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The Synthesis and Reactions of Some α , β -Unsaturated Diazoketones

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THE SYNTHESIS AND REACTIONS
OF SOME α,β -UNSATURATED
DIAZOKETONES

by

Virendra K. Sood

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
December 1973

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I am also thankful to my wife for her moral support.

Virendra K. Sood

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HISTORICAL

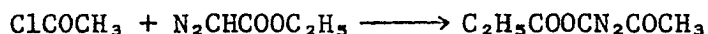
Several original papers, reviews and monographs¹⁻⁴ have appeared in the literature, underlining the remarkable part, which the diazo-ketones have played in the development of organic chemistry. The methods of preparation of diazoketones may be divided into seven principal groups:

- 1) C-acylation of aliphatic diazo-compounds
- 2) Reaction of organic azides with active methylene compounds
- 3) Oxidation of monohydrazones of α -aldehydoketones and α -diketones
- 4) Diazotization of primary amines containing a carbonyl group
- 5) Diazotization of ketoximes
- 6) Alkaline cleavage of N-acyl-N-nitrosamines
- 7) Alkaline cleavage of tosylhydrazones of α -carbonyl compounds

From our point of view the first two methods are of interest.

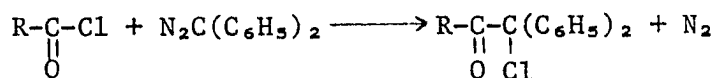
C-Acylation of Aliphatic Diazocompounds

This method consists of direct acylation of diazo derivatives by carboxylic acid halides and acid anhydrides. The nature of the product formed depends considerably on the reaction conditions and on the structure of the diazo-compounds and acylating agents. For example, acetyl chloride reacts with ethyl diazoacetate as follows:⁵



The reaction of carboxylic acid chlorides with diazo-compounds with-

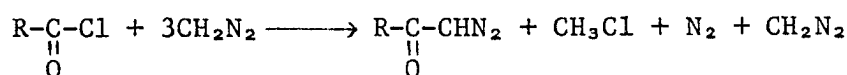
out an activated α -hydrogen atom takes place differently⁵.



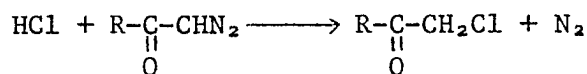
The reaction of aromatic carboxylic acid chlorides with diazomethane at room temperature using equimolar amounts of reactants leads to the formation of aryl chloromethyl ketones^{6,7}.



C-Acylation of diazoalkanes takes place in the presence of carboxylic acid chlorides at 0°C and may be described as below⁸⁻¹⁰.

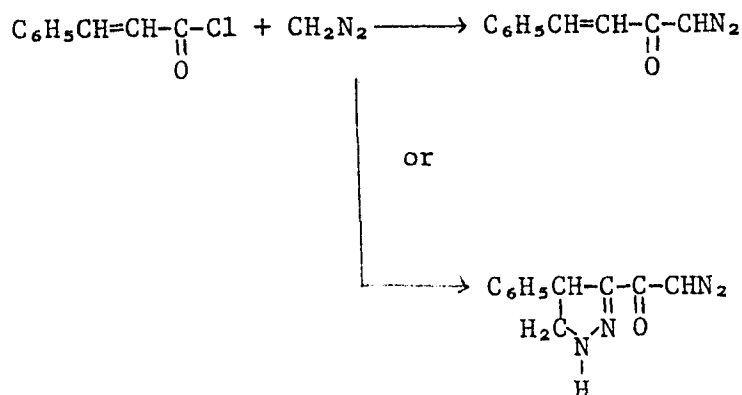


When less than 3 moles of diazoalkane are used, a side reaction leading to the formation of a chloromethyl ketone is possible.

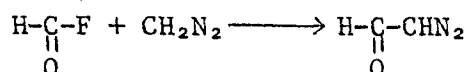


Triethylamine may be used to combine with hydrogen chloride formed in the reaction¹¹. The method of C-acylation of diazo-compounds (the Arndt-Eistet method) has been developed in fair detail and is widely used to synthesize not only primary but also secondary diazoketones¹². It constitutes the basis of the synthesis of mono, bis-, and tris-diazoketones^{13,14}. Thus, 1,3,5-tris (diazoacetyl) benzene has been obtained by treating trimesitoyl chloride with an excess of diazomethane¹⁴.

Wotiz and Buco¹⁵ reported that it was possible to prepare α,β -unsaturated diazoketones or diazoacetyl pyrazolines using different amounts of reactants by the following method.



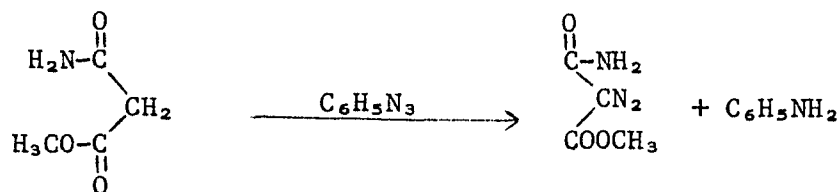
While C-acylation of diazo-compounds by carboxylic acid chlorides and acid bromides have been investigated in fair detail, carboxylic acid fluorides are rarely used for this purpose. The synthesis of diazoacetaldehyde may serve as an example¹⁶.



There are only a few examples of the C-acylation of diazo-compounds by carboxylic anhydrides^{17,18}. Benzoic anhydride reacts with diazomethane to form diazoacetophenone.

Reaction of Organic Azides with Active Methylene Compounds

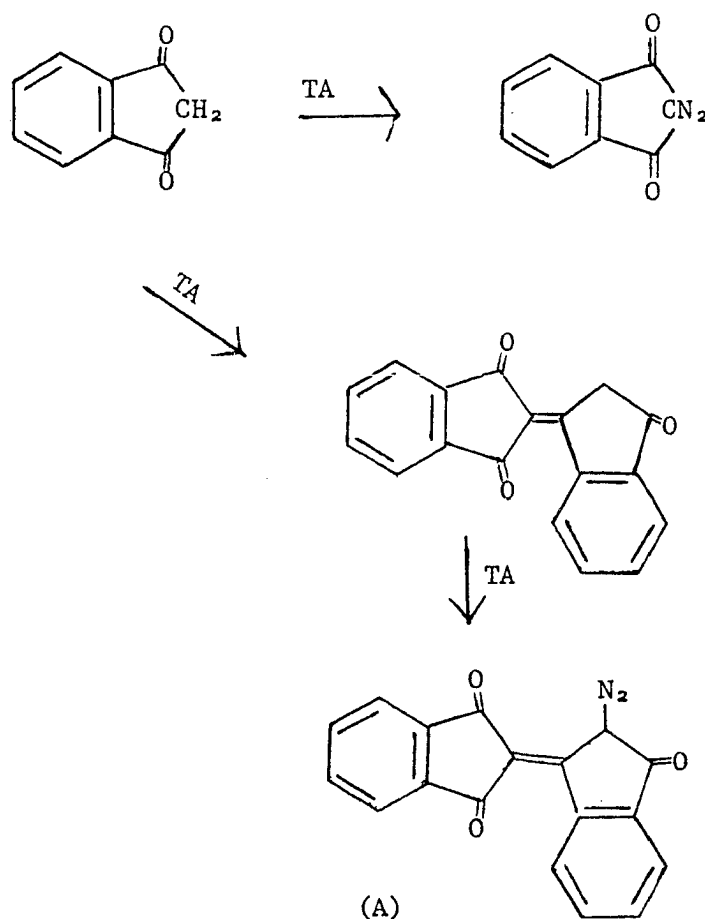
The reaction involving the introduction of diazo groups into an active methylene group with the aid of phenyl azide was discovered by Dimorth¹⁹ in 1910.



Later it was shown that p-tosyl azide can also be used to transfer the diazo group²⁰. However, at that time, this interesting method of preparing diazo compounds did not attract much attention and its

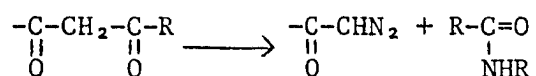
detailed development began as late as 1953^{21,22}. The method proved to be suitable for the synthesis of cyclic diazo compounds including diazoketones^{22,23}. The reaction is carried out in ethanol in the presence of sodium or potassium ethoxide, triethylemine or potassium hydroxide.

The formation of a mixture of diazo-compounds was also noted in the synthesis of 2-diazoindan-1,3-dione. The principal reaction product is 2-diazo-1,3,3-trioxo-1,2-bisindanylidene (A) which arises as a result of the self condensation of indan-1,3-dione under the influence of a base. The self condensation product reacts further with *p*-tosylazide (TA)²⁴.



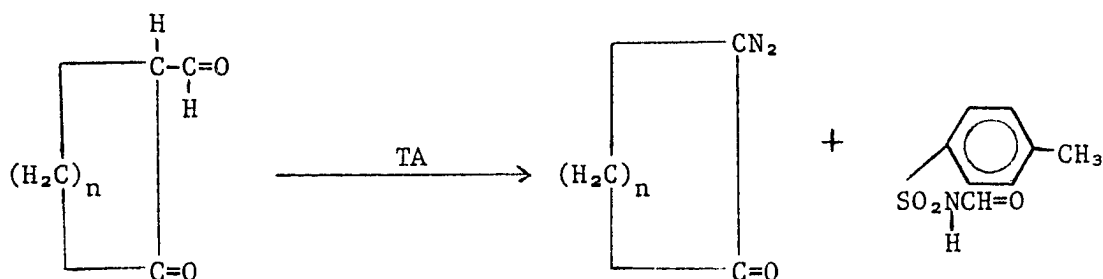
Carbonyl compounds of the type $-\text{CH}_2-\text{C}=\text{O}$ react with sulfonyl azides to form diazo derivatives, when the C-H group is sufficiently activated^{25,26}.

Dicarbonyl compounds are convenient acceptors of the diazo group. Ketones, which are unsuitable for the direct introduction of the diazo group, are converted by Claisen condensation into β -dicarbonyl compounds. The latter smoothly converted into diazoketones, with elimination of substituted carboxamides^{27,28}.

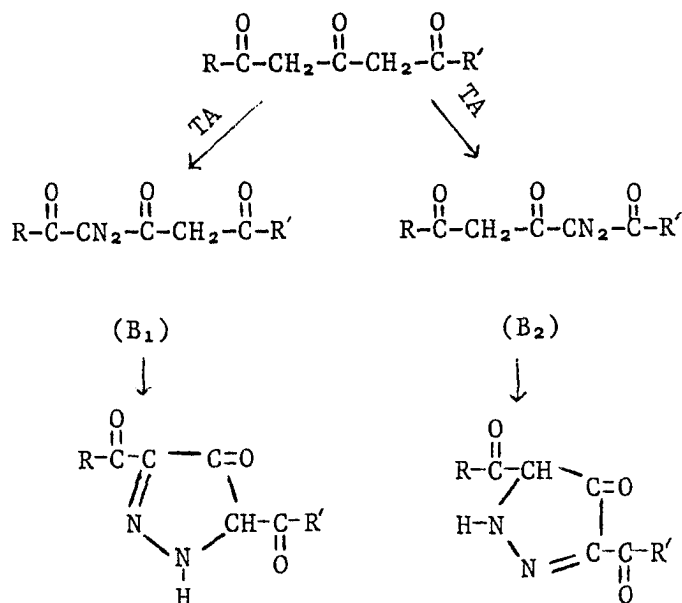


R = H, alkyl group or aryl group

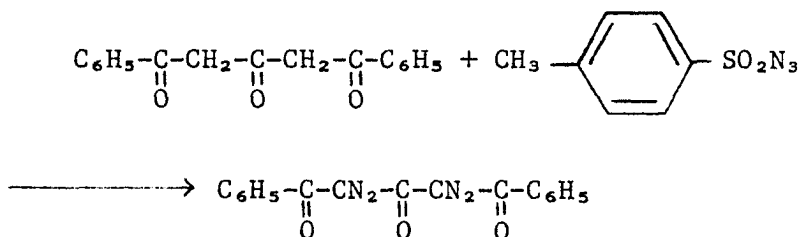
α -Formylcycloalkanones are also readily converted into diazocycloalkanones^{27,29}.



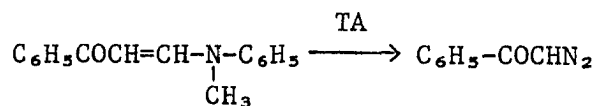
In the reaction of 1,3,5-triketones with tosylazide, pyrazolones are isolated in high yields, instead of the expected bis diazoketones. The formation of the pyrazolones is due to an intramolecular reaction of the intermediate diazoketone (B_1 and B_2)³⁰.



However, when the reactants are mixed slowly, the reaction can be driven towards the formation of bis diazoketones³¹.



Diazoketones are formed in the reaction of enamines with arenesulfonyl azides^{32,33}.



Reactions of Diazketones

An intense investigation of the chemical reactions of diazoketones was begun in 1928, when Arndt and Amende discovered the reaction in which diazoalkanes are acylated by carboxylic acid halides⁹. Since then diazoketones have become readily available. They undergo

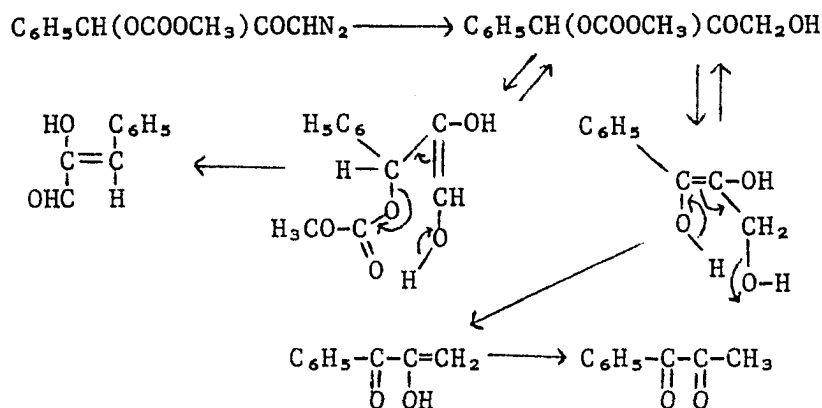
reactions of the following characteristic types:

- 1) Reactions with evolution of nitrogen
- 2) Reactions involving the nitrogen atoms of the diazo group
- 3) Reactions in which the mobile α -hydrogen atom is substituted

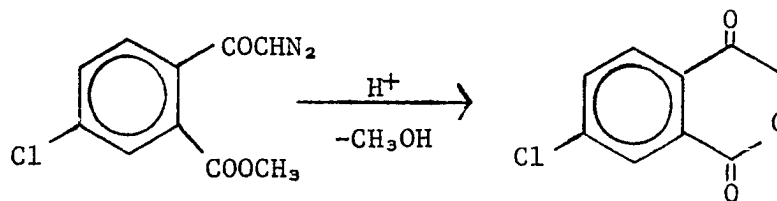
Reactions involving acid catalysis

This group of reactions includes the reactions of diazoketones with water, alcohols, acids, halogens, N-halogeno derivatives and nitrogen oxides. Under the usual conditions, diazoketones are, as a rule, inert to water. However, a few drops of acid (usually inorganic) are sufficient for the evolution of nitrogen to begin, and an α -hydroxyketone to form. Sometimes the reaction takes place on heating. For example, an acetylmethanol may be obtained from diazoacetone³⁴.

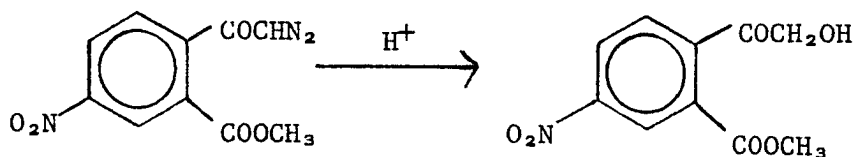
Acid hydrolysis of primary diazoketones does not result in the formation of α -hydroxymethylketones only. In the decomposition of 3-diazo-1-methoxycarbonyl-1-phenyl-propane-2-one by dilute sulfuric acid, Bradley and Eaton isolated benzylglyoxal in 12% yield, the formation of which they believe may be due to an anionotropic migration of the phenyl group and the elimination of the second substituent³⁵. Dahn et al³⁶ investigated this reaction in greater detail and employed 10% phosphoric acid for hydrolysis and obtained benzylglyoxal in 44% yield. In addition to the aldehyde, benzoyl-acetyl was also isolated. They explained the formation of the above products by the intermediate formation of a hydroxyketone and a diol.



In the acid hydrolysis of diazoketones, the stabilization of the carbonium ion depends both on the nature of the substituents and on their distribution relative to the diazo group. For example, p-chloro-w-diazo-o-methoxycarbonyl-acetophenone gives 7-chloro-1,4-diketetoisochroman on treatment with 3% sulfuric acid³⁷.



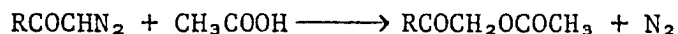
Under the hydrolysis conditions, 2-diazo-o-carbomethoxy-p-nitroacetophenone is converted into w-hydroxy-o-carbomethoxy-p-nitroacetophenone³⁸.



The acidity of alcohols is insufficient for the decomposition of diazoketones, therefore, the reaction with alcohols is, as a rule, carried out in the presence of catalysts. Inorganic acids, boron trifluoride or metallic copper are employed for this purpose³⁹.

The reaction results in the formation of O-alkyl-derivatives of α -hydroxyketones.

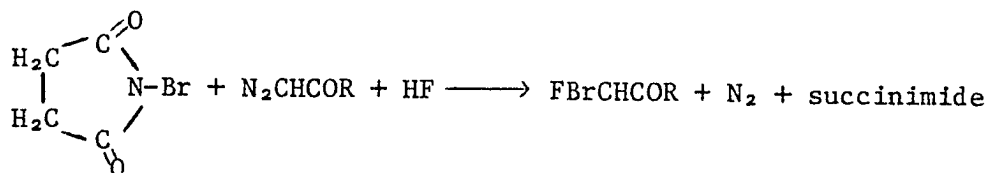
In contrast to diazoalkanes, diazoketones are more stable in relation to electrophilic reagents. The inertness of diazoketones with respect to cold acetic acid makes it possible to carry out certain reactions in it⁴⁰. On heating with acetic acid, diazoketones form ketoesters⁴¹.



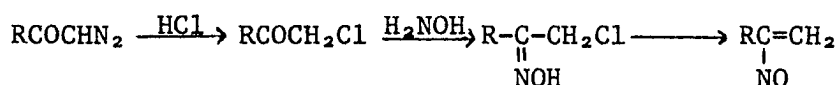
Strong organic acids decompose diazoketones at room temperature.

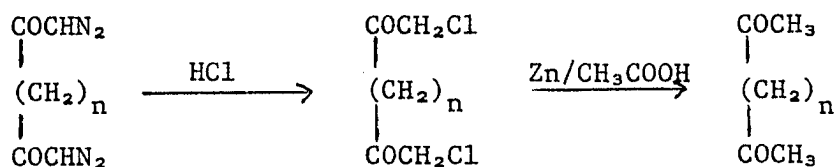
ω -Nitro- α -diazoketones react with polynitro-carboxylic acids when the reactants are fused together⁴³.

Hydrogen halides, except hydrogen fluoride, readily decompose diazoketones. Interesting experiments have been performed on the decomposition of diazoketones in hydrofluoric acid in the presence of N-bromosuccinimide⁴⁴.



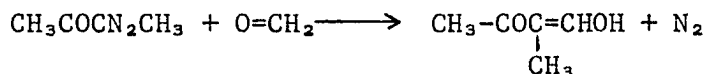
When diazoketones are treated with dry hydrogen chloride α -chloromethyl ketones, which are starting materials for various syntheses, are obtained⁴². For example, nitrosolefins, diketones, and other compounds have been obtained from diazoketones via α -chloromethylketones.



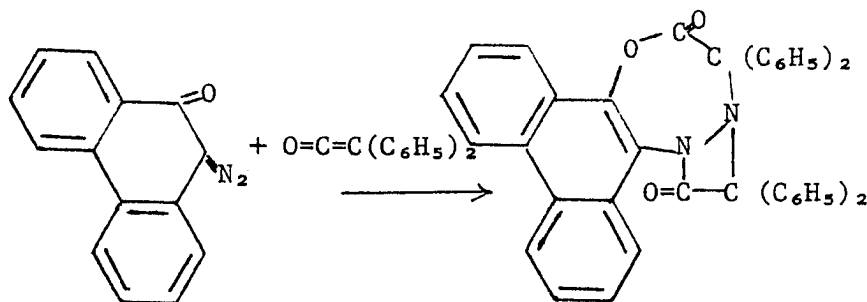


Reaction of diazoketones with carbonyl compounds

The reaction of diazoketones with aldehydes was investigated for the first time by Diels and Ilberg⁴⁵. On mixing 2-diazo-3-butanone with formaldehyde, they observed a vigorous evolution of heat and nitrogen. The reaction resulted in the isolation of 4-hydroxy-3-methylbut-3-en-2-one.

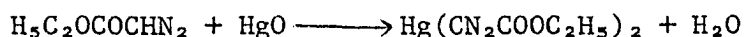


Diazoketones readily react with ketenes. After allowing azibenzil to react with diphenylketene, Staudinger and Reber isolated a nitrogen containing crystalline adduct⁴⁶. Ried and Dietrich made a detailed study of the reaction of *o*-quinone diazide with ketenes and showed that it resulted in the formation of polycyclic nitrogen-containing systems^{47,48}.

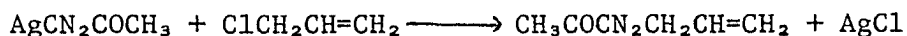
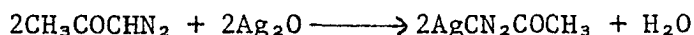


Electrophilic substitution involving diazoketones

Diazoketones are known to undergo a reaction in which silver or mercury replaces the hydrogen at the carbon atom linked to the diazo group. The reaction was first discovered by Buchner⁴⁹ when he allowed diazoacetic ester to react with yellow mercury (II) oxide.



Silver oxide can also be employed as a deprotonating agent for diazoketones. The reaction is performed in tetrahydrofuran at temperatures between -15° and 0° . Silver derivatives of diazoketones are excellent alkylating agents and serve as intermediates for the synthesis of unsaturated diazoketones⁵⁰.



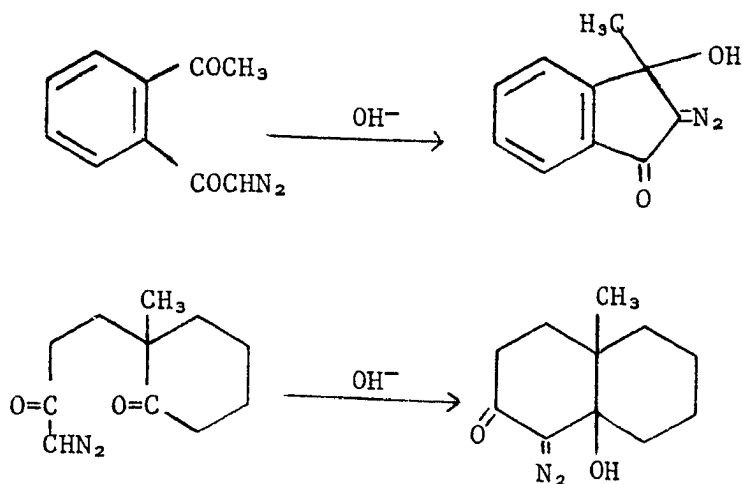
Organotin derivatives of diazoacetic ester, formed in the reaction of the latter with organotin derivatives of alkylamines, have been recently described⁵¹.

Reactions of diazoketones under the influence of bases

The reactions of diazoketones with bases have not been adequately investigated, evidently due to their complexity. The reaction takes place unambiguously in the case of the diazoacetamide⁵² and 2-diazo-3-pentanone⁵³. In the first case the product is 5-keto-1,2,3-triazole and in the second 1-(3,3-dimethyl-2-butyroyl)-5-(2,2-dimethyl-1-ketopropyl) tetrazole. The reaction of diazoacetophenone with potassium *t*-butoxide yields a dimer of diazoacetophenone, 5-benzoyl-1-phenyltetrazole, and 5-benzoyl-2-phenacyltetrazole. 1-Phenacyltetrazole is obtained in ether in the presence of ammonium

chloride⁵⁴.

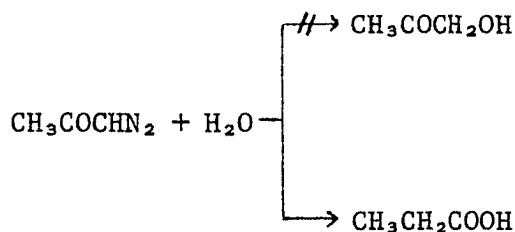
It was found recently that diazoketones undergo intramolecular condensation on treatment with alkalis⁵⁵.



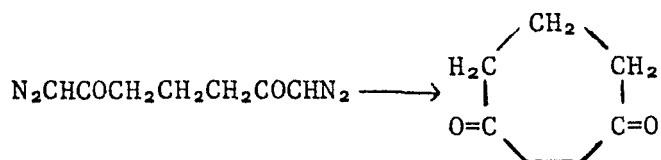
Reactions of diazoketones via ketocarbenes

A characteristic reaction of diazoketones is decomposition via ketocarbenes on irradiation and under the influence of heat and light. The intermediate species with an incomplete octet at the α -carbon atom, formed after the elimination of nitrogen, can be stabilized in different ways.

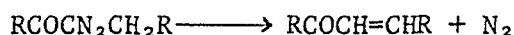
Wolff, who studied the reaction of diazoacetone and diazoacetophenone with water in the presence of silver oxide, isolated, instead of the expected α -hydroxyketones, propionic and phenylacetic acids³⁴.



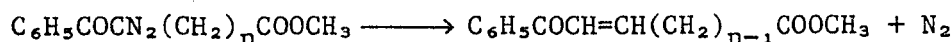
oxide leads to the formation of cyclohept-2-ene-1,4-dione⁵⁹.



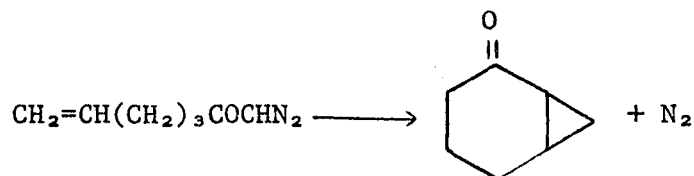
Under analogous conditions, cyclic diazoketones form polymeric products in addition to the dimers⁶⁰. When diazoketones in which a CH group adjoins the diazo group decompose under the influence of light or Ag_2O , α,β -unsaturated ketones are formed as a rule⁶¹. These are formed by the migration of a hydride ion from the β -carbon atom to the α -carbon atom.



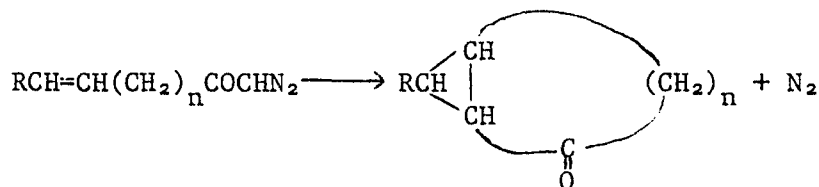
Recently a number of unsaturated ketoesters have been synthesized in this way⁶².



If the decomposition of unsaturated diazoketones is carried out in inert solvents, the ketocarbene formed may be stabilized in yet another way, namely via intramolecular addition of the carbon atom with an incomplete octet to the double bond, resulting in the formation of a cyclic product. Thus, when 1-diazo-oct-7-ene-2-one is refluxed in cyclohexane in the presence of copper bronze, bicyclo-[4,1,0]-2-heptanone is formed⁶³.

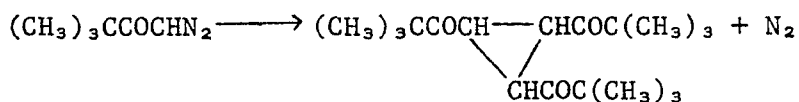


The intramolecular reaction of unsaturated diazoketones was investigated in greater detail by Fawzi and Gutsche⁶⁴, who noted that the substituents at the double bond do not have a significant influence on this reaction.

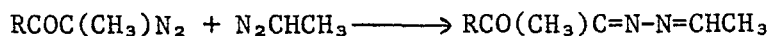


If the diazomethyl group is separated from the double bond by a benzene ring or if the double bond is located in a ring, polycyclic systems are formed⁶⁵.

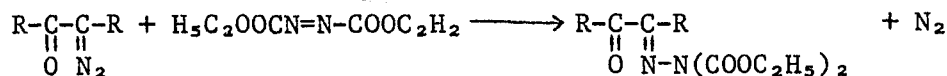
Low yields of cyclopropanes may be obtained by the thermal decomposition of diazoketones⁶⁶. When the reaction is carried out in thianisole in nitrogen and in the presence of copper bronze, the yield of the cyclic compound may be increased⁶⁷.



The decomposition of diazoketones in the presence of diazoalkanes leads to the formation of azines⁶⁸.

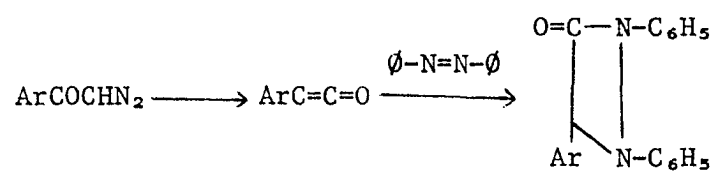


α -Diazoketones react with azodicarboxylic acid diesters on heating with the formation of the monohydrazones of 1,2-dicarbonyl compounds⁶⁹.



The reaction with azobenzene takes place under the influence of ultraviolet light. This involves the formation of ketenes which are

subsequently coupled to the azo-group with formation of heterocyclic compounds⁷⁰.

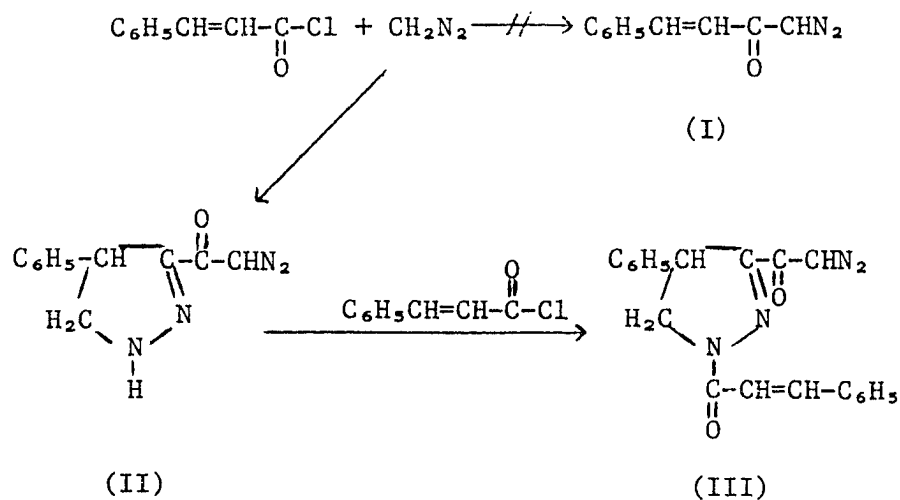


2-Diazo-1,3-dicarbonyl compounds react similarly with azo derivatives.

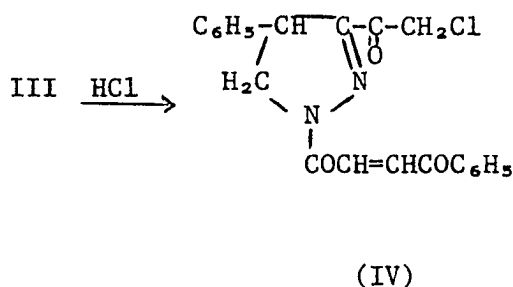
DISCUSSION

The diazomethyl ketones can be very easily prepared by the reaction of acid chlorides with diazomethane. Wotiz and Buco¹⁵ reported in 1955 that cinnamoyl diazomethyl ketone could be prepared by the reaction of cinnamoyl chloride and diazomethane at 0°C. Kapoor and Gupta⁷² in 1961 also reported the preparation of cinnamoyl diazomethyl ketone by the above procedure.

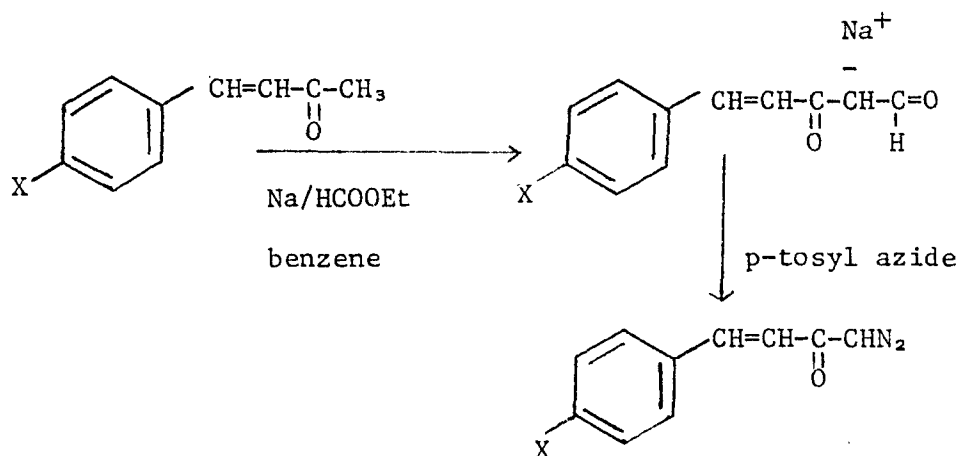
Moore⁷³ in 1969 repeated the above reaction and reported that they did not get cinnamoyl diazomethyl ketone (I) but got Compound III instead as shown below:



Compound III on treatment with HCl gave IV.

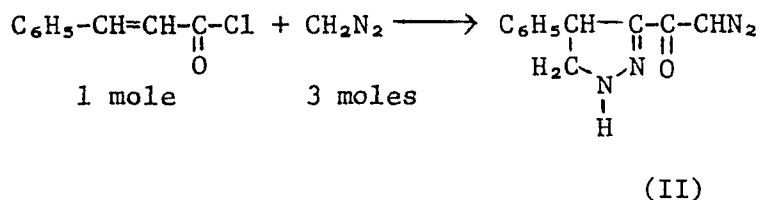


Regitz⁷⁴ referred to Moore's⁷³ work about the failure to get cinnamoyl diazomethyl ketone by the cinnamoyl chloride and diazomethane reaction and proposed that α,β -unsaturated diazoketones could be prepared by the following method.



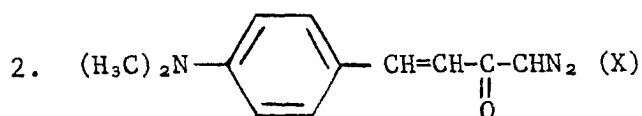
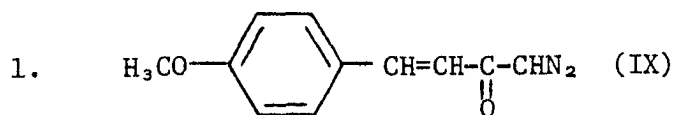
The only two substituted diazomethyl ketones prepared by this method⁷⁴ were those in which $\text{X} = -\text{OCH}_3$ and $-\text{N}(\text{CH}_3)_2$. The authors did not mention in the above paper whether or not they tried to prepare cinnamoyl diazomethyl ketone.

We repeated the cinnamoyl chloride and diazomethane reaction and found that not only did we not get cinnamoyl diazomethyl ketone (I), but we got compounds which were different from those obtained by Moore et al.



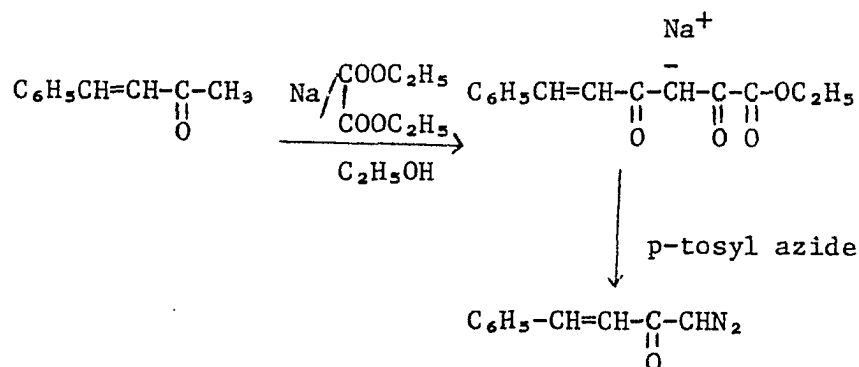
If 2 moles of CH_2N_2 were used instead of 3 moles as above, we got IV and not III.

We then attempted the preparation of cinnamoyl diazomethyl ketone by Regitz's method. We were able to repeat the reaction and prepared the two diazoketones he had reported.



However we failed to get the cinnamoyl diazomethyl ketone or p-nitro-cinnamoyl diazomethyl ketone. The preparation of the sodium salts of α -formyl ketones in the case of p-anisalacetone and p-dimethylaminobenzal acetone took several days. Evidently the scope of the Regitz method did not include the preparation of cinnamoyl diazomethyl ketone.

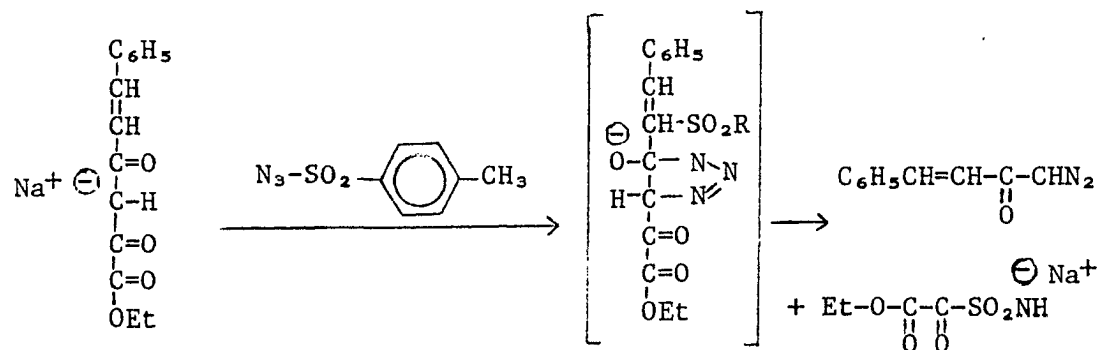
We then attempted to modify the above reaction and tried to make, instead of the sodium salt of α -formyl ketone, the sodium salt of the α -ethyl oxalyl ketone as follows:



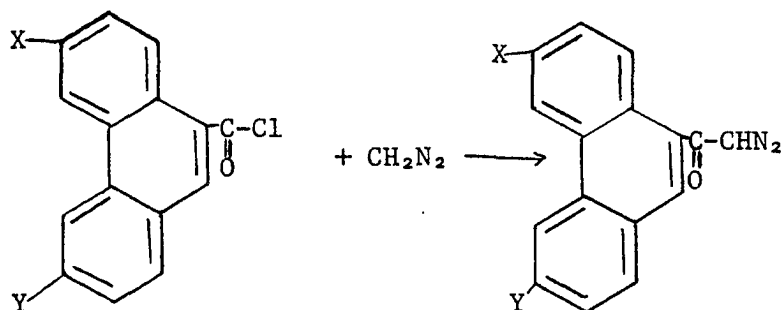
We were able not only to prepare the two diazoketones made by Regitz

by this method in equal or better yields but were also able to prepare cinnamoyl diazomethyl ketone for the first time and in fairly good yield. In the above case the sodium salt could be formed in only two hours.

The identity of $\text{C}_6\text{H}_5\text{CH}=\text{CH}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CHN}_2$ was confirmed by ir and nmr spectroscopy and the mass spectrum gave an m/e ratio of 172. The compound analyzed correctly for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}$. It melted at $64-66^\circ\text{C}$. The mechanism for the formation of the diazoketone is believed to be the following: In the first stage the diazo-group acceptor is converted under the influence of base into a carbanion in which a double bond may be formed. The subsequent addition of the sulfonyl azide to the anion leads to the formation of a triazoline intermediate which dissociates into a diazo-compound and a sulfonamide.

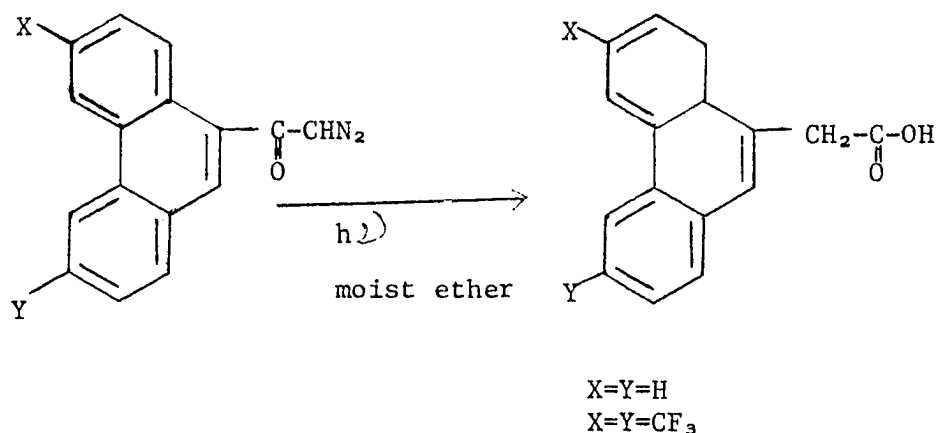


We prepared two other diazoketones of the phenanthrene series by the usual method as follows:



- i) $X=Y=H$ (V)
- ii) $X=Y=CF_3$ (VI)

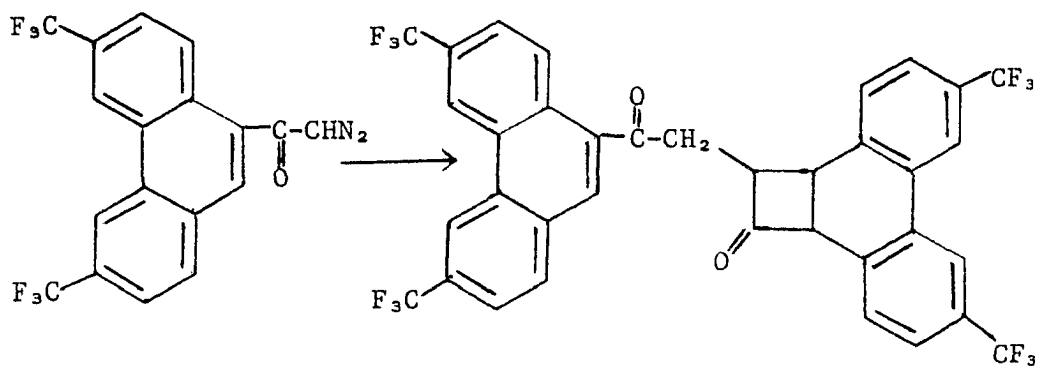
These two diazoketones of the phenanthrene series were irradiated with ultraviolet light in moist ether and we obtained the corresponding 9-acetic acids (VII, VIII).



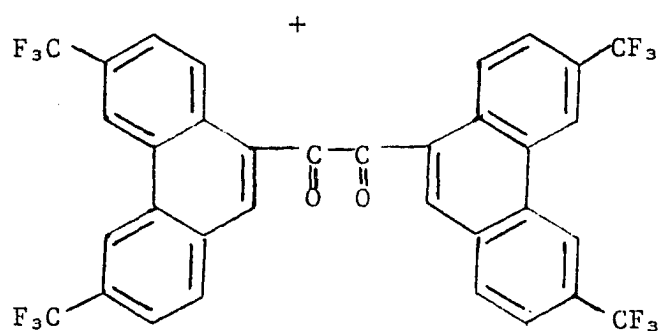
Bistrifluoromethyl-9-diazoacetylphenanthrene was treated with copper bronze in dry benzene under nitrogen. The reaction mixture showed several spots on the thin layer chromatography.

Infrared spectrum of the reaction mixture showed that the diazo-peak at 2100 cm^{-1} had disappeared and two new peaks at 1630 and 1680 cm^{-1} , appeared.

Two products were obtained by separation on a dry column packed with silica gel G and based on the mass spectrographic evidence and elemental analysis data (see Experimental) we believe that they have the following structures.



VI (A)



VI (B)

The nmr spectrum of these compounds could not be obtained because they were not soluble in conventional nmr solvents. 9-Diazoacetyl-phenanthrene, when heated under reflux in dry benzene, with copper bronze in an atmosphere of nitrogen gave a very complex mixture of products, which could not be separated.

EXPERIMENTAL

All melting points, expressed in degrees Centigrade, are corrected. The elemental analyses were performed by Midwest Microlabs, Inc., Indianapolis, Indiana and Micro-Analyses Inc., Wilmington, Delaware. Chemicals were used as obtained unless stated otherwise. Thin-layer chromatography was carried out on micro-slides, using Silica Gel-G (Dermstadt) or precoated thin-layer plates, and column chromatography was performed in a column 30 cm. in length with an inside diameter of 2 cm. using Silica Gel-G (Dermstadt) with automatic fraction collector for collecting the fractions. Infrared spectra were measured with a Beckman IR-8 spectrophotometer and the assignments were made according to Rao⁷⁸. The nuclear magnetic resonance spectra were obtained with a Varian A-60. The mass spectrometer used was Atlas CH-4.

Preparation of 9-diazoacetylphenanthrene (V)

This was prepared by the method of Israelashvile et. al.,⁷⁴ m.p. 121-122°C, (lit.⁷⁴ 122°), yield 85%.

Anal. calcd for $C_{16}H_{10}N_2O$: C, 78.1; H, 4.1; N, 11.4.

Found: C, 78.0; H, 4.2; N, 11.4.

9-Phenanthroylchloride was prepared by the method of Goldberg et. al.⁷⁵.

Preparation of 1-cinnamoyl-3-chloroacetyl-4-phenyl-2 pyrazoline (IV)

Cinnamoyl Chloride, 1.67 g (0.01 mole) was dissolved in 30 ml.

of chloroform and added dropwise to a solution of diazomethane, 0.84 g (0.02 moles) in 75 ml. of ether at 0°C (diazomethane was prepared from diazald). After the addition was complete (15-20 minutes) the reaction mixture was stirred for 1 hour at low temperature and then kept in the refrigerator for 24 hours. Excess diazomethane was destroyed by keeping the solution briefly in warm water (45°C). On evaporation of the ether under reduced pressure, a solid was obtained, which on recrystallization with methanol yielded colorless prisms, m.p. 179-180° (lit.⁷³ 178°), yield 2.5 g (70%), ir (Nujol): 1700, 1650, 1620 cm.⁻¹

Anal. calcd for C₂₀H₁₇ClN₂O₂: C, 68.10; H, 4.86; N, 7.94.

Found: C, 68.40; H, 4.86; N, 7.97.

Preparation of 3-diazoacetyl-4-phenyl-2-pyrazoline (II)

Cinnamoyl chloride, 1.67 g (0.01 mole) was dissolved in 30 ml. of dry ether and added dropwise to a solution of diazomethane 1.25 g (0.03 moles) in 120 ml. ether at 0°C. After the addition was complete (15 minutes), the solution was stirred at the same temperature for 1 hour and then kept in the refrigerator overnight. Excess of diazomethane was destroyed by keeping the solution in warm water (45-50°C) for a short time. After evaporating the ether, a yellow crystalline solid was obtained. It was recrystallized from ethanol-water to give bright yellow plates, m.p. 113-114°C.

Anal. calcd for C₁₁H₁₀N₄O: C, 61.67; H, 4.71; N, 26.16.

Found: C, 61.85; H, 4.70; N, 26.05.

Preparation of Cinnamoyl Diazomethyl Ketone (I)

(a) Preparation of sodium salt of α -ethyl oxalyl-4-phenyl-3-butene-2-one

Benzalacetone, 2.92 g (0.02 moles) and diethyl oxalate, 1.46 g (0.02 mole) were dissolved in 50 ml. of absolute ethanol and the resulting solution was added to 20 ml. of ethanol in which 0.46 g (0.02 mole) of Na metal had been dissolved, dropwise in such a way that the temperature of the solution did not rise above 5-10°C. After the addition was complete (15-20 minutes), the resulting mixture was stirred at room temperature for 2-3 hours. Then 100 ml. of ether was added to it and the resulting precipitate was filtered on a Buchner funnel. m.p. 180°d.

(b) Preparation of the diazoketone

P-toluene-sulfonylazide, 2.0 g (0.01 mole) was added dropwise with stirring and cooling in an ice bath to a suspension of 2.95 g (0.011 mole) of the Na salt of α -oxalyl ketone in 25 ml. of ethanol in such a way that the temperature did not rise above 5-10°C. The mixture was stirred at room temperature for 2-3 hours. The solvent was removed at room temperature under reduced pressure and the residue was taken up in 25 ml. of water and extracted with 50 ml. of ether. The ether extract was washed first with a solution of 1 g of NaOH in 25 ml. of water and then with 25 ml. of water. It was then dried over anhydrous Na₂SO₄. Ether was then removed under vacuum and the yellowish solid recrystallized from pentane to give light

yellow plates m.p. 64-66°C., yield 2.54 g (73%), ir (Nujol) = 2096 cm^{-1}
m/e parent peak 172. (theoretical m/e=172).

Anal. calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}$: C, 69.76; H, 4.65; N, 16.27.

Found: C, 69.72; H, 4.70; N, 16.21.

Preparation of phenanthrene-9-acetic acid (VII)

Phenanthryl-9-diazomethyl ketone, (400 mg.) was dissolved in 250 ml. of wet ether and irradiated for 24 hours using 2757 Å uv source. After the reaction was complete, the ether solution was dried over anhydrous Na_2SO_4 . Then ether was removed under vacuum and the solid obtained was redissolved in a minimum amount of ether and kept in the refrigerator for 12 hours. A light fluffy crystalline solid was obtained. Yield 350 mg., m.p. 223-225° (lit.⁷⁷ 224°).

Method for the Preparation of p-dimethylamino Cinnamoyl Diazomethyl Ketone and p-Methoxy Cinnamoyl Diazomethyl Ketone

Method A

(a) Preparation of sodium salt of α -formyl ketone

The α,β -unsaturated ketone (0.1 mole) was taken up in 100 ml. of dry benzene and to this was added 0.12 mole of ethyl formate and the resulting solution was added dropwise with stirring and cooling to 0.1 mole of sodium metal in 50 ml. of dry benzene, in such a way that the solution temperature did not exceed 10-15°C. After the addition was complete, the reaction mixture was stirred at room temperature for 48 hours or more. 100 ml. of dry ether was then

added to the solution. A solid separated out and was filtered.

(b) Preparation of the diazoketone

.011 mole of the above α -formyl ketone was suspended in 25 ml. of ethanol and the solution was cooled to 0°C in a bath of ice-salt mixture. To this was added dropwise 2.0 g (0.01 mole) of *p*-toluene sulfonyl azide in such a way that the temperature did not exceed 5-10°C. After the addition was complete (15 minutes), the reaction mixture was stirred at room temperature for 2-3 hours. The solvent was removed under vacuum and the residue taken up in 25 ml. of water and extracted with 50 ml. of ether. The ether extract was washed with a solution of 1 g of NaOH in 25 ml. of water and then with 25 ml. of water, dried over anhydrous Na₂SO₄ and the ether was removed under vacuum. The solid thus obtained was recrystallized from ethanol water. Yield for (IX) 50%, for (X) 72%. m.p., (IX) 122-123° (lit.⁷⁶ 123°), (X) 127-129° (lit.⁷⁶ 128°). ir diazobands (IX) 2096 cm⁻¹, (X) 2096 cm⁻¹.

Method B

(a) Preparation of sodium salt of α -ethyl oxalyl ketone

0.1 mole of α - β -unsaturated ketone was dissolved in 100 ml. of absolute ethanol and to this was added 0.1 mole of diethyloxalate. This solution was added dropwise to 0.1 mole of sodium metal in 25 ml. of absolute ethanol with cooling and stirring so that the temperature did not exceed 10°C. This was then stirred at room temperature for 2-3 hours. 100 ml. ether was then added and the

resulting solid filtered.

(b) Preparation of the diazoketone

The sodium salt of α -ethyl oxalyl ketone thus obtained was treated with *p*-toluene sulfonyl azide as in (b) above of Method A. Yield (IX) 70%, m.p. 122-123°. Yield (X) 75%, m.p. 127-128°C.

Preparation of 3,6-bis trifluoromethyl-9-diazoacetyl phenanthrene (VI)

The acid chloride, 3.7 g (0.01 mole) was dissolved in 50 ml. of dry ether and the resulting solution was added dropwise to 300 ml. of ether containing 0.03 mole of diazomethane at 0°C. The addition was complete in about 15 minutes. The resulting solution was stirred for about 1 hour at 0°C and then kept overnight in the refrigerator. The excess diazomethane was removed by keeping the solution briefly in warm water (45-50°C). The ether was evaporated and the resulting solid melted at 153-154°. Yield 3.5 g (95%).

Anal. calcd for $C_{18}H_8N_2OF_6$: C, 56.6; H, 2.1; N, 7.3.

Found: C, 57.11; H, 2.25; N, 6.67.

Copper bronze reaction of the above diazoketone (VI)

1.4 g (.0038 mole) of the 3,6-bistrifluoromethyl-9-diazoacetyl phenanthrene was taken up in 600 ml. of dry benzene. 0.3 g of copper bronze powder was added to it and the mixture was refluxed under N_2 atmosphere for 3 hours. The solvent was removed under vacuum. The resulting oily residue was chromatographed over a dry column packed with silica Gel-G using cyclohexane as a solvent.

Two compounds were obtained. Compound VI A Yield 8%, m.p. 173-176°C.

Anal. calcd for $C_{36}H_{17}O_2F_{12}$: C, 61.0; H, 2.25.

Found: C, 61.06; H, 2.36.

m/e (parent peak), 708

Compound VI B Yield 54%, m.p. 280-285°

Anal. calcd for $C_{34}H_{14}O_2F_{12}$: 59.82; H, 2.05.

Found: 60.1; H, 1.9.

m/e (parent peak), 682

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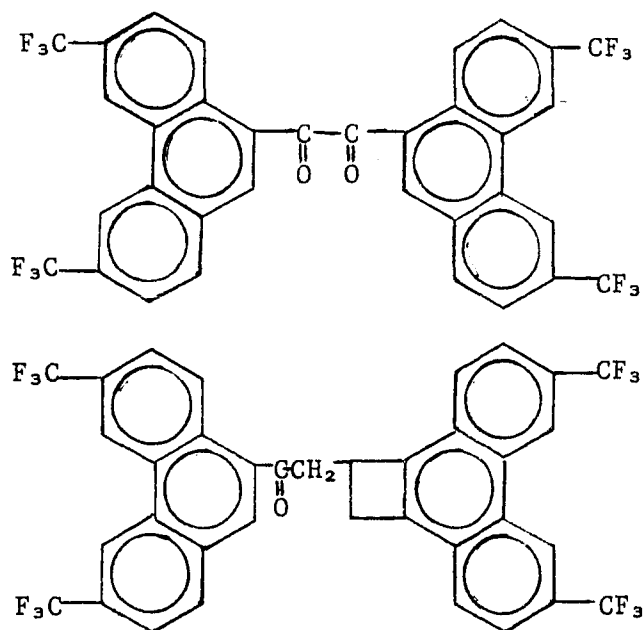
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SUMMARY

Several syntheses of cinnamoyl diazomethyl ketone (1-diazoacetyl-4-phenyl-3-butene-2-one), using the Arndt Eistert method have appeared in the literature. On repeating these procedures in our laboratory, we were unable to obtain the desired compound. By using an alternate procedure, we were able to obtain the above compound, and have established its structure unequivocally. Phenanthrene-9-diazomethyl ketones were obtained from the corresponding acid chlorides by using the Arndt Eistert method. When 2,6-bistrifluoromethyl-9-diazoacetylphenanthrene and 9-diazoacetylphenanthrene were irradiated with ultra-violet light in moist ether they gave the corresponding 9-acetic acids. Two compounds were isolated from the reaction mixture when bistrifluoromethyl-9-phenanthrene was treated with copper bronze, which have been tentatively assigned the following structures.



VITA

The author was born at Bahjoi (U.P.) India on July 11, 1943. He, after studying at several different schools in different cities, due to the nature of his father's job involving transfers after every 2-3 years, passed High School from D.A.V. Inter College Azamgarh in 1957. He passed Intermediate from Government Inter College Meerut in 1959 and received a B.S. in 1962 from Government College Rampur.

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