

quantitative electrolysis was carried out with the circulating pump operating. The electrolysis current was integrated electronically. When the electrolysis current had decreased enough to indicate essentially complete reaction, another current-voltage curve at the dropping mercury electrode was recorded to verify the completion of reaction. The sample bulb was then closed off and removed for infrared analysis of the gaseous reaction products contained therein.

The n value of the reaction was calculated from the integrated electrolysis current (converted to equivalents by use of Faraday's law) and the known number of moles of material reacted.

Analytical Methods.—The gases were monitored by analyzing 0.2-ml samples with the gas chromatographic equipment described previously.¹ The relative molar responses of the fluoronitrogens to detection by thermal conductivity are the following: N_2 (1.00), CF_2N_2 (1.5), $F_2NCF=NF$ (1.85), $(F_2N)_2C=NF$ (2.22), and $(F_2N)_3CF$ (2.40). The final gaseous products were also analyzed by infrared and mass spectrometry with the apparatus described previously.⁷ The iodine-containing solutions were analyzed by the conventional thiosulfate titration. Fluoride ion was determined by thorium nitrate titration. Cyanate degradation products were identified by comparing the infrared spectra of the solids in question to reference spectra of the solids obtained from aged solutions of cyanate, iodide, and fluoride.

Registry No.—Tris(difluoroamino)fluoromethane, 14362-68-6; tetrafluoroformamidine, 14362-70-0; penttafluoroguanidine, 10051-06-6.

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The Reaction of Diazomethane with a Methylene-cyclopropene

R. SCOTT PYRON^{1a,b} AND W. M. JONES^{1c}

Department of Chemistry, University of Florida,
Gainesville, Florida 32601

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As a possible source of the highly strained spiro-pentene ring system,² the reaction of diazoalkanes with the *exo* double bond of a suitable methylenecyclopropene appeared attractive.³ We therefore undertook an examination of the reaction of diazomethane with a methylenecyclopropene (1) which was available to us from previous work in these laboratories.⁴ The purpose of this paper is to report our finding that this reaction does not proceed by attack of the diazomethane on the exocyclic double bond but, instead, by attack on the *endo* double bond to give the unstable ring-opened diazoalkene 3, which isomerizes under very mild conditions to pyrazole 5 *via* what we believe to be the pyrazolenine 4.

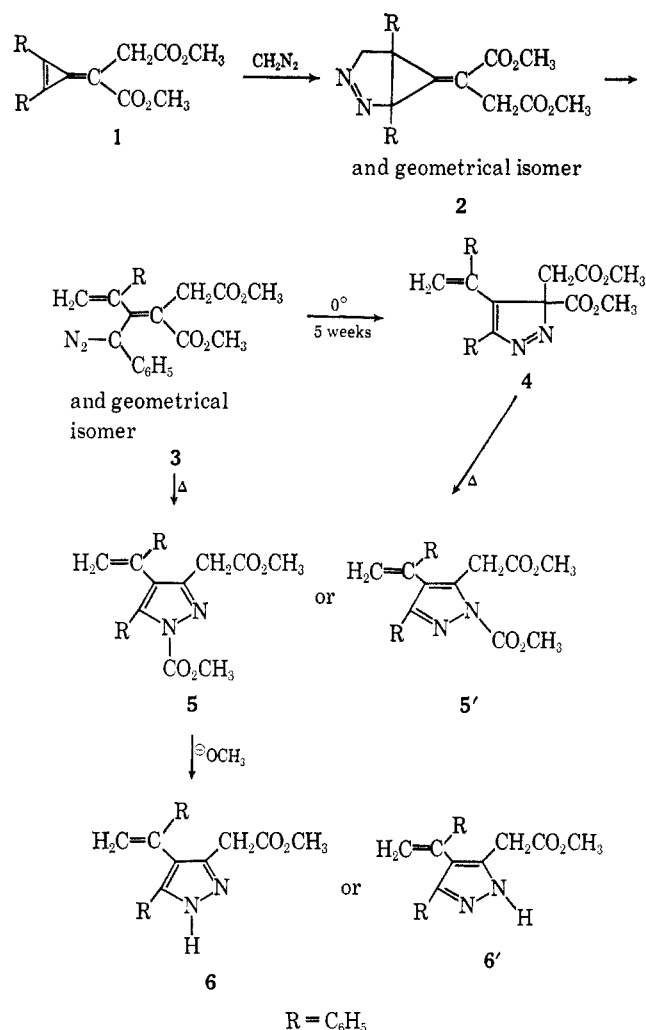
Since the expected products of reaction with either olefinic bond in 1 would be colorless, it was surprising to find that reaction of the yellow triafulvene with diazomethane produces a deep red, uncrystallizable oil.

(1) (a) Danforth Fellow, 1960–1964. (b) This paper comprises a portion of the dissertation submitted by R. Scott Pyron in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Florida. (c) Alfred P. Sloan Fellow, 1963, 1967.

(2) W. M. Jones and M. Stowe, *Tetrahedron Letters*, 3459 (1964).

(3) T. V. Van Auken and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **84**, 3736 (1962), and references included therein.

(4) W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964).



Although its thermal instability precluded analyses, it is assigned structure 3 on the basis of the following spectrometric observations as well as elemental analysis of a subsequent rearrangement product (see below). Infrared absorptions suggested the presence of conjugated and unconjugated ester groups. Both infrared (absorption at 4.85μ) and visible (absorption of $485 m\mu$) spectra argued for the phenyldiazomethane group.⁵ Finally, a terminal methylene was suggested by infrared absorptions and confirmed by the nmr spectrum (see Experimental Section).

The probable route for the formation of 3 is *via* 2. This suggestion finds sample precedents in the reports of Wiberg and Bartley,⁶ and Izzo and Kende,⁷ who found that cyclopropene and diphenylcyclopropenone were attacked by diazomethanes at the endocyclic double bond. However, whereas their intermediates opened to six-member heterocycles, 2 apparently undergoes what amounts to a X exchange between alkyl groups^{8,9} to give the observed phenyldiazomethane.

Refluxing a carbon tetrachloride solution of the diazoalkane for 1 hr effected complete decolorization to give a single crystalline product (76%) which has been

(5) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).

(6) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(7) P. T. Izzo and A. S. Kende, *Chem. Ind. (London)*, 839 (1964).

(8) D. G. Farnum and P. Yates, *Proc. Chem. Soc.*, 224 (1960).

(9) For a thorough discussion of diazo exchanges, see H. M. Walborsky and C. G. Pitt, *J. Am. Chem. Soc.*, **84**, 4831 (1962).

assigned the pyrazole structure (**5** or **5'**).¹⁰ The structural assignment was based on analyses, spectral properties, and its rather interesting reaction with base. Its infrared spectrum showed a carbonyl absorption at 5.71μ with a slight shouldering at 5.71^{11} and showed no N-H absorption. Nmr and infrared spectra indicated persistence of the terminal double bond and resonances for the aliphatic and aromatic protons were also consistent with structure **5** (see Experimental Section).

Further evidence for structure **5** was obtained by examination of products from its reaction with base in methanol. Hydrolysis in refluxing methanolic potassium hydroxide gave 86% of the carboxylic acid of **6** (or **6'**) which was converted with diazomethane to its methyl ester **6** (or **6'**). This same ester was also formed by simply treating **5** with a trace of methoxide in methanol. This reaction was rather remarkable in that it occurred essentially quantitatively almost instantaneously even at very low base concentrations ($10^{-5} M$). Furthermore, as expected, it gave a by-product, dimethyl carbonate. The structure of **6** derived from analytical data on the acid and spectra of both the acid and its methyl ester. Thus the acid showed infrared absorptions characteristic of N-H, unconjugated acid, and terminal methylene. A broad absorption at $250 m\mu$ further supported the proposed structure (see below). The nmr spectrum of the methyl ester **6** supported the assigned structures in that it showed a low-field resonance at τ 1.41 which is particularly strong evidence for the pyrazole core in the molecule.¹²

Furthermore, the single maxima at 258, 250, and $248 m\mu$ in the ultraviolet spectra of esters **5** and **6** and the acid of **6**, respectively, are also reasonable for the assigned pyrazole structure.¹³ Study of molecular models of these compounds suggests that the styryl group is prevented by steric interactions from being coplanar with the pyrazole system and thus probably has its absorption masked by the stronger absorption of the latter.

As the structure of the pyrazole (**5**) became apparent, possible routes to this material were explored. As a possible intermediate, pyrazolenine **4** was particularly attractive, not only because of the straightforward mechanism that would explain its formation from **3** but also because it would be expected to undergo facile rearrangement to the observed pyrazole.¹⁴ In fact, when the thermal isomerization of the diazoalkane **3** to the pyrazole was followed by tlc, an intermediate compound was indeed detected. This unstable intermediate was actually isolated in good yield by allowing the diazoalkane to isomerize over a 38-day period at -15° . The resulting oil was almost quantitatively converted to pyrazole **5** on heating.

(10) For other examples of isomerization of α,β -unsaturated diazoalkenes to pyrazoles, see (a) W. Adamson and J. Kenner, *J. Chem. Soc.*, **286** (1935); (b) C. D. Hurd and S. C. Lui, *J. Am. Chem. Soc.*, **57**, 2656 (1935); and (c) G. L. Closs, L. E. Closs, and W. A. Boll, *ibid.*, **85**, 3798 (1963).

(11) See E. Wahlberg, *Arkiv Kemi*, **16**, 369 (1960), for infrared spectra of similar systems.

(12) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 84-87.

(13) For model compounds, see I. I. Grandberg and A. N. Kost, *J. Gen. Chem., USSR*, **29**, 650 (1959); and D. H. R. Barton and T. Bruun, *J. Chem. Soc.*, 603 (1953).

(14) J. Van Alphen, *Rec. Trav. Chim.*, **62**, 485, 491 (1943).

On the basis of its spectra and its facile conversion to **5** we have assigned the pyrazolenine structure **4** to this product. Disappearance of the internal double bond and the diazo group of **3** were evidenced by the infrared spectrum. Nmr resonances for the aromatic and aliphatic protons of the pyrazolenine appeared in acceptable proportions and positions (see Experimental Section). The ultraviolet spectrum showed absorption at $242 m\mu$ with a much weaker absorption at $303 m\mu$. This is consistent with structure **4** since the absorbing chromophores are probably the styrene and the 1,2-diaza-3-phenyl-1,3-butadiene systems.

Experimental Section¹⁵

Reaction of Diazomethane and 1,2-Diphenyl-4-carbomethoxy-4-carbomethoxymethylmethylenecyclopropene (1).—A 0.252-g (0.75 mmole) portion of methylenecyclopropene (**1**) (prepared by the method of Jones and Denham)⁴ was dissolved in 2.5 ml of tetrahydrofuran, which had been dried over 4A sieves and passed through Woelm basic alumina (activity 1). The yellow solution was cooled in an ice-salt bath and a 10% excess of diazomethane in ether (*ca.* 0.4 *M* solution) was added. During the course of the reaction, the color changed from bright yellow to deep red. The progress of the reaction was followed by the loss of methylenecyclopropene peaks in the ultraviolet spectrum and by thin layer chromatography (tlc) on silica gel. After 3 hr tlc indicated that the yellow starting material was still present, so another small portion of diazomethane was added. After 4.75 hr, when the methylenecyclopropene was indicated to be all consumed, the mixture was evacuated with stirring and the solvent and excess diazomethane were removed. A second evacuation was performed after addition of 0.7 ml of carbon tetrachloride. The flask remained in the bath during both evacuations.

Tlc of the red oil with ether-hexane (3:2) as developer showed a deep red species with a large R_f value as the major product with small amounts of methylenecyclopropene **1** and another species at smaller R_f values. An nmr spectrum, at -13° , of the freshly prepared oil in carbon tetrachloride showed unresolved resonances at τ 2.67 and 2.82 (aromatic protons) and two smaller ones at 4.47 and 4.74 (terminal olefin protons) (relative areas 10.0, 0.87, 0.87). Much smaller broad resonances appeared at τ 4.23 and 4.59, and between 6.43 and 6.90 (aliphatic region) were six absorbances of varying intensity with their total area about the same as that in the aromatic region. There was a quintet at τ 8.29 of *ca.* $1/3$ of the area of the aromatic proton resonances. Significant peaks were present in the infrared region (CCl_4) at 4.85 ($C=N_2$), 5.71 (unconjugated $C=O$), 5.85 (conjugated $C=O$), 10.98μ . Absorption in the ultraviolet and visible regions ($MeCN$) was present at 226, 241 shoulder, 286, 330 shoulder, and $485 m\mu$ (relative ϵ 1.49, 1.42, 1.00, 0.46, and 0.01).

A red solution of this product, **2** in carbon tetrachloride was essentially decolorized in 0.5 hr at reflux temperature, overnight at room temperature, or in a month in a freezer. All attempts to crystallize the red material met with failure.

1-Carbomethoxy-3- (or 5-) carbomethoxymethyl-4-(β -styryl)-5- (or 3-) phenylpyrazole (5).—The residual red oil from 200 mg of methylenecyclopropene **1** was dissolved in 30 ml of carbon tetrachloride and brought rapidly to reflux temperature in a dark flask with a septum-covered side arm. Periodic samples were cooled rapidly and stored in a freezer prior to analysis by tlc. The latter technique demonstrated that the initial red product **2** is converted successively to a second compound and then to a third compound **5** which was stable under these conditions. The conversion to pyrazole **5** was complete in 1 hr leaving a yellow solution due to traces of methylenecyclopropene **1**. The solution was concentrated and chromatographed on 20 g of silica gel, eluting with pentane-ether (9:1, 4:1, and then 2:1). The latter solvent mixture gave several yellow cuts and washing their residues with pentane-ether gave

(15) Melting points were taken in a Thomas-Hoover Uni-melt apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infracord. Ultraviolet-visible spectra were recorded with a Cary Model 14 spectrophotometer with methanol as a solvent. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

171 mg (76%) of off-white solid, mp 100–105°. Recrystallization from 95% ethanol gave 160 mg of pyrazole 5, mp 103.5–104.5°. Some other apparently identical preparations melted at 112–114°. The lower melting form could be converted to the higher melting form by finely pulverizing it. Its nmr spectrum (CDCl₃) showed absorption at τ 2.41 and 2.79 (ten aromatic protons in unresolved multiplets), 4.09 and 4.72 (one olefinic proton in each doublet, $J = 1.35$ cps), 5.96 and 6.05 (total of five protons—one methoxyl group and the methylene group), and 6.35 (three protons in methoxyl group). Significant peaks in the infrared region (KBr) were at 5.71 (with slight shouldering) (C=O), 10.97 μ . However, in the Nujol mull the carbonyl peak was distinctly shouldered absorbing at 5.71 and 5.74 μ (shoulder). In methylene chloride it was sharp at 5.71 μ . The ultraviolet spectrum showed one rather broad peak: $\lambda_{\text{max}}^{\text{MeCN}}$ 257 μm ($\log \epsilon$ 4.40), $\lambda_{\text{max}}^{\text{MeOH}}$ 258 μm ($\log \epsilon$ 4.37).

Anal. Calcd for C₂₂H₂₀N₂O₄: C, 70.20; H, 5.36; N, 7.44. Found: C, 69.92; H, 5.57; N, 7.29.

Hydrolysis of Pyrazole 5.—A solution of 89 mg (0.23 mmole) of pyrazole 5 and 0.58 mmole of KOH in 2.6 ml of methanol was heated at reflux for 4.5 hr. After the solvent was removed under vacuum, the residue was dissolved in 6 ml of water and extracted two times with ether. The aqueous solution was acidified with 2 *N* hydrochloric acid and extracted with methylene chloride. After drying the solution, evaporation of the solvent and washing the residue with pentane–ether gave 62 mg (86% yield) of 3- (or 5-) carboxymethyl-4-(β -styryl)-5- (or 3-) phenylpyrazole (6). The melting point was 166–168° and two recrystallizations gave an analytically pure sample, mp 167–168.5°. Significant infrared absorptions (KBr) were at 2.99 (N–H), 3.27 (aromatic C–H), 3.41 (aliphatic C–H), 4.05 (broad) (acid O–H), 5.31 (broad), 5.85 (acid C=O), and 11.09 μ . The ultraviolet spectrum (MeOH) shows absorption at 248 μm ($\log \epsilon$ 4.29).

Anal. Calcd for C₁₉H₁₆N₂O₂: C, 74.98; H, 5.30; N, 9.20. Found: C, 75.10; H, 5.44; N, 8.97.

Base-Catalyzed Reaction of Pyrazole 5 in Methanol.—The progress of the hydrolysis of 5 with equivalent amounts of KOH in methanol was followed by tlc with visualization by quenching of the fluorescent indicator in the adsorbent. Development of the spots with ether–acetone (1:1) on silica gel showed compound 6 having an R_f value of 0.80 and the hydrolysis product having an R_f value 0.05. However, when the basic solution was spotted immediately after dissolution of 5, a spot was present at 0.75 which disappeared during the course of the hydrolysis with concurrent increase in the area of the low R_f value spot. A solution of 5 and KOH in methanol in an equivalent ratio of 20:1 gave similar results when analyzed by tlc, *i.e.*, only one spot was visible under ultraviolet light and that was of lower R_f value than that of 5.

A suspension of pyrazole 5 (75 mg, 0.189 mmole) in 1.5 ml of dry methanol was treated with a solution of 1 mg of sodium methoxide in 1 ml of methanol at room temperature. The solid dissolved rapidly and tlc of a sample of the solution showed one spot of R_f value 0.62 (pyrazole 5; R_f value 0.70). The solution was concentrated and diluted with carbon tetrachloride prior to preparative tlc on silica gel (*ca.* 1.0-mm layer) with acetone–ether (1:1). Extraction of the front band with acetone gave 55 mg of a viscous oil (6) which could not be induced to crystallize. It had significant peaks in the infrared region (CCl₄) at 3.14 (N–H), 5.71 (C=O), and 11.05 μ . The nuclear magnetic resonances (CCl₄) were at τ 1.14 (N–H singlet), 2.61 and 2.90 (unresolved aromatic multiplets), 4.29 and 4.85 (slightly split olefinic resonances), 6.57 (methoxyl and methylenic protons), and 8.78 (complex resonances). The relative areas were 1.2, 10 (total aromatic), 0.8, 0.8, 4.3, and 0.6. The ultraviolet spectrum was obtained by dissolving a known amount of pyrazole 5 in methanol, measuring the absorbances, and then adding a trace of sodium methoxide to the solution. After shaking the solution for a few seconds, the spectrum of monomer was obtained, $\lambda_{\text{max}}^{\text{MeOH}}$ 250 μm ($\log \epsilon$ 4.33). This peak was unchanged in position or intensity after several hours. When a small portion of the carboxylic acid described in the previous experiment was treated with diazomethane, tlc showed a single spot. This spot had an R_f value the same as that of the oil described above.

In one case, a small-scale, base-catalyzed reaction was run in a methanol–ether mixture. Tlc of the solution again showed only one spot. However, upon vapor phase chromatography (5 ft \times 1/8 in. column of 6% Apiezon L on Chromosorb Z at 30°)

of the solution, a peak appeared at a retention time that was the same as that of dimethyl carbonate.

3-Phenyl 4-(β -Styryl)-5-carbomethoxy-5-carbomethoxy-methylpyrazolenine (?) (4).—A carbon tetrachloride solution of the red diazomethane 3 was allowed to remain in a freezer for 38 days. The faintly colored solution was then chromatographed on 20 g of silica gel in an ice-water-jacketed column. Elution with pentane–ether (9:1, followed by 4:1) gave some small oily fractions followed by several cuts which were indicated by tlc to contain only one component in appreciable amounts. Its colorless thin layer spot became deep red when treated with 50% H₂SO₄ and heated. The R_f value of the compound was slightly less than that of 3 when developed with hexane–ether. This product was obtainable only as a moderately stable oil which could be maintained with little loss only at freezer temperatures or below.

The purest chromatography cuts were concentrated and the solvents were replaced with carbon tetrachloride for spectral data. Tlc indicated the presence of two minor impurities in the resulting solution. The nmr spectrum of the solution at –5° showed absorptions at τ 1.99 and 2.83 (aromatic protons) and at 4.26 and 4.80 (terminal olefinic protons) with areas in the ratio of 2:8:1:1. Two resonances of unequal area at τ 6.55 (methoxyl protons) and 6.70 (methoxyl and methylenic protons) had a total area of 7.6 relative to 10 for the aromatic protons. In addition there were small unassigned absorptions at τ 6.35, 7.17, 7.48, 8.02, and 8.83 (total relative area *ca.* 2.7). The infrared spectrum (CCl₄) exhibited significant peaks at 5.71 (sharp) (unconjugated C=O) and 10.95 μ . Absorption in the ultraviolet spectrum (MeCN) appeared at 242 and 303 μm with relative extinction coefficients *ca.* 1.0:0.2.

Registry No.—1, 1669-47-2; 2, 14565-27-6; 3, 14638-75-6; 4, 14638-76-7; 5, 14565-28-7; 6, 14565-29-8; diazomethane, 334-88-3.

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Chemistry of Furazan Derivatives. II.¹

The Reaction of Dibenzoylfuroxanes with Diazomethane

A. R. DANIEWSKI, M. WITANOWSKI,

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw 10, Poland

AND T. URBAŃSKI²

Warsaw Institute of Technology (Politechnika), Warsaw 10, Poland

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It is known³ that diazomethane reacts with aldehydes and ketones to give oxides or homologous ketones. The reaction occurs with liberation of nitrogen and is catalyzed by alcohols or water. We have now investigated the reaction of dibenzoylfuroxanes with diazomethane. No reaction occurs in dry carbon tetrachloride or chloroform, but addition of a small amount (0.5%) of methanol results in initiation of the evolution of nitrogen. Larger amounts of methanol cause degradation to the corresponding methyl benzoate derivatives. The main products of the reaction of 1 and 2 with diazomethane were isolated in about

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(2) To whom inquiries should be addressed.

(3) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).