From the mother liquors the following additional crops were obtained after treatment with activated carbon and several recrystallizations from ethanol: 1.18 g., m.p. 152–155°; resolidified, m.p. 224–245°, λ_{max} 223 mμ (ε 4650), 260 mμ (ε 96); 0.37 g., m.p. 153–157°; resolidified, m.p. 227–243°; 0.47 g., m.p. 207–242°.

Reduction using lithium instead of sodium afforded 76% of the pure pyrazole II.

17β-Hydroxy-17α-methylandrost-4-eno[3,2-*c*]-2′-methylpyrazole (III).[2b]—To a solution of 4.00 g. of 2-hydroxymethylene-17α-methylandrost-4-en-17β-ol-3-one, m.p. 179–180°,[12] in 350 ml. of ethanol was added a solution of 7.36 g. of sodium acetate trihydrate and 3.50 g. of methylhydrazine sulfate in 50 ml. of water. After the mixture was stirred and refluxed for 3.5 hr., it was concentrated under reduced pressure to a small volume and poured into 300 ml. of cold water. The mixture was filtered and the collected white solid was recrystallized from acetonitrile to yield 2.65 g. of light yellow crystals, m.p. 202–205°. Three additional recrystallizations from benzene–acetonitrile afforded 1.40 g. of fine cream colored plates, m.p. 203.6–205.8°; $[\alpha]_D$ +123.4° (chloroform); λ_{max} 219 (ε 11,100), 250 sh (ε 6300), 278 mμ (ε 10,500); δ p.p.m. (20%, $CDCl_3$), 1.45 ($C_{18}CH_3$), 1.50 ($C_{19}CH_3$), 1.77 (CH_3 at C-17), 4.30 (N–CH_3), 6.55 ($-\overset{|}{\underset{|}{C}}-$CH=), 7.72 ($-\overset{|}{N}-$CH=).

Anal. Calcd. for $C_{22}H_{30}N_2O$: C, 77.60; H, 9.47; N, 8.23. Found: C, 77.45; H, 9.33; N, 8.49.

Thin layer chromatography (2% methanol in chloroform) showed only one spot as detected by iodine, sulfuric acid, followed by heat. The previously reported sample [m.p. 175.2–193.2°; $[\alpha]_D$ +103.6° (chloroform); λ_{max} 272 mμ (ε 10,400)[2b]] was apparently a mixture of the 1′-methyl- and 2′-methylpyrazoles. The compound, whose preparation is described here, is now believed to be the 2′-methyl isomer rather than the 1′-methyl isomer because of its reduction to the known 5α-2′-methylpyrazole IV[2b] (see next paragraph). Its ultraviolet spectrum compared favorably with the spectrum [λ_{max}^{MeOH} 277.5 mμ (ε 10,200)] of 17α,20;20,21-bismethylenedioxy-11β-hydroxy-2′,16α-dimethyl-4-pregneno[3,2-*c*]pyrazole.[13]

Reduction of 17β-Hydroxy-17α-methylandrost-4-eno[3,2-*c*]-2′-methylpyrazole (III).—To a solution of 100 mg. of 17β-hydroxy-17α-methylandrost-4-eno[3,2-*c*]-2′-methylpyrazole (III), m.p. 203.6–205.8°, in 25 ml. of dry tetrahydrofuran and 35 ml. of dry *t*-butyl alcohol and 50 ml. of liquid ammonia was added 150 mg. of lithium wire. The dark blue mixture with bronze liquid floating on top was stirred and refluxed for two hours. The mixture turned colorless in 1.5 hr. Methanol (10 ml.) was added and the ammonia was allowed to evaporate. The mixture was concentrated to dryness under reduced pressure and the residue was taken up in ethyl acetate–water. The organic layer was washed with water and saturated sodium chloride solution and filtered through anhydrous sodium sulfate. Concentration of the solution under reduced pressure afforded colorless crystals, m.p. 217--222°. Recrystallization from acetone afforded 75 mg. of colorless flakes, m.p. 221.4–222.2°; $[\alpha]_D$ +37.6° (ethanol); λ_{max} 229 mμ (ε 4800); δ p.p.m. (10%, $CDCl_3$), 1.25 ($C_{18}CH_3$), 1.40 ($C_{19}CH_3$), 1.75 (CH_3 at C-17), 4.25 ($-\overset{|}{N}-CH_3$), 7.79 (–N=CH–).

Anal. Calcd. for $C_{22}H_{34}N_2O$: C, 77.14; H, 10.01. Found: C, 77.13; H, 10.08.

Thin layer chromatography (2% methanol in chloroform) showed only one spot as detected by iodine, sulfuric acid, followed by heat. The previously reported sample,[2b] prepared by the pyrolysis of the N-methylsemicarbazone of 2-hydroxymethylene-17α-methylandrostan-17β-ol-3-one [m.p. 186.6–198.0°, $[\alpha]_D$ +38.3° (EtOH), λ_{max} 229 mμ (ε 4900)] was apparently a mixture of mostly the 2′-methylpyrazole contaminated with the 1′-methylpyrazole. An examination of the n.m.r. spectrum of this sample (in chloroform, internal tetramethylsilane standard) shows two N-methyl peaks at 3.77 and 3.80 p.p.m. in a 3:2 ratio.

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[12] H. J. Ringold, E. Batres, O. Halpern, and E. Necoechea, *J. Am. Chem. Soc.*, **81**, 427 (1959).

[13] R. Hirschmann, N. G. Steinberg, P. Buchschacher, J. H. Fried, G. J. Kent, M. Tishler, and S. L. Steelman, *ibid.*, **85**, 120 (1963). The 1′-methyl isomer had λ_{max}^{MeOH} 266.5 mμ (ε 13,100).

Pyrazolines. VIII. The Syntheses of 5,5-Diaryl-2-pyrazolines from the Reaction of Diazoalkanes with Methyl Acrylate[1]

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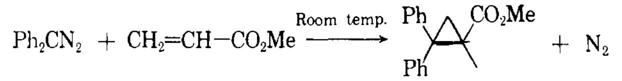
Received March 26, 1963

In the course of some kinetic studies on the thermal decomposition of selected 2-pyrazolines[2] we needed a sample of 5,5-diphenyl-3-carbomethoxy-2-pyrazoline I. However, a literature check showed that although the reaction of diphenyldiazomethane with methyl acrylate had been effected,[3] the actual isolation of the pyrazoline was not reported. This might not have been particularly surprising since this type of reaction has been often used for the synthesis of cyclopropanes[4] without concern for the presumed intermediate pyrazoline. However, the surprising feature of this observation was the fact that spontaneous nitrogen evolution is observed when diphenyldiazomethane is added to methyl acrylate.[3] This is in contrast to the fact that in most cases where the reaction of a diazoalkane with an *alpha,beta*-unsaturated addend is used to effect the synthesis of a cyclopropane, the pyrazoline is first formed and then must be heated to varying temperatures to give the desired products.



A more careful perusal of the literature very quickly showed that although diphenyldiazomethane does lead to pyrazolines with some addends,[5-9] spontaneous cyclopropane formation has also been observed in several cases.[3,6,7,10,11] Furthermore, many cases of spontaneous cyclopropane formation in this type of reaction have been observed with the closely analogous diazofluorene.[12]

Spontaneous nitrogen evolution from reactions of diazoalkanes with *alpha,beta*-unsaturated addends has been recognized as being anomolous and has been discussed.[11-13] In general, the available evidence indicates that spontaneous formation of nitrogen-free products in this type of reaction involves initial formation of the 1-pyrazoline which then decomposes under

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[1] For the previous paper in this series, see W. M. Jones and W. T. Tai, *J. Org. Chem.*, **27**, 1324 (1962).

[2] Unpublished work of D. G. Baarda.

[3] H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955).

[4] *Cf.* T. L. Jacobs in R. C. Elderfield, "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, New York, 1957, Chap. 2.

[5] H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, **49**, 1928 (1916).

[6] J. van Alphen, *Rec. trav. chim.*, **62**, 210 (1943).

[7] J. van Alphen, *ibid.*, **62**, 334 (1943).

[8] W. M. Jones, *J. Am. Chem. Soc.*, **81**, 3776 (1959).

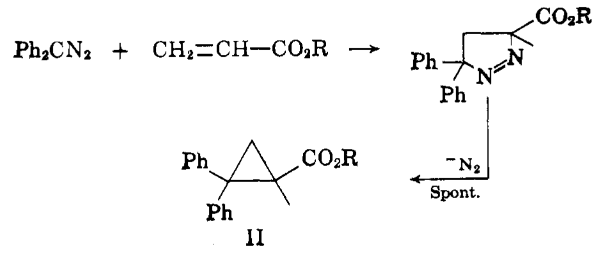
[9] L. F. Fieser and M. A. Peters, *ibid.*, **53**, 4080 (1931).

[10] F. J. Impasto, L. Barash, and H. M. Walborsky, *ibid.*, **81**, 1514 (1959).

[11] L. I. Smith and K. L. Howard, *ibid.*, **65**, 159 (1943).

[12] L. Horner and E. Lingnau, *Ann.*, **591**, 21 (1955).

[13] W. G. Young, L. J. Andrews, S. L. Lindenbaum, and S. J. Cristol, *J. Am. Chem. Soc.*, **66**, 810 (1944).



the reaction conditions (usually room temperature) to the cyclopropane.[14]

In view of the probable formation of the 1-pyrazoline in the reaction of diphenyldiazomethane with methyl acrylate, we felt that we might be able to find conditions under which the reaction would either stop at this point or, possibly be diverted to the desired 2-pyrazoline. The purpose of this note is to report experimental conditions under which a high yield of 5,5-diphenyl-3-carbomethoxy-2-pyrazoline I can be isolated from the reaction of diphenyldiazomethane with methyl acrylate.

Table I reports the results of a series of experiments under a variety of conditions on the reaction of diphenyldiazomethane with methyl acrylate. Gas evolution was generally taken as a semiquantitative measure of the relative amounts of cyclopropane and 2-pyrazoline formed except in those cases where either no nitrogen or nearly quantitative nitrogen was observed. In the latter two cases, the products were actually isolated. In the cases where nearly quantitative nitrogen was observed, up to 91% of the cyclopropane II was isolated. In the cases where no gas evolution was observed, up to 70% of the pure (recrystallized to 2° melting point range) 2-pyrazoline I was isolated.

TABLE I

REACTIONS OF DIPHENYLDIAZOMETHANE WITH METHYL ACRYLATE

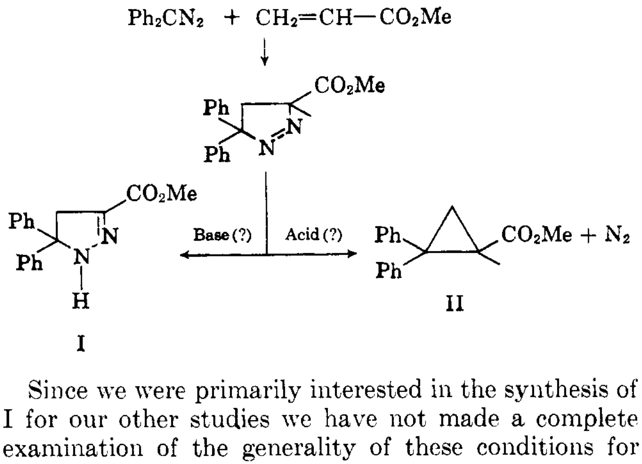
	Flask I[a]		Flask II[b]		Flask III[c]	
Temp., °C.	% N_2 evol.	Product	% N_2 evol.	Product	% N_2 evol.	Product
0°	60 ± 9[d]	[f]	0	Pyraz.[e]	30 ± 9[d]	[f]
20°	80 ± 12[d]	Cyclopropane[g]	10 ± 2[d]	Pyraz.[e]	20 ± 4[d]	Pyraz.[e]
0°			0[h]	Pyraz.[e]	0[h]	Pyraz.[e]
20°	20 ± 5[d,h]	[f]	0[h]	Pyraz.[e]	0[h]	Pyraz.[e]

[a] Flask washed with dichromic acid and rinsed three times with distilled water and dried. [b] Flask washed with trisodium phosphate and rinsed three times and dried. [c] New flask, washed with distilled water and dried. [d] Average of at least five runs. [e] 5,5-Diphenyl-3-carbomethoxy-2-pyrazoline. [f] Product not isolated. [g] Methyl-2,2-diphenylcyclopropyl carboxylate. [h] Run in the presence of an equimolar quantity of triethylamine.

Several features of the experimental conditions investigated deserve some mention. First, we found it most interesting that the preparation of the reaction flask was very important. For example, if the flask was washed with acid, rinsed three times with distilled water and dried, it invariably led to large quantities of nitrogen and cyclopropane. On the other hand, rinsing the flask with a saturated solution of trisodium phosphate, followed by three rinses with distilled water and drying, led to high yields of the pyrazoline. When the reaction was carried out in a new flask or in a polyethylene vessel, apparently a large amount of pyrazoline was formed, although this was invariably accompanied by some nitrogen evolution (usually corresponding to about 30% of the calculated). Finally, it was found that as a synthetic method, the most consistent results were obtained when the reaction was conducted in a base-washed flask in the presence of an added base (triethylamine).

A second feature of the reaction that we found to be interesting was the fact that the course of the reaction was apparently affected by the temperature. However, for synthetic purposes it was found that so long as the temperature was maintained at room temperature or below and the reaction run in a base-washed flask in the presence of triethylamine, the reaction gave good yields of the pyrazoline.

The results outlined in Table I lead to certain conclusions regarding the course of the spontaneous formation of cyclopropanes in the reactions of diazoalkanes with unsaturated compounds. In particular, either the traces of acid that are probably present on the inside surface of the acid washed glassware catalyze the loss of nitrogen from an unlikely intermediate zwitterion[14] or the cyclopropane formation requires initial formation of the 1-pyrazoline. It is obvious that the former of these two possibilities is unlikely. The point of real interest is the function of the acid on the decomposition of the 1-pyrazoline. It could either be acting as a catalyst for the decomposition of the 1-pyrazoline or it could simply remove base from the reaction. The latter possibility requires a particular function of the base and the most obvious one is as a proton transfer agent to competitively convert the 1-pyrazoline to the thermally more stable 2-pyrazoline. The fact that the 2-pyrazoline actually precipitated out of solution in many instances in the presence of base certainly suggests the latter function of the base. However, this does not exclude the possibility of acid catalyzing the decomposition of the 1-pyrazoline. This fascinating possibility is presently under investigation.



Since we were primarily interested in the synthesis of I for our other studies we have not made a complete examination of the generality of these conditions for other reported cases of spontaneous cyclopropane for-

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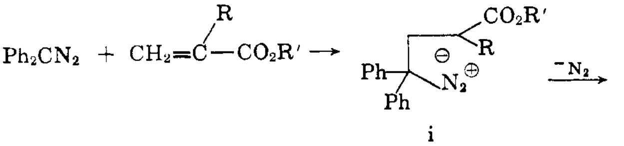
(14) Impastato, Barash, and Walborsky (see ref. 10) have suggested the possibility that the reaction of diphenyldiazomethane with menthyl acrylate and menthyl methacrylate leads to initial formation of a zwitterion i that loses nitrogen before closing to the pyrazoline. However, in light of the



i

kinetic studies of Horner and Lingnau (see ref. 12) and Huisgen and his group [R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961)], the isolation of pyrazolines from certain other addends (see ref. 5-9) and the results reported in this note, there can be little doubt that their alternate suggestion of the 1-pyrazoline as a distinct intermediate is the correct one.

mation. However, we felt that it would be most interesting to examine at least one example involving diazofluorene. We felt that this would be particularly interesting since Horner and Lingnau[12] have found that of the many addends that they investigated, in no case were they able to isolate the pyrazoline. Under the conditions of a base-washed flask in the presence of triethylamine, methyl acrylate gave a 75% yield of the corresponding recrystallized 2-pyrazoline.

It, therefore, appears that the conditions discussed above might be fairly general for the synthesis of 2-pyrazolines with two phenyl rings attached to the number five carbon.

Experimental[15]

Diphenyldiazomethane.—Diphenyldiazomethane was prepared by the method of Miller[16] with one modification. The oxidation was conducted in an open flask at room temperature with vigorous stirring.

Diazofluorene.—Diazofluorene was prepared according to the method of Schonberg, Awad, and Liatif,[17] m.p. 93–94.5°, lit. m.p. 94–95°.

General Procedure for the Reaction of Diphenyldiazomethane with Methyl Acrylate.—Reactions were run in stock, three-neck 100-ml. flasks. The flask was equipped with a pressure-equalizing addition funnel, a ball joint Herschberg stirrer, and an outlet to a gas buret. The flask was immersed in a 30-gal. tank equipped with a thermostatically controlled refrigerating unit and a continuous duty recirculating pump. This apparatus was capable of maintaining a preset temperature of ±0.5°. In a typical run, 0.55 g. (6.4 mmoles) of freshly distilled methyl acrylate and 25 ml. of the reaction solvent (usually pentane or hexane) were placed in the previously prepared reaction flask. In the runs using base, 0.571 g. (6.43 mmoles) of freshly distilled triethylamine was introduced into the reaction flask at this point. Diphenyldiazomethane (1.13 g., 5.83 mmoles) was dissolved in 25 ml. of the solvent and placed in the addition funnel. When the closed system had come to equilibrium, the solution of diazoalkane was added rapidly to the reaction mixture. The mixture was then stirred until either the color had disappeared or until gas evolution ceased. In general, at 20° in the presence of triethylamine, the reaction required approximately 16 hr. to reach completion.

The reaction mixture was worked up only if the amount of nitrogen evolved was negligible or nearly quantitative.

5,5-Diphenyl-3-carbomethoxy-2-pyrazoline.—The pyrazoline ester was obtained by removing the solvent on a Roto-Vac at room temperature from the above mixture (from which no gas evolution had been observed) and crystallizing the residue from methanol-water. In this manner, as high as 70% of the calculated amount of pure pyrazoline was obtained, m.p. 138–140° dec. Instability of the ester (apparently due to small quantities of oxygen) precluded sending the material off for analysis. However, nitrogen analysis was effected in these laboratories.

Anal. Calcd. $C_{17}H_{16}N_2O_2$: N, 10.01. Found: N, 10.09. The 2-pyrazoline was further characterized by its infrared and ultraviolet spectra. In the infrared, the compound showed strong absorptions at 3.00 (N–H), 6.00 (conjugated C=O), 6.42 μ (C=N). In the ultraviolet, the product showed one absorption at 298 mμ (log ϵ 4.02), in methanol.

5,5-Diphenyl-2-pyrazoline-3-carboxylic Acid.—A reaction mixture obtained by the above synthetic method using diphenyldiazomethane in the presence of triethylamine was worked up by first removing the solvent on a Roto-Vac, being careful to keep the temperature at 0°. The residue was then treated with cold methanol containing a slight excess of the calculated amount of potassium hydroxide. This mixture was then placed in the refrigerator overnight. The alcohol was removed from the reaction mixture and the residue taken up in water. Following acidification, the pyrazoline acid crystallized on the side of the flask on gentle warming. The crystalline acid was collected and recrystallized from methanol-water to give 70% (average of several runs) of acid, m.p. 187–189° dec. Several recrystallizations from methanol–water gave an analytical sample, m.p. 188–189° dec. Infrared absorptions appeared at 3.00 (N–H), 3.8 (broad absorption, O–H), 6.00 (conjugated carbonyl), 6.40 μ, (C=N). The acid showed a maximum in the ultraviolet at 292 mμ, (log ϵ 3.89), in methanol. Due to the sensitivity of the pyrazoline to oxygen, the recrystallized samples were stored under dry argon.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.28; H, 5.40; N, 10.51.

2,2-Diphenylcyclopropanecarboxylic Acid.—This known acid[3,10] was isolated in high yield (average of several runs, 86%) from crude reaction mixtures from which nearly quantitative nitrogen evolution had been observed. Isolation was effected by evaporating the reaction mixture *in vacuo* to near dryness. The residue was dissolved in methanol containing a slight excess of the calculated amount of potassium hydroxide and allowed to remain at room temperature overnight. The alcohol was removed from the reaction mixture and the residue taken up in water. The acid precipitated upon acidification of the aqueous solution, m.p. 161–163°, lit.[10,3] m.p. 163–164.5°, 170–171°. Recrystallization from acetone–water gave a product, m.p. 167–169°.

Reaction of Diazofluorene with Methyl Acrylate.—The reaction between diazofluorene and methyl acrylate was carried out in the manner as described for the reaction with diphenyldiazomethane with a few minor changes. Enough benzene was used in the reaction mixture to bring all of the diazofluorene into solution. It was also found that 20–24 hr. were generally required to complete the reaction. The pyrazoline ester was isolated by filtering a reaction mixture (run in a base-washed flask in the presence of triethylamine) in which no nitrogen evolution had been observed (75% yield, m.p. 187–189° dec.). Recrystallization from methanol–water gave colorless crystals, m.p. 188–189° dec. Significant infrared absorptions appeared at 2.99, 6.01 and 6.51 μ.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.10; H, 5.41; N, 10.03. Found: C, 73.17; H, 5.15; N, 10.10.

The acid was isolated in exactly the same manner as described above. The recrystallized acid (75% calcd., m.p. 169–171° dec.) decomposes so rapidly that analysis was not possible. However, its infrared spectrum was typical of a 2-pyrazoline acid showing a sharp N–H absorption at 3.00, a broad O–H band centering about 3.9, a conjugated carbonyl at 6.09 and a C=N peak at 6.49 μ. Further evidence for the structure was obtained by converting the acid back to the analyzed and characterized ester by adding the acid to a solution of diazomethane in ether and evaporating to dryness.

Acknowledgment.—The authors are most grateful to the National Science Foundation for its support of this work.

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[15] Melting points are uncorrected.

[16] J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

[17] A. Schonberg, W. Awad, and N. J. Liatif, *J. Chem. Soc.*, 1368 (1951).

Organoboron Compounds. XV. Equilibrium in the Thermal Isomerization of Secondary and Tertiary to Primary Alkyl Groups in Trialkylboranes[1,2]

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In connection with a detailed study of the kinetics of the thermal isomerization[3] of secondary and tertiary alkyl to primary alkyl groups in trialkylboranes, it was necessary to establish if equilibrium existed among

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[1] Previous paper, P. A. McCusker, P. L. Pennartz, and R. C. Pilger, Jr., *J. Am. Chem. Soc.*, **84**, 4362 (1962).

[2] Contribution from the Radiation Laboratory operated by the University of Notre Dame under contract with the Atomic Energy Commission.

[3] Reviewed by H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chap. 9, pp. 136–149.