Table IV

Summary of the Physical Constants of the Diazonium Salts

Amine used	Yield of diazonium fluoroborate, %	Recrystn. solvent	Dec. temp., °C. (uncor.)	% C[a] Calcd.	% C[a] Found	% H[a] Calcd.	% H[a] Found	% N[a] Calcd.	% N[a] Found
o-Anisidine[b]	40	Methanol	95–97	37.9	37.5	3.16	3.33	12.6	12.4
m-Anisidine[c]	30	Methanol	80–81	37.9	38.0	3.16	3.44	12.6	12.4
p-Anisidine[d]	72	Methanol	143	37.9	38.0	3.16	3.39	12.6	12.6
2,4-Dimethoxyaniline	40	Methanol	*e*	38.2	38.5	3.58	3.62	11.1	11.3
2,5-Dimethoxyaniline	55	Methanol–ether	109	38.2	37.9	3.58	3.53	11.1	11.2
2,6-Dimethoxyaniline	52	Methanol	*e*	38.2	38.2	3.58	3.67	11.1	11.1
3,4-Dimethoxyaniline	60	Methanol	116	38.2	38.4	3.58	3.58	11.1	11.1
2,4,6-Trimethoxyaniline	62	Water	*e*	38.4	37.8	3.91	3.94	9.95	9.98
2,3,5-Trimethoxyaniline	65	Methanol	127	38.4	38.4	3.91	3.88	9.95	10.2
3,4,5-Trimethoxyaniline	62	Methanol–water	116	38.4	38.6	3.91	3.95	9.95	10.2
2,4,5-Trimethoxyaniline	74	Ethanol–water	*e*	38.4	38.4	3.91	3.83	9.95	9.92

[a] Footnote 18. [b] G. Schiemann and M. Seyhan, *Ber.*, 70, 2396 (1937). [c] B. C. Berker and R. Adams, *J. Am. Chem. Soc.*, 54, 2973 (1932). [d] A. Roe, *Org. Reactions*, 5, 205 (1957). [e] Not determined.

Table V

Buffer Solutions Measured at 27° and $\mu = 0.25$

	pH	Components (g./l.)
A	4.27	$CH_3CO_2Na \cdot 3H_2O$ (1.3), CH_3CO_2H (0.60), KCl (18.9)
B	5.95	KH_2PO_4 (23.2), Na_2HPO_4 (4.3), KCl (3.7)
C	6.40	$Na_2HPO_4 \cdot 12H_2O$ (1.8), $Na_2HPO_4 \cdot 2H_2O$ (1.5), KCl (16.7)
D	7.95	Boric acid (11.8), borax (9.1), KCl (3.7)
E	9.08	Boric acid (6.2), borax (38.1), KCl (3.7)

system that was described by Zollinger[8] to obtain pseudo-first-order rate constants was used in these experiments, except that the actual rate data were obtained by a continuous measurement of the optical density of the dyes formed. We followed Zollinger's method for evaluating the true second-order rate constant from the observed first-order rate constant. The first-order rate constant, k_1, comes from a coupling reaction where the concentration of the coupler is kept relatively constant in a buffer-controlled equilibrium.

$$k_1 \text{ (observed)} = k_2 \text{ (diazonium) (naphtholate anion)} \quad (1)$$

$$\frac{\text{(naphtholate anion) }(\text{H}^+)}{\text{(naphthol)}} = K_{\text{equil}} \quad (2)$$

The second-order constant can be calculated from the preceding relationships (eq. 1 and 2). The appropriate amount of diazonium salt was dissolved in water such that a 1.0-ml. aliquot would produce enough dye to give a final optical density of approximately 2.0 in the 5000-Å. region. This aliquot and 3.0 ml. of .012 *M* sodium 6-naphthol-2-sulfonate were added to 26 ml. of buffer solution. The final ionic strength was 0.22. The kinetic data were analyzed by taking the final optical density as proportional to the initial diazonium ion concentration and ($\text{O.D.}_{\infty} - \text{O.D.}_t$) as proportional to the diazonium concentration at any time, *t*. Clean, first-order plots were obtained in all cases. The details of the individual kinetic runs are given in Table III.

The Preparation and Properties of Some Salts of 2,2-Diphenylcyclopropyldiazonium Hydroxide[1]

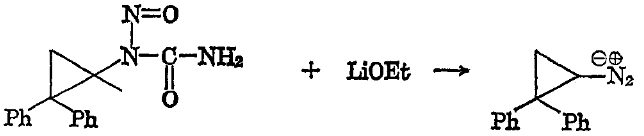
T. K. Tandy, Jr., and W. M. Jones[2]

Department of Chemistry, University of Florida, Gainesville, Florida

Received May 10, 1965

In the course of our investigation of the base-induced decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)urea, we have succeeded in isolating several salts of 2,2-diphenylcyclopropyldiazonium hydroxide. The methods of preparation of this unusual and interesting type of compound are discussed as are their reactions with acylating agents and benzoic acid.

In the course of our investigations on the base-induced conversion of N-nitroso-N-(2,2-diphenylcyclopropyl)urea to 2,2-diphenyldiazocyclopropane,[3,4] we have succeeded in isolating several salts of 2,2-diphenylcyclopropyldiazonium hydroxide (III).



I II

The purpose of this paper is to report the method of synthesis of this interesting and relatively rare type of molecule[5] and to report some of the chemical properties of these salts that do not relate directly to the course of the conversion of N-nitroso-N-(2,2-diphenylchloropropyl)urea to 2,2-diphenyldiazocyclopropane. In another paper,[4] we reported the properties of these salts that do pertain to the mechanism of this specific reaction.

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[1] Based upon a dissertation submitted by Thomas King Tandy, Jr. in 1964 to the Faculty of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Alfred P. Sloan Fellow.

[3] *Cf.* W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963), and references cited therein.

[4] W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *ibid.*, in press.

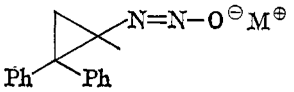
[5] To the best of our knowledge, the only other aliphatic diazotates that have been reported are some salts of methyl and benzyl diazonium hydroxide.[6-9]

[6] A. Hantzsch and M. Lehman, *Ber.*, **35**, 897 (1902).

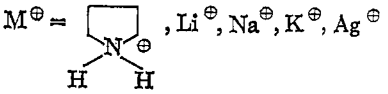
[7] J. Thiele, *Ann.*, **376**, 239 (1910).

[8] E. Mueller, W. Hoppe, H. Hagenmaier, H. Haiss, R. Huber, W. Rundel, and H. Suhr, *Ber.*, **96**, 1712 (1963); E. Mueller, W. Rundel, H. Haiss, and H. Hagenmaier, *Z. Naturforsch.*, **b15**, 751 (1960).

[9] For a general discussion on both aliphatic and aromatic diazotates, see H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 44–67.

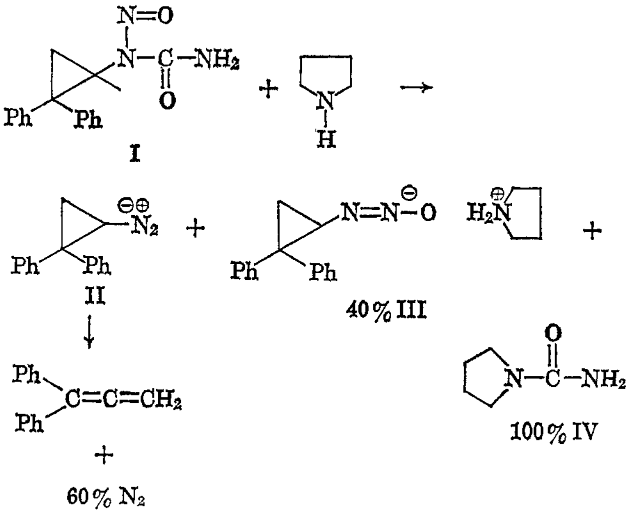


III

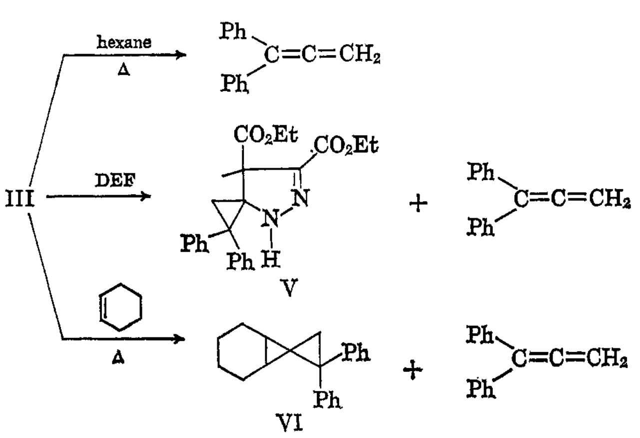


Preparation of Pyrrolidinium 2,2-Diphenylcyclopropyldiazotate.—Pyrrolidinium 2,2-diphenylcyclopropyldiazotate (III) was isolated in 40% yield from the reaction of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea (I) with an excess of pyrrolidine in ether at 0°. The diazotate formation was accompanied by *ca.* 60% nitrogen evolution (apparently owing to the formation of 2,2-diphenyldiazocyclopropane which spontaneously decomposes to 1,1-diphenylallene and nitrogen[3]) and quantitative precipitation of N-pyrrolidinylcarboxamide (IV).

Pyrrolidinium 2,2-diphenylcyclopropyldiazotate (III) is a white solid that melts sharply with decomposition at 85°. It is unstable to moisture, decomposing rather rapidly in aqueous solution and slowly when exposed as a solid to the atmosphere. Decomposition either thermally or by moisture is accompanied by the liberation of pyrrolidine. Reproducible analyses could not be obtained. The infrared spectrum was instructive in that it showed a group of rather broad peaks between 3.5 and 4.5 μ that can be assigned to the NH_2^+ stretching vibrations. It also showed typical monosubstituted phenyl absorptions.



Perhaps the strongest evidence for the suggested diazotate structure is the fact that, upon heating, III gives products that would be expected from 2,2-diphenyldiazocyclopropane (II).[10] Thus, in hot hexane, the diazotate is thermally unstable and gives 1,1-diphenylallane. Thermal decomposition in the presence of an olefin acceptor gave the spiropentane VI and 1,1-diphenylallene. Finally, decomposition in the presence of diethyl fumarate (DEF) gave the pyrazoline V and 1,1-diphenylallene. Thus, in summary, the primary points favoring the suggested diazotate structure are the following. The salt is formed in a reaction that gives a quantitative yield of N-pyrrolidinylcarboxamide. This indicates quantitative loss of the carboxamide group from the nitrosourea.[11] The infrared spectrum and the liberation of pyrrolidine upon aqueous decomposition of the salt indicate the presence of the pyrrolidinium cation. Conversion to the pyrazoline V and the spiropentane VI is strong evidence that the 2,2-diphenylcyclopropyl ring is intact in the salt and, furthermore, is highly suggestive of the diazotate structure. Finally, the pyrrolidinium salt is readily converted to alkali metal salts for which there is additional evidence for the diazotate structure (see below).



Preparation of Alkali Metal Salts of 2,2-Diphenylcyclopropyldiazonium Hydroxide.—When a sample of the pyrrolidinium diazotate was added to a small amount of 5% aqueous sodium, potassium, or lithium hydroxide, the salt completely dissolved. However, after standing for a few minutes, white crystals began to form. Similar to the pyrrolidinium salt, these white solids are stable in aqueous base but decompose slowly when dissolved in tap water. The decomposition is accompanied by the evolution of a gas. Acidification of a freshly prepared aqueous solution of any of these salts gave a precipitate (probably the diazonium hydroxide) which very rapidly decomposed with the evolution of a gas (presumably nitrogen). Moreover, when dry carbon dioxide was passed through an ether slurry of the lithium salt, 1,1-diphenylallene, the decomposition product of 2,2-diphenyldiazocyclopropane, was formed. All of these properties are consistent with those reported for sodium methyldiazotate.[6-8] Difficulty in the manipulation and drying of the salts prepared in the above manner prompted efforts to synthesize the alkali metal derivatives alternatively.

It was found that the potassium (or lithium) salt could be rather easily prepared by reduced-pressure evaporation of a solution of the pyrrolidinium diazotate in methanol containing 1 equiv. of potassium (or lithium) hydroxide. When the resulting thick brown oil was leached with anhydrous ether, the potassium (or lithium) diazotate crystallized as a pale yellow solid, normally in yields of about 75%. The infrared spectra (KBr) showed that these salts are probably alcoholates. This is consistent with the observations of other investigators who have found that diazotates commonly crystallize as alcoholates.[9] The lithium salt was also conveniently prepared by the addition of 1 equiv. of lithium ethoxide to an ether solution of

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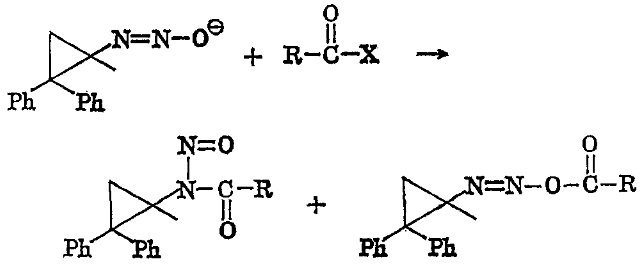
[10] This is despite the fact that it has been clearly shown[4] that this is *not* the precursor of 2,2-diphenyldiazocyclopropane in the pyrrolidine-induced conversion of the nitrosourea to this diazo compound.

[11] For a suggested mechanism for this conversion, see ref. 4.

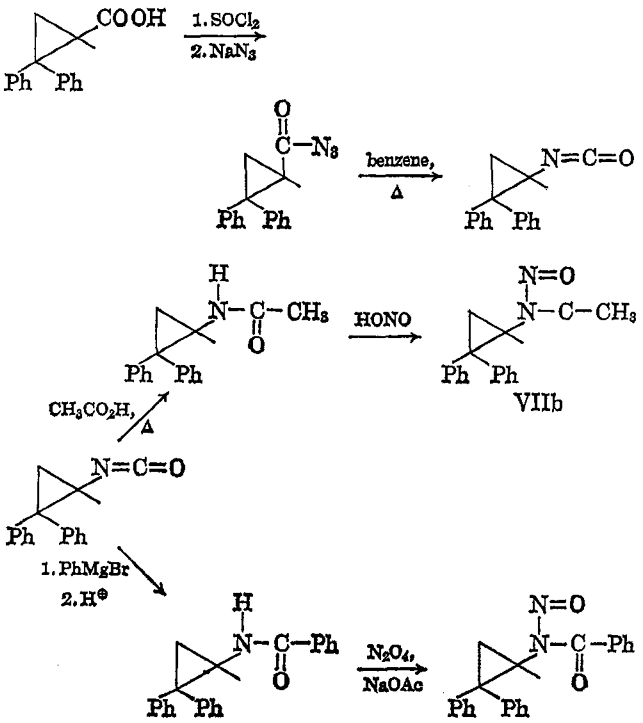
pyrrolidinium diazotate. Upon stirring overnight, the lithium salt precipitated in nearly quantitative yield.

Reaction of Lithium 2,2-Diphenylcyclopropyldiazotate with Acylating Agents.—In an attempt to obtain additional evidence for the diazotate structures, the lithium salt was treated with benzoyl chloride, acetyl chloride, and acetic anhydride. By analogy with the acylation of potassium methyldiazotate[8] and aromatic diazotates,[8,12] we anticipated the formation of a mixture of the corresponding nitrosoamides (VII) and the products that would result from the decomposition of the diazo ester VIII (presumably the diazocyclopropane[13,14]). To our initial surprise, infrared spectra of the product oils from all of these reactions showed no absorption maxima between 5.75 and 5.85 μ or around 6.65 μ, thus suggesting that virtually none of the nitrosoamides were formed. Alternate synthesis of both nitrosamides by the preceding scheme and demonstration of their stability to reaction conditions eliminated the possibility that they had been formed and then decomposed. The absence of these products was further confirmed by chromatography of the crude reaction mixtures of silica gel, using conditions which were independently shown to be effective for isolating the nitrosoamides.



VII VIII

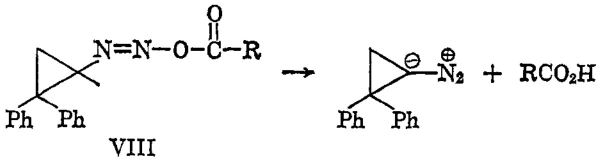
a, $R = C_6H_5$; $X = Cl$
b, $R = CH_3$; $X = Cl$
c, $R = CH_3$; $X = O-\overset{O}{\overset{\|}{C}}-CH_3$



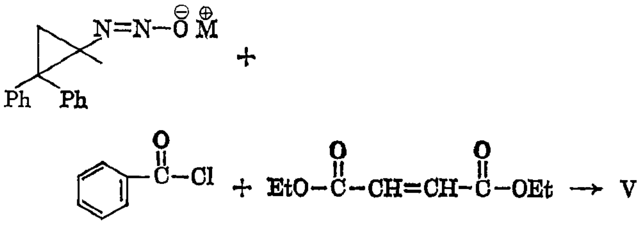
VIIb

VIIa

The search for products that would be expected to arise from O-acylation proved to be more fruitful. Acylation on the diazotate oxygen would give rise to a diazo ester (VIII). In line with the rather extensive studies that have been reported on this type of compound,[13,14] the diazo ester would be expected to decompose rapidly to give 2,2-diphenyldiazocyclopropane and the corresponding carboxylic acid. The formation of 2,2-diphenyldiazocyclopropane was suggested with the detection of 1,1-diphenylallene in all of the acylation reactions and was confirmed by effecting the acylation of the diazotate in the presence of diethyl fumarate. Under these conditions, the pyrazoline (V) was isolated.



VIII



Additional evidence for the formation of 2,2-diphenyldiazocyclopropane from the acylation of the diazotate was obtained from the reaction of lithium or potassium 2,2-diphenylcyclopropyldiazotate with excess benzoyl chloride in ether at 0°. Under these conditions, a yellow-orange color developed almost immediately and persisted throughout the reaction. Evaporation of the reaction mixture to dryness gave an unstable orange oil. The infrared spectrum of this oil showed, in addition to the absorptions that are typical of 1,1-diphenylallene and benzoyl chloride, two peaks at 4.75 and 6.2 μ, absorptions that suggested a diazo ketone structure.[15] Unfortunately, this particular component of the mixture was too unstable to isolate in pure form. For example, all attempts to chromatograph the crude reaction mixture led to nitrogen evolution and loss of the unknown. We also attempted to characterize this material by Wolff rearrangement,[16] pyrazoline formation and tosylate formation by the method of Crowther and Holt.[17] All of these attempts were unsuccessful. However, we did succeed in gaining some insight into the structure of this material by approaching the problem from an entirely different direction. As a working hypothesis, we assumed that the diazo ketone resulted from reaction of 2,2-diphenyldiazo-

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[12] Reference 9, p. 154.

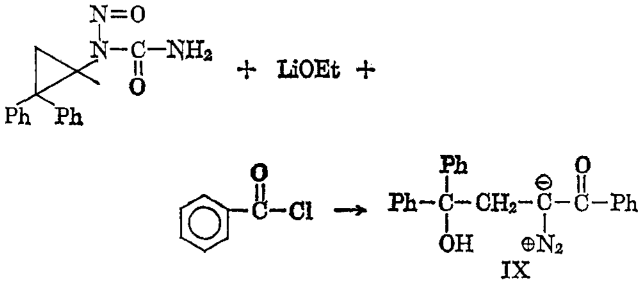
[13] W. M. Jones, M. H. Grasley, and D. G. Baarda, *J. Am. Chem. Soc.*, **86**, 912 (1964).

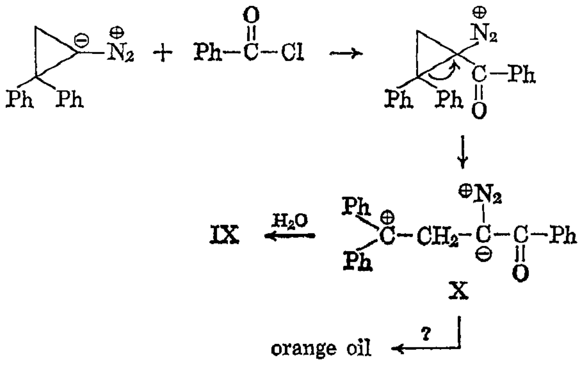
[14] For many examples of the thermal conversion of diazo esters to diazoalkanes, see E. H. White and R. J. Baumagarten, *J. Org. Chem.*, **29**, 2070 (1964); E. H. White, and C. A. Aufdermarsh *J. Am. Chem. Soc.*, **83**, 1174 (1961); E. H. White, *ibid.*, **77**, 6013 (1955); A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957); A. R. Huisgen and R. Reimlinger, *Ann.*, **599**, 183 (1956).

[15] P. Yates, B. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

[16] W. E. Bachmann and W. S. Struve, *Org. Reactions*, **1**, 39 (1942).

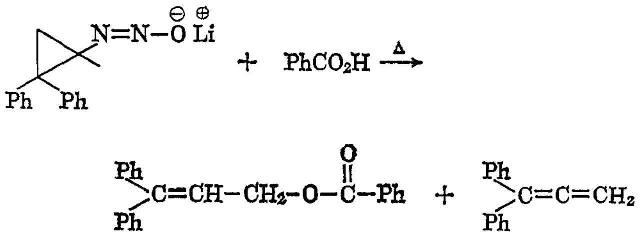
cyclopropane with benzoyl chloride. To test this, 2,2-diphenyldiazocyclopropane was generated [from reaction of the nitrosourea (I) with lithium ethoxide] in the presence of benzoyl chloride and, indeed, under these conditions, we again observed the orange oil. However, in addition, there was isolated a yellow solid which showed proper analysis and infrared and n.m.r. spectra for the hydroxy diazo ketone IX. Furthermore, when the same reaction was run in the presence of magnesium sulfate (to assure anhydrous conditions), the unknown orange oil was formed at the expense of hydroxydiazo ketone IX. These observations are readily rationalized by the following reaction scheme[18] in which the orange oil and the hydroxydiazo ketone have the common precursor X. Furthermore, the similarity between the spectra (infrared and ultraviolet) of the two compounds suggests that the orange oil is the product of reaction of the carbonium ion with some available nucleophile (*e.g.*, Cl$^-$, benzoic acid) and/or, possibly, loss of a proton to give the olefin. Nonetheless, whatever its complete structure, there can be little doubt but that it also contains an α-diazo ketone group which arose from reaction of 2,2-diphenyldiazocyclopropane with benzoyl chloride.


IX

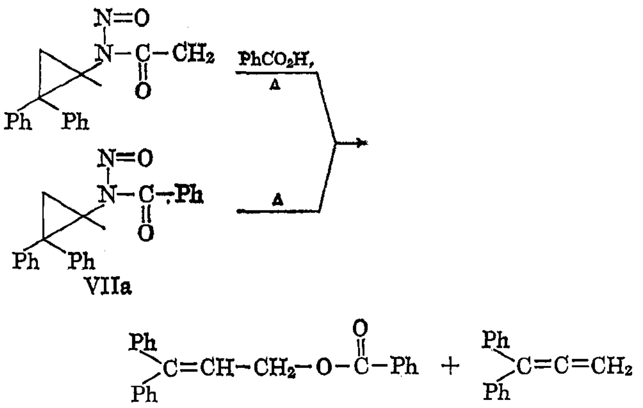

X

All of these acylation results not only present additional evidence for the suggested diazotate structures for the salts but also point up an interesting anomalous behavior of these salts: whereas the methyl and benzyl diazotates undergo acylation almost exclusively on the nitrogen,[8] the 2,2-diphenylcyclopropyldiazotate apparently undergoes acylation exclusively on the oxygen. Actually, the reason for this is probably quite simple since the nitrogen of the diazotate in the 2,2-diphenylcyclopropyl system is bonded to a rather bulky secondary carbon that could easily retard attack of the acylating group on the nitrogen.

Reaction of Lithium 2,2-Diphenylcyclopropyldiazotate with Benzoic Acid.—The reaction of the lithium diazotate with benzoic acid in refluxing benzene resulted in the formation of the ring-opened ester, 1,1-diphenylpropen-3-yl benzoate (XII), and 1,1-diphenylallene.


XII

The benzoate probably arises from reaction of 2,2-diphenyldiazocyclopropane with benzoic acid. Consistent with this suggestion is the fact that both the thermal decomposition of N-nitroso-(2,2-diphenylcyclopropyl)urea in the presence of benzoic acid[20] and the thermal decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)benzamide (VIIa), both of which probably proceed through 2,2-diphenyldiazocyclopropane, give the same mixture of products.



Experimental Section

The melting points were taken in a Thomas-Hoover Unimelt apparatus and are uncorrected. The infrared spectra were recorded with a Perkin-Elmer Infracord spectrophotometer and the ultraviolet spectra were recorded with a Cary 14 spectrophotometer. The elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. G.l.p.c. analyses were performed with an Aerograph Hy-Fi Model 600-B or Aerograph Model A-350-B converted to an Autoprep. The n.m.r. spectra were determined in deuterated chloroform solution employing a Varian 4300-2 high-resolution spectrometer operating at 56.4 Mc.

Materials.—The solvents used in this work were all Fisher Certified reagents and were used without further purification as were the diethyl fumarate (Eastman White Label), benzoyl chloride (Allied), acetyl chloride (Allied), glacial acetic acid (Allied), acetic anhydride (Baker), phenylmagnesium bromide (Peninsular ChemResearch), and vinylmagnesium bromide (Peninsular ChemResearch). The pyrrolidine (Eastman Practical grade) and cyclohexene (Eastman White Label) were purified by fractional distillation before use.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Pyrrolidine in Ethyl Ether.—To 0.600 g. (0.00214 mole) of N-

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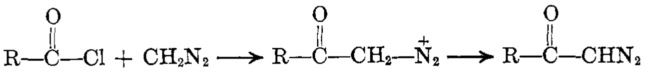
[17] A. L. Crowther and G. Holt, *J. Chem. Soc.*, 2818 (1963).

[18] There is excellent analogy for this suggested scheme in the well-known Arndt-Eistert[19] reaction in which diazomethane reacts with an acid chloride to give a diazo ketone. The difference between the Arndt-Eistert and our reaction rests in the manner in which the intermediate diazonium ketone collapses. In the former case, it loses a proton and in the latter, which does not have a proton to lose, the ring opens to give the delocalized diphenylmethyl type of carbonium ion.



$$R-\overset{O}{\overset{\|}{C}}-Cl + CH_2N_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{+}{N}_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-CHN_2$$

[19] See H. Staudinger and C. Machling, *Ber.*, **49**, 1973 (1916).

[20] D. L. Muck, unpublished results.

nitroso-N-(2,2-diphenylcyclopropyl)urea dissolved in 25 ml. of anhydrous ether stirred at 0° was added 0.4 ml. (0.34 g., 0.0048 mole) of pyrrolidine (and usually 0.60 g. of anhydrous $MgSO_4$). Nitrogen evolved for 13 min. (usually about 28 cc., 58%) after which the reaction mixture was filtered to give a quantitative yield of N-pyrrolidinylcarboxamide, m.p. 216–225°. Successive recrystallizations from ethanol gave a pure white solid: m.p. 220–221° (lit.[21] m.p. 218°); significant infrared absorptions (KBr) 2.95, 3.1, 6.1, 6.3, 6.75, 6.9, 7.4, and 12.9 μ.

Anal. Calcd. for $C_5H_{10}N_2O$: C, 52.61; H, 8.83; N, 24.54. Found: C, 52.39; H, 8.65; N, 24.37.

When the above ether filtrate was evaporated under reduced pressure while allowing the flask to get very cold, pyrrolidinium 2,2-diphenylcyclopropyldiazotate usually crystallized to a white solid. Sometimes, however, it was necessary to add pentane very slowly to effect crystallization. This solid was filtered, washed with a small volume of cold, anhydrous ether, and dried to give an average yield of 265 mg. (40%), m.p. 79–83° dec. Recrystallization from anhydrous ether gave the pyrrolidinium diazotate: m.p. 85° dec.; significant infrared absorption bands (Nujol) 4.05 (broad), 6.05, 6.15, 6.25, 8.8, 9.5, 9.9, 10.8 (very broad), 11.6 (very broad), 13.15, and 14.35 μ.

An elemental analysis of this compound was precluded by its instability.

The ether solution from which the pyrrolidinium diazotate had crystallized was evaporated under reduced pressure to a yellow oil. An infrared spectrum (neat) of this oil was superimposable on that of 1,1-diphenylallene.

Thermal Decomposition of Pyrrolidinium 2,2-Diphenylcyclopropyldiazotate in Hexane.—A 50-mg. sample of pyrrolidinium 2,2-diphenylcyclopropyldiazotate was heated in hexane to reflux. Reduced pressure evaporation of the solvent gave a brown-yellow oil whose infrared spectrum (film) was superimposable on that of 1,1-diphenylallene.

Thermal Decomposition of Pyrrolidinium 2,2-Diphenylcyclopropyldiazotate in the Presence of Diethyl Fumarate.—A solution of 240 mg. of pyrrolidinium 2,2-diphenylcyclopropyldiazotate and 0.546 ml. (0.574 g., 4 equiv.) of diethyl fumarate in 30 ml. of anhydrous ether was stirred overnight at room temperature. Evaporation of the solvent to a small volume and filtration yielded 145 mg. (47.6%) of white solid, m.p. 140–143°, whose infrared spectrum (KBr) was superimposable on that of a known sample of pyrazoline V.[3]

Thermal Decomposition of Pyrrolidinium 2,2-Diphenylcyclopropyldiazoacetate in Cyclohexene.—A mixture of 100 mg. (0.324 mmole) of pyrrolidinium 2,2-diphenylcyclopropyldiazoacetate in 10 ml. of cyclohexene was heated under reflux for 1 hr. The resulting solution was cooled, dried over anhydrous $MgSO_4$, filtered, and evaporated to an oil. After 5.42 mg. of methyl α-methylcinnamate (internal standard) was added, the product oil was analyzed by g.l.p.c. (10 ft. × $^1/_8$ in. column charged with 5% Apiezon L on 60–80 mesh Gas Chrom Z) which showed a 23.3% yield of 2,2-diphenyl-4,5-tetramethylenespiropentane. The adduct was identified by comparison of its retention time with that of a known sample.[3]

Preparation of Sodium 2,2-Diphenylcyclopropyldiazotate.—A small portion of freshly prepared pyrrolidinium 2,2-diphenylcyclopropyldiazotate was added to a few drops of 5% NaOH. After the sample completely dissolved, crystals of sodium 2,2-diphenylcyclopropyldiazotate precipitated out of solution upon standing. This precipitate was filtered and dried to give a white solid; characteristic infrared absorption maxima (Nujol and KBr) were at 6.1, 6.24, 6.7, 8.5, 8.8, 9.1, 9.3, 9.75, 11.3, 13.0, 13.3, and 14.3 (broad) μ.

When this sodium diazotate was dissolved in water and acidified with 5% HCl, a white precipitate formed which rapidly evolved a gas (presumably nitrogen).

The lithium and potassium diazotates were prepared in the same manner.

Decomposition of Lithium 2,2-Diphenylcyclopropyldiazotate with Carbon Dioxide.—Dry carbon dioxide (Linde) was bubbled through an ether slurry of lithium 2,2-diphenylcyclopropyldiazotate for 15 min. The ether solution was then filtered and evaporated to an oil. An infrared spectrum of the product oil was superimposable with that of pure 1,1-diphenylallene, the decomposition product of 2,2-diphenyldiazocyclopropane.

Preparation of Potassium 2,2-Diphenylcyclopropyldiazotate.—To freshly prepared pyrrolidinium 2,2-diphenylcyclopropyldiazotate was added an equimolar amount of KOH dissolved in anhydrous methanol and cooled to 0°. This solution was stirred magnetically as the solvent was evaporated *in vacuo* to a very thick brown oil. Upon adding a small amount of anhydrous ether, the potassium diazotate crystallized to a pale yellow solid (normally 75% yield). When the product was heated in an oil bath, it slowly darkened up to its melting point (208°), but did not decompose as evidenced by loss of gas from the cooled melt on acidification with acetic acid. A strong and broad infrared absorption maximum in the OH region indicated that the potassium salt was probably an alcoholate. The lithium diazotate was also prepared in this manner.

Preparation of Lithium 2,2-Diphenylcyclopropyldiazotate.—To an ether solution of pyrrolidinium 2,2-diphenylcyclopropyldiazotate was added 1 equiv. of lithium ethoxide.[4] After stirring overnight at room temperature, the white solid was filtered, giving the lithium diazotate (contaminated with lithium ethoxide) in good yield.

Reaction of Lithium 2,2-Diphenylcyclopropyldiazotate with Benzoyl Chloride.—To an ether suspension of lithium 2,2-diphenylcyclopropyldiazotate stirred magnetically at 0° was added 1.5 equiv. of benzoyl chloride. After several hours the yellow reaction mixture was washed with 5% $NaHCO_3$ and water and dried over anhydrous $MgSO_4$. An infrared spectrum (neat) of the orange oil obtained upon evaporation of the solvent showed strong absorption bands at 4.75, 6.2, and 6.35 μ in addition to those consistent with a mixture of benzoyl chloride and 1,1-diphenylallene. There was a distinct absence of absorption bands at 5.85 and 6.65 μ. This eliminates N-nitroso-N-(2,2-diphenylcyclopropyl)benzamide as a possible product.[22,23]

The orange product oil containing the above mixture was dissolved in acetonitrile and stirred at room temperature overnight. The precipitate which formed was filtered, washed with ether, and recrystallized from benzene–pentane to give white crystals, m.p. 197–198°. An infrared spectrum of this solid was superimposable on that of the $C_{44}H_{32}O_2$ material obtained by the decomposition of α-diazo ketone XI prepared by decomposing N-nitroso-N-(2,2-diphenylcyclopropyl)urea with lithium ethoxide in the presence of benzoyl chloride (see below).

Preparation of N-(2,2-Diphenylcyclopropyl)acetamide.—An ether solution of 2,2-diphenylcyclopropanecarboxylic acid azide was prepared in the reported manner from 10 g. (0.042 mole) of 2,2-diphenylcyclopropanecarboxylic acid. To a refluxing mixture of 100 ml. of anhydrous benzene and 100 ml. of glacial acetic acid was added the anhydrous ether solution of acid azide at such a rate that the ether was distilled away. When the temperature of the refluxing vapor reached 75°, the water to the condenser was turned on and the reaction mixture was heated under reflux overnight. After gas evolution stopped, about 15 hr., the reaction mixture was cooled, neutralized with a saturated sodium carbonate solution, and diluted with ether. A white solid which precipitated at this point was removed by filtration and identified as the symmetrically disubstituted urea.

The organic layer was separated, washed twice with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to a small volume. After the oil was dissolved in ether, a white solid precipitated which was filtered, washed with ether, and dried to give 5.5 g. (0.0219 mole, 52.2% from acid) of the desired amide, m.p. 125–127°. Recrystallization from benzene–ether yielded 3.5 g. of product: m.p. 125.5–126°; infrared maxima (Nujol) at 3.02, 6.05, 6.52, 6.67, 7.24, 9.8, 10.63, 13.27, 14.17, and 14.35 μ.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.17; H, 6.80; N, 5.44.

Preparation of N-Nitroso-N-(2,2-diphenylcyclopropyl)acetamide.—Method B of White[24] was employed in this nitrosation. A mixture of 0.8 g. (3.2 mmoles) of N-(2,2-diphenylcyclopropyl)-acetamide, 3.2 ml. of glacial acetic acid, and 16 ml. of acetic anhydride was stirred at 0° as 4.8 g. (0.07 mole) of solid sodium nitrite was added over a 5-hr. period. After stirring an additional 5 hr. at that temperature, the solution was warmed to 15°, poured into a mixture of ice and water, and extracted with ether.

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(21) V. W. Reppe, *et al.*, *Ann.*, **596**, 150 (1955).

(22) Despite the fact that the infrared spectrum did not show a detectable amount of the nitrosobenzamide, a subsequent reaction mixture was carefully chromatographed on silica gel (Fisher) using the conditions known to isolate this compound. None was obtained.

(23) Completely analogous results were obtained when acetyl chloride or acetic anhydride was used as the acylating reagent.

(24) E. H. White, *J. Am. Chem. Soc.*, **77**, 6009 (1955).

These ether extracts were washed successively with water, 5% $NaHCO_3$, and water again before being dried over anhydrous $MgSO_4$. The yellow oil obtained upon solvent evaporation was recrystallized twice from a pentane–ether mixture at Dry Ice–acetone temperature. The viscous yellow oil was unstable enough at room temperature to preclude elemental analyses. However, it was stable in solution at 0° for long periods of time. It was found that elution chromatography on silica gel using 90% pentane–ether as eluent also purified the nitrosoamide. Significant infrared absorption maxima (neat) were at 3.22, 3.36, 5.73, 6.25, 6.6, 6.9, 7.3, 7.5, 8.67, 9.2, 10.65, 11.05, 13.0, and 14.36 μ.

Preparation of N-(2,2-Diphenylcyclopropyl)benzamide.—A benzene solution of 2,2-diphenylcyclopropyl isocyanate, made in the usual manner from 2,2-diphenylcyclopropanecarboxylic acid (10.0 g., 0.042 mole), was cooled to 0° and maintained in an atmosphere of dry argon as a slight excess of phenylmagnesium bromide in ether was slowly added with stirring. After stirring 1 hr., the reaction mixture was allowed to warm to room temperature and stirred an additional hour. The solution was then cooled to 0° and an aqueous solution of 2.61 g. (0.0488 mole) of ammonium chloride was added. The organic layer was separated, washed successively with 5% HCl, 5% $NaHCO_3$, and water, dried over anhydrous magnesium sulfate, and evaporated to a solid residue. The solid was leached with pentane and filtered to give 9.53 g. (72.5% from acid) of product amide, m.p. 156–158°.

Successive recrystallizations from hot benzene or benzene–pentane gave analytically pure product: m.p. 157–158°; infrared maxima (KBr) at 2.95, 3.25, 6.1, 6.25, 6.35, 6.56, 6.72, 6.93, 7.68, 7.75, 9.33, 9.75, 10.12, 10.85, 11.33, 11.55, 12.47, 13.14, 13.37, 13.9, 14.17, and 14.5 μ.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.27; H, 6.08; N, 4.31.

Preparation of N-Nitroso-N-(2,2-diphenylcyclopropyl)benzamide.—A solution of 0.5 g. (0.0017 mole) of N-(2,2-diphenylcyclopropyl)benzamide in 40 ml. of ether was stirred magnetically and cooled to −20°. To this was added 0.394 g. (0.0048 mole) of sodium acetate and 0.0024 moles of N_2O_4 (Matheson C.P.) dissolved in ether. The mixture was allowed to stir until all the green color had disappeared. The yellow reaction mixture was washed successively with water, 5% $NaHCO_3$, and water again, dried over anhydrous $MgSO_4$, and evaporated to an oil. This oil was chromatographed on silica gel (Fisher), and the nitrosobenzamide separated as a bright yellow band with 95% pentane–ether as eluent. The nitrosoamide crystallized from pentane at Dry Ice temperature, but was a liquid at room temperature. The product was unstable enough at ordinary temperature to preclude elemental analyses. Characteristic infrared absorptions (neat) were at 3.25, 5.85, 6.65, 6.7, 6.9, 7.5, 7.85, 9.35, 10.5, 11.35, 11.5, 12.7 (broad), 13.3, and 14.4 μ (broad).

Reaction of Potassium 2,2-Diphenylcyclopropyldiazotate with Benzoyl Chloride in the Presence of Diethyl Fumarate.—To 0.163 g. (0.591 mmole) of potassium 2,2-diphenylcyclopropyldiazotate and 0.385 ml. (0.406 g., 2.36 mmoles) of diethyl fumarate (Eastman Organic Chemicals) at 0° was added an ether solution of 68 μl. (0.591 mmole) of benzoyl chloride over a 2-hr. period. Although a white solid had precipitated by this time, the reaction mixture was stirred for an additional 2 hr. After enough ether had been added to dissolve the white solid, the solution was washed with water, 5% $NaHCO_3$, and water, dried over anhydrous $MgSO_4$, and evaporated to a small volume. This mixture was filtered to give 53 mg. (23%) of white solid, m.p. 135°. Recrystallization of the solid from hot methanol gave white crystals, m.p. 146–147° (lit.[3] m.p. 147–149°), whose infrared spectrum matched perfectly with that of a known sample of pyrazoline V.

Reaction of N-Nitroso-N-(2,2-diphenylcyclopropyl)urea with Lithium Ethoxide in the Presence of Benzoyl Chloride.—To an ether solution of 0.60 g. (0.00214 mole) of N-nitroso-N-2,2-diphenylcyclopropyl)urea and 0.5 ml. (0.61 g., 0.00434 mole) of benzoyl chloride cooled to 0° and stirred magnetically was added 0.50 g. (0.00408 mole) of lithium ethoxide. When nitrogen evolution ceased (usually 12–15 cc. evolved within 1 hr.), the reaction mixture was filtered and the filtrate was evaporated to an oil. When this oil was dissolved in a small amount of ether, and pentane was very slowly added with stirring, a yellow solid (usually 40–80 mg., m.p. *ca.* 140° dec.) precipitated from solution. Repeated recrystallizations from ether gave pure yellow solid IX: m.p. 135–135.5° dec.; λ_{max} (*i*-PrOH) 302 mμ (ε 7280); infrared absorption maxima (KBr) at 2.85, 4.75, 6.2, 6.35, 6.7, 6.9, 7.25, 7.76, 8.45, 9.45, 9.85, 12.7, 12.85, 13.32, 13.72, and 14.3 μ; n.m.r., resonances at τ 2.34, 2.47, and 6.06.

Anal. Calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.12; H, 5.41; N, 8.13.

The pentane–ether solution from which the yellow α-diazo ketone IX had precipitated was evaporated to an oil. An infrared spectrum (neat) of the oil showed strong absorption bands with maxima at 4.75 and 6.2 μ and the absence of a 2.85-μ band. The ultraviolet spectrum showed a maximum at 303 mμ (*i*-PrOH) (ε 5670).[25] Repeated attempts to crystallize this second diazo ketone (XI) were unsuccessful. Attempts to purify the oil by elution chromatography (neutral alumina or silica gel) resulted in decomposition to a solid, m.p. 198–201°. Successive recrystallizations of this decomposition product from benzene–pentane gave a pure white solid: m.p. 199.5–200° (very dark melt); infrared absorption maxima (KBr) at 3.21, 5.98, 6.25, 6.35, 6.7, 6.9, 7.4, 8.12, 8.47, 9.77, 10.2, 10.85, 11.4, 11.66, 13.0 (broad), 13.72, and 14.4 μ (broad).

Anal. Calcd. for $C_{44}H_{32}O_2$: C, 89.16; H, 5.44; mol. wt., 593. Found: C, 88.78; H, 5.82; mol. wt., 590 (Rast).

When the above reaction was run taking no precautions to exclude moisture, 5.47% of diazo ketone IX was isolated. Treatment of the remaining reaction product dissolved in acetonitrile with *p*-toluenesulfonic acid gave 45.2% nitrogen evolution. When another run was made under strictly anhydrous conditions, no diazo ketone IX was isolable. Treatment of the reaction product dissolved in acetonitrile with *p*-toluenesulfonic acid gave 56.6% nitrogen evolution.

Reaction of Lithium 2,2-Diphenylcyclopropyldiazotate with Benzoic Acid.—To a refluxing benzene solution of benzoic acid (3 molar excess) was added dropwise a slurry of lithium 2,2-diphenylcyclopropyldiazotate in chloroform. After the addition was complete, the reaction mixture was heated under reflux for an additional 2 hr. The lithium benzoate precipitate was then filtered and the filtrate was washed twice each with water, 5% $NaHCO_3$, and water again before being dried over anhydrous $MgSO_4$. Evaporation of the solvents under reduced pressure gave a yellow oil. When this oil was dissolved in pentane, white needles very slowly formed. These were filtered and washed with pentane, m.p. 87–89°; no depression on admixture with the material obtained from the reaction of 1,1-diphenylpropen-3-ol with benzoyl chloride[20] was observed. The infrared spectra of the two materials were also identical.

G.l.p.c. analysis (5 ft. × 1/8 in. column charged with S.E.-30 Silicone Fluid on 60–80-mesh Chromosorb W) of the reaction product oil showed peaks with retention times identical with those of 1,1-diphenylallene and 1,1-diphenylpropen-3-yl benzoate in the ratio 63:79. There was no peak observed with a retention time corresponding to that of 3,3-diphenylpropen-3-yl benzoate.[26] An infrared spectrum of the product oil was consistent with the g.l.p.c. results in that all absorption peaks could be explained by a simple mixture of the allene and 1,1-diphenylpropen-3-yl benzoate.

Thermal Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)benzamide.—Approximately 100 mg. of nitrosoamide was heated at 100° for 30 min. to effect decompostion. An infrared spectrum of the crude oil showed the product to be almost entirely 1,1-diphenylpropen-3-yl benzoate with small amounts of 1,1-diphenylallene and benzoic acid also present. The result of g.l.p.c. analysis (5 ft. × 1/8 in. column charged with PDEAS fluid on 60–80 mesh Gas Chrom Z) was consistent with the above mixture. When the product oil was dissolved in ether and the solvent was allowed to evaporate slowly, the benzoate crystallized, m.p. 87–89°. No melting point depression was observed on admixture with the material obtained from the reaction of benzoyl chloride and 1,1-diphenylpropen-3-ol, and their infrared spectra were superimposable.

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[25] Since the infrared spectrum of this oil showed a considerable amount of benzoyl chloride, this extinction coefficient is only a minimum value.

[26] Prepared by reacting 3,3-diphenylpropen-3-ol and benzoyl chloride.