hydrochloric acid, filtered, and recrystallized from petroleum ether (b.p. 90–100°); m.p. 113–114°, lit.[8] m.p. 111.5–113°; yield 14.5 g. (73%).

*δ-Methylaminovaleric acid hydrochloride.* Crude 1-methyl-2-iminopiperidine hydrochloride (1.55 g.) (m.p. 140–147°[44]) was converted into the amino acid hydrochloride by a described procedure[19]; m.p. 96–97°, lit.[19,20] m.p. 93°; yield 0.4 g. (approximately 24%).

*Anal.* Calcd. for $C_6H_{14}O_2NCl$: C, 42.98; H, 8.42; N, 8.36; Cl, 21.15. Found: C, 42.95; H, 8.43; N, 8.60; Cl, 21.06.

*α-Phenyl-δ-butylaminovaleramide.* A mixture of 2.7 g. (0.01 mole) of 1-butyl-2-imino-3-phenylpiperidine hydrochloride, 2.0 g. (0.05 mole) of sodium hydroxide, and 20 ml. of water was stirred, refluxed for 3 hr., cooled, and extracted with ether. The extract was dried over magnesium sulfate and the solvent was removed. The oily residue, which partially solidified, was triturated with ether and filtered; the product melted at 90–91°; yield 1.5 g. (60%). Recrystallization from absolute ethanol did not raise the melting point.

*Anal.* Calcd. for $C_{15}H_{24}ON_2$: C, 72.54; H, 9.74; N, 11.28. Found: C, 72.59; H, 9.79; N, 11.45.

The hydrochloride, prepared in absolute ethanol-ether, was recrystallized from isopropyl alcohol–ether; m.p. 135–136°.

*Anal.* Calcd. for $C_{15}H_{25}ON_2Cl$: C, 63.25; H, 8.85; N, 9.84; Cl, 12.45. Found: C, 63.24; H, 8.60; N, 9.96; Cl, 12.45.

*α-Phenyl-δ-butylaminovaleric acid.* After the hydrolysis described above had been carried out for 17 hr., ether was added and three layers formed. The middle layer was neutralized with hydrochloric acid whereupon a white precipitate formed. Without filtration, the mixture was evaporated to dryness and extracted with absolute ethanol. The crude valeric acid obtained, upon concentration and refrigeration of the extract, was recrystallized from absolute ethanol; m.p. 184°; yield 30%.

*Anal.* Calcd. for $C_{15}H_{23}O_2N$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.28; H, 9.40; N, 5.60.

Identifiable products were not obtained from the top or lower layers.

*1-Butyl-3-phenyl-2-piperidone.* α-Phenyl-δ-butylaminovaleric acid (3.5 g.) was placed in a distillation flask to which a condenser was attached and heated at 190–200° for 15 min. Water collected in the condenser. The residue in the flask, the piperidone, was distilled; b.p. 138–140° (0.4 mm.); yield 2.9 g. (90%).

*Anal.* Calcd. for $C_{15}H_{21}ON$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.68; H, 8.99; N, 6.18.

When an attempt was made to obtain the piperidone by treatment of 1-butyl-2-imino-3-phenylpiperidine hydrochloride with nitrous acid[15] at 85° for 10 hr., 1-butyl-2-imino-3-phenylpiperidine nitrate precipitated in 68% yield when the reaction mixture was cooled; m.p. 149–150° after recrystallization from absolute ethanol.

*Anal.* Calcd. for $C_{15}H_{23}O_3N_3$: C, 61.41; H, 7.90; N, 14.33. Found: C, 61.54; H, 7.73; N, 14.10.

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[44] The monohydrate of this substance melted at 157°.[19]

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# Reaction of Diazo Compounds with Nitroolefins. VII. The Thermal Decomposition of Nitropyrazolines

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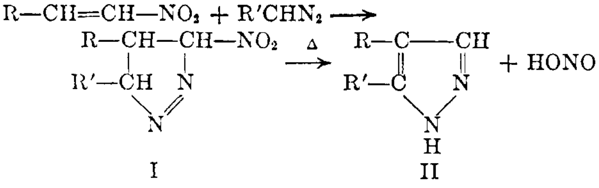
*Received September 19, 1960*

The course of thermal decomposition of nitropyrazolines of type III, in which the diazonitrogen is attached to the β-carbon of the nitroolefin from which the pyrazoline was prepared, is dependent upon the nature of the substituent in the 3-position. When this substituent is alkyl (methyl or ethyl), thermal decomposition leads to nitrocyclopropanes. When the substituent is hydrogen, the intermediate pyrazoline has not been isolated, and the nitrocyclopropane results directly from the reaction of diphenyldiazomethane and the nitroolefin. When the substituent is phenyl, nitrocyclopropanes do not result. Products isolated from the thermal decomposition of 4-nitro-3,3,5-triphenylpyrazoline are discussed.

The thermal decomposition of nitropyrazolines (I), derived from nitroolefin and diazomethane or diazoacetic ester, is known[2] to result in the elimination of the elements of nitrous acid with the formation of pyrazoles of type II.[3] The conversion of I to II is also known to be catalyzed by acid or base.[2] Hitherto the only nitrocyclopropanes that have been prepared by the reaction of nitroolefin with diazo compounds are those reported by Mustifa[4] from diazofluorene and nitroolefins.



I II

We have recently shown that diphenyldiazomethane adds to nitroolefins to give pyrazolines of type III, in which the diazo nitrogen atom is attached to the *beta*-carbon atom of the nitroolefin.[5,6]

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[1] From the Ph.D. theses of Henry G. Braxton, Jr., and Carl Serres, Jr., The University of Minnesota, 1960 and 1956, respectively.

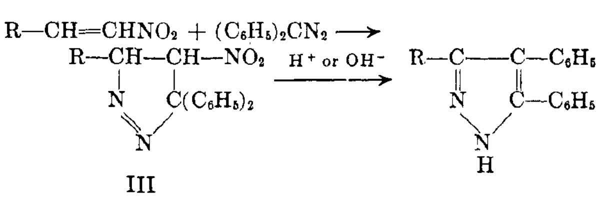
[2] W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **72**, 3813 (1950); **73**, 4664 (1951).

[3] Type II pyrazoles are designated as those in which the diazonitrogen becomes attached to the α-carbon of the nitroolefin. The double bonds in such pyrazoles can lie in any of the three possible positions.

[4] A. Mustifa and A. Harbash, *J. Am. Chem. Soc.*, **76**, 1383 (1954).

[5] W. E. Parham, C. Serres, Jr., and, P. R. O'Connor, *J. Am. Chem. Soc.*, **80**, 588 (1958).

[6] W. E. Parham, H. G. Braxton, Jr., and, P. R. O'Connor, *J. Org. Chem.*, **26**, 1805 (1961).

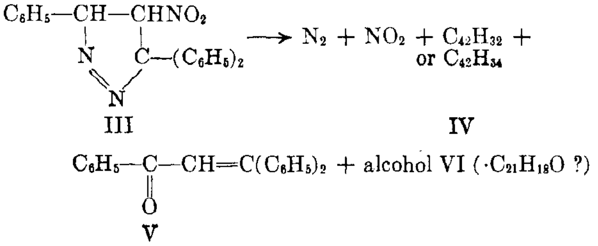


III

These pyrazolines are converted to pyrazoles by reaction with acid or base[5,6,7]; however, unlike similar reactions with pyrazolines of type I, such conversions must involve molecular rearrangement accompanying loss of nitrous acid.

The purpose of this investigation was to study the thermal degradation of pyrazolines of type III, and to determine what structural requirements are needed in order to obtain nitrocyclopropanes.

4-Nitro-3,3,5-triphenylpyrazoline (III) was prepared in 41% yield from diphenyldiazomethane and ω-nitrostyrene. Although this compound was originally considered[7] to be the isomeric 3-nitro-4,5,5-triphenyl pyrazoline, more recent studies[5] establish structure III for such products. When III was heated to its melting point (137–138°), in the absence of oxygen, an instant and rather violent decomposition occurred. The exhaust gases were colorless and turned a solution of ferrous ammonium sulfate dark brown. When the reaction was carried out in the presence of air, the exhaust gases were brown and contained nitrogen dioxide. Thus, one of the products of the decomposition was considered to be nitric oxide. The residue from the decomposition was a dark-brown oil which was nitrogen-free. Thus, the nitro group and the two nitrogen atoms were eliminated.



III IV

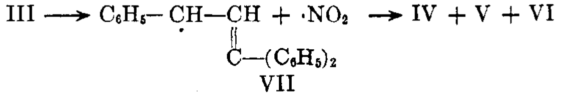
V

The residual oil was separated into three components, of almost equal weight, by partition chromatography. The first of these contained a hydrocarbon with the molecular formula $C_{42}H_{32}$ or $C_{42}H_{34}$, which was isolated in 12% yield. This material melted at 185–215° after recrystallization from several solvents, and thus was a mixture.

Another product, isolated pure in 12% yield, was a solid melting at 87–88°. This material was identified as phenylbenzalacetophenone (V) by reduction to β,β-diphenylpropiophenone, and by the independent synthesis of both phenylbenzalacetophenone and β,β-diphenylpropiophenone.

The third component was an oil which was not obtained pure and which was not fully characterized. The composition and infared spectrum of this material suggested that it contained an alcohol of the formula $C_{21}H_{18}O$; however, molecular weight values were high for this assignment (360 found, 286 calcd.).

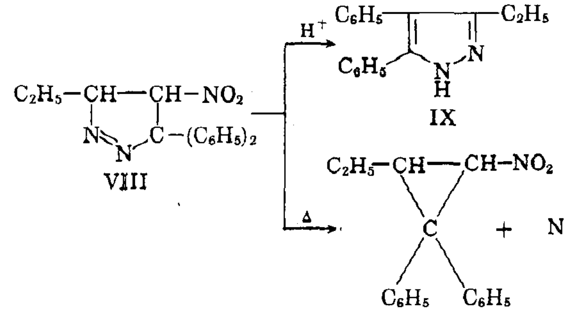
Obviously no decision can be made as to the exact mechanism for the thermal degradation of III on the basis of the present data. Failure to isolate 3,4,5-triphenylpyrazole,[5,7,8] together with the nature of the products, suggests a free radical reaction of the type outlined below. Dimerization



VII

of VII would give a $C_{42}H_{34}$ hydrocarbon; disproportionation of VII and dimerization of a possible allene intermediate would give a $C_{42}H_{32}$ hydrocarbon. Oxidation of VII (or the saturated derivative formed from it by disproportionation) by nitric oxide might logically lead to alcohols of the type suspected ($C_{21}H_{18}O$), and to the ketone V actually obtained.

3 - Ethyl - 4 - nitro - 5,5 - diphenylpyrazoline (VIII) was prepared (45% yield) by the addition of diphenyldiazomethane to 1-nitrobutene, and was characterized by conversion (75% yield) to 3-ethyl-4,5-diphenylpyrazole (IX) by reaction with hydrochloric acid in ethanol.



VIII IX X

The pyrolysis of VIII was in sharp contrast to that observed for III. The decomposition was moderate, and a relatively high yield of 1-nitro-2-ethyl-3,3-diphenylcyclopropane (X, 64%) resulted. The infrared spectrum of X showed no evidence for olefinic unsaturation, and was consistent with structure X. The cyclopropane gave a negative test for unsaturation with potassium permanganate, and reacted slowly with bromine in carbon tetrachloride in light at room temperature.

The rather startling difference noted for the pyrolysis of III and VIII is apparently a function of the substituent in the 3-position. 3-Methyl-4, nitro-5,5-diphenylpyrazoline (XI)[5] was prepared and decomposed thermally as described above for III and VIII. A moderate decomposition with evolu-

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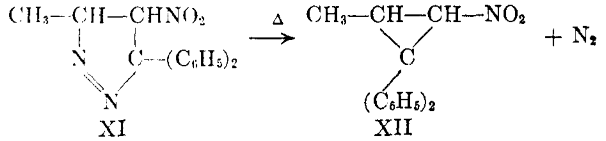
[7] W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 799 (1954).

[8] The acid or base-catalyzed decomposition of III is known to give 3,4,5-triphenylpyrazole.

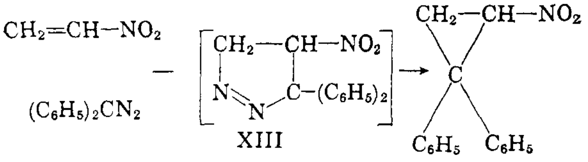


XI XII

tion of nitrogen was noted, and the cyclopropane XII was isolated from the reaction mixture in 36% yield (pure).

A nitrogen-containing by-product was also isolated (about one-fifth the quantity of XII) which has not been identified. These two cyclopropanes are the first examples of nitrocyclopropanes prepared directly by thermal decomposition of a nitropyrazoline.

We next investigated the reaction of diphenyldiazomethane with nitroethylene, for this, it was anticipated, would give a pyrazoline (XIII) with only hydrogen in the three position. Nitrogen was, however, evolved at ice-bath reaction temperatures, and 1-nitro-2,2-diphenylcyclopropane (XIV) was formed directly and isolated in 67% yield.



XIII XIV

Some preliminary attempts were made to reduce 2-phenyl-3-nitrospiro(cyclopropane-1-9′-fluorene)[4] (XV) and XII to the corresponding amines by reaction with hydrogen in the presence of Raney nickel. The quantity of hydrogen absorbed, and the composition of the derived hydrochloride and picrate, suggest that hydrogenolysis of the cyclopropane ring accompanied reduction of XV.

## EXPERIMENTAL

*4-Nitro-3,3,5-triphenylpyrazoline* (III). This material (m.p. 138–139°) was prepared in 41% yield from ω-nitrostyrene and diphenyldiazomethane.[7] The structure of the pyrazoline was originally designed as either III or the isomer 3-nitro-4,5,5-triphenylpyrazoline, with preference for the latter structure. However, more recent work of Parham, Serres, and O'Connor[5] established inverse orientation of addition for such reactants, and concluded that the product is 4-nitro-3,3,5-triphenylpyrazoline.

*Thermal decomposition of 4-nitro-3,3,5-triphenylpyrazoline.* (a) The pyrazoline (III, 5.9 g., 0.0167 mole) was placed in a 250-ml flask. Dry oxygen-free nitrogen was slowly passed through the flask, the outlet leading through a freshly prepared solution of ferrous ammonium sulfate. The flask was slowly heated; and at the melting point of the pyrazoline (138–140°), a rather violent decomposition occurred. Exhaust gases caused the ferrous sulfate solution to turn brown, presumably due to the formation of a ferrous ion–nitric oxide complex. The reaction flask was heated at 145–150° for 30 min. to ensure complete reaction. The dark-brown tarry residue weighed 4.40 g. and gave a negative test for nitrogen.

The residue was dissolved in petroleum ether (b.p. 30–60°) and the insoluble residue (0.25 g.) was discarded. The extract was placed on a column of alumina (30 g.) which was developed with (a) petroleum ether (b.p. 30–60°) (b) petroleum ether–ether (50:50), and (c) ether.

1. *Hydrocarbon.* The first two fractions, eluted with petroleum ether, were greenish-yellow solids and weighed 1.25 g. Addition of ethanol caused the precipitation of a white solid; removal of the ethanol from the extract left 0.15 g. of a deep-yellow oil. The infrared spectrum of the oil showed it to be impure phenylbenzalacetophenone (V, see latter section).

The white solid was recrystallized from benzene to give a product (0.55 g., 12.3% yield) melting over a range 185–215°. The melting point was not changed by further recrystallization from benzene or from ethanol.

*Anal.* Calcd. for $C_{42}H_{32}$: C, 94.03; H, 5.97; mol. wt. 536. For $C_{42}H_{34}$: C, 93.68 H, 6.32; mol. wt. 538. Found: C, 94.06; H, 6.56; mol. wt. (benzene) 514 ± 26 (f.p. in benzene).

The remaining fraction, eluted from the column with petroleum ether, weighed 0.55 g. and was an oil. This was probably a mixture of hydrocarbon and phenylbenzalacetophenone; however, this material was not processed.

2. *Phenylbenzalacetophenone.* The combined oily fraction eluted with petroleum ether–ether weighed 1.0 g. Trituration of this material with ethanol afforded a solid, which weighed 0.41 g. and melted at 87–88° after additional recrystallization from ethanol.

*Anal.* Calcd. for $C_{21}H_{16}O$: C, 88.70; H, 5.65. Found: C, 88.24, 88.25; H, 5.65, 5.63.

This material was subsequently identified as phenylbenzalacetophenone.

3. *The more polar fraction.* The oily fraction eluted with ether could not be induced to crystallize.

*Anal.* Calcd. for $C_{21}H_{8}O$: C, 87.81; H, 6.33; mol. wt. 286. Found: C, 88.11; H, 6.29; mol. wt. 360 ± 18 (f.p. benzene).

The infrared spectrum revealed hydroxyl absorption at 3525 cm.$^{-1}$ and weak carbonyl absorption at 1658 cm.$^{-1}$.

(b) The thermal pyrolysis was repeated using 1.35 g. of polished platinum per 0.5 g. of pyrazoline, as catalyst. The results were similar to those described in (a); there was no evidence for cyclopropane formation.

*Proof of structure of phenylbenzalacetophenone.* 1. *Authentic phenylbenzalacetophenone.* Authentic V was prepared, in low yield, by the procedure described by Kohler.[9,10] The product melted at 83–84° instead of 92°, as previously reported. A mixture melting point with the phenylbenzalacetophenone (m.p. 87–88°) obtained by pyrolysis of III was 84–87°. The infrared spectra of both samples were almost identical; however, the authentic sample possessed a band of medium intensity at 975 cm.$^{-1}$ not present in the spectrum of the other.

2. *β,β-Diphenylpropiophenone.* β,β-Diphenylpropiophenone (m.p. 93–94°) was prepared by reduction (hydrogen, platinum) of authentic phenylbenzalacetophenone, and by reduction of the product obtained by pyrolysis of III. β,β-Diphenylpropiophenone was also prepared (56% yield), as described by Kohler.[9,10] These three samples were identical (melting point, mixture melting point, and infrared spectra).

*3-Ethyl-4-nitro-5,5-diphenylpyrazoline* (VIII). A mixture of 1-nitrobutene (19.7 g., 0.195 mole, $n_D^{25.6}$ 1.4484),[11] prepared in 52% yield from 1-nitro-2-butyl acetate, diphenyldiazomethane (14.3 g., 0.195 mole) and petroleum ether (b.p. 30–60°, 50 ml.) was allowed to stand in a refrigerator. The solid that formed after 4 days weighed 7.5 g. (m.p. 137–140°), and the total after 8 days weighed 15.5 g. (m.p. 137–140°, 45% yield). The pyrazoline melted at 139–141° after further crystallization from ethanol.

*Anal.* Calcd. for $C_{17}H_{17}N_3O_2$: C, 69.13; H, 5.80; N, 14.23. Found: C, 69.41; H, 5.85; N, 14.41.

*3-Ethyl-4,5-diphenylpyrazole* (IX). 3-Ethyl-4-nitro-5,5-diphenylpyrazoline (4.0 g., 0.0136 mole) was dissolved in

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[9] E. P. Kohler, *Am. Chem. J.*, **29**, 352 (1903).

[10] E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904).

[11] E. Schmidt and G. Rutz, *Chem. Ber.*, **61**, 2142 (1928).

warm ethanol (50 ml.) and concentrated hydrochloric acid (2.5 ml.) was added dropwise at the reflux temperature. Test for oxides of nitrogen were negative after 24 hr. Additional hydrochloric acid (1 ml.) was added and the mixture was heated at the reflux temperature for an additional 12 hr. The solution was nearly neutralized with methanolic potassium hydroxide, and the inorganic salts were removed by filtration. Ethanol was removed from the filtrate; the oily residue was chromatographed on alumina (50 g.) using petroleum ether as eluent. 3-Ethyl-4,5-diphenylpyrazole (2.52 g., 74.4% yield) melted at 132–136° after further crystallization from ethanol.

*Anal.* Calcd. for $C_{17}H_{16}N_2$: C, 82.22; H, 6.50; N, 11.28. Found: C, 82.15; H, 6.55 N, 11.11.

*Thermal decomposition of 3-Ethyl-4-nitro-5,5-diphenylpyrazoline. 1-Nitro-2,ethyl-3,3-diphenylcyclopropane* (X). The pyrazoline (VIII, 7.446 g., 0.0252 mole) was decomposed as described earlier for III, with the exception that 4.0 g. of platinum scrap was added. The mixture was maintained at 147–166° for 2 hr. The crude orange tar (6.30 g.) was triturated with ether, and the solid (m.p. 85–98°) weighing 3.23 g. was removed. The ether extract was processed by chromatography and the solid recovered (2.75 g., m.p. ~100°) was combined with the original precipitate. The crude yield was 87% (5.98 g.). Further purification was achieved by crystallization of the crude product from ether and from ethanol. Pure 1-nitro-2-ethyl-3,3-diphenylcyclopropane melted at 104–105° (4.39 g., 64% yield).

*Anal.* Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.34. Found: C, 76.27; H, 6.16; N, 5.24.

Infrared spectrum: bands at 1540 $cm.^{-1}$ and 1365 $cm.^{-1}$ [12] characteristic of the nitro group. Band at 1020 $cm.^{-1}$ characteristic of cyclopropyl group. No evidence for olefinic unsaturation.

This cyclopropane derivative did not react with potassium permanganate (2% in acetone-water), and slowly decolorized bromine in carbon tetrachloride, in light, at room temperature.

*Thermal decomposition of 5-methyl-4-nitro-3,3-diphenylpyrazoline* (XI). (a) This pyrazoline (2.65 g., 0.0094 mole) was decomposed as described for IV. The additional heating time at 145–160° was 45 min. The tarry residue (2.25 g.) contained nitrogen and was dissolved in petroleum ether (0.1 g. insoluble) and chromatographed as described for X. The column was eluted with a mixture composed of two parts petroleum ether, b.p. 30–60°, and one part ether; the separation is discussed in 1, 2, and 3 below.

1. *3-Methyl-2,2-diphenyl-1-nitrocyclopropane* (XII). The first two fractions (1.25 g.) solidified, and the solid (0.85 g., 36% yield) melted at 95–96° after several recrystallizations from ethanol.

*Anal.* Calcd. for $C_{16}H_{15}NO_2$: C, 75.88; H, 5.93; N, 5.53; mol. wt., 253. Found: C, 76.08; H, 6.29; N, 5.64; mole. wt., (benzene) 250 ± 2.

Infrared spectrum: showed no evidence for olefinic unsaturation; absorption at 1550 $cm.^{-1}$ and 1360 $cm.^{-1}$ characteristic of the nitro group; absorption at 1020 $cm.^{-1}$ thought to be characteristic of the cyclopropane group.[12]

The product did not react with potassium permanganate (2% aqueous or water-acetone mixture) hot or cold, and reacted only slowly with bromine in carbon tetrachloride at room temperature.

2. The next two fractions from the chromatogram weighed 0.25 g., and subsequent to recrystallization from ethanol, was obtained as small pale-yellow crystals melting at 164–165°.

*Anal.* Found: C, 87.77, 87.81; H, 5.86, 6.39; N, 7.97.

The identity of this material has not been established.

3. The remaining fractions from the chromatogram were not characterized (0.25 g., dark oil).

(b) The thermal decomposition was repeated using 2.5 g. of polished platinum scraps as catalyst. The mixture was processed as described above. The yield of crude and pure pyrazoline was essentially the same as described in (a).

*1-Nitro-2,2-diphenylcyclopropane.* Nitroethylene[13] (2.8 g., 0.038 mole) was added slowly to a stirred solution of diphenyldiazomethane (9.7 g., 0.050 mole) in petroleum ether (b.p. 30–60°, 100 ml.) cooled to ice-bath temperature. There was an immediate evolution of gas. The solid which had separated after 3 hr. weighed 4.0 g. and melted at 72–99°. An additional quantity of solid precipitated during the next 24 hr., and the total yield of crude product was 5.1 g. (67%). Pure 1-nitro-2,2-diphenylcyclopropane, m.p. 117–118°, was obtained by several recrystallizations of the crude product from ethanol.

*Anal.* Calcd. for $C_{15}H_{13}NO_2$ C, 75.43; H, 5.58; N, 5.84. Found: C, 75.30; H, 5.48; N, 5.84.

Infrared spectrum: bands at 1540 $cm.^{-1}$ and 1360 $cm.^{-1}$ characteristic of the nitro group; absorption at 1020 $cm.^{-1}$ thought to be characteristic of the cyclopropane group. There was no evidence for olefinic unsaturation.

The cyclopropane did not decolorize potassium permanganate (2% in acetone-water), and slowly decolorized bromine in carbon tetrachloride in light at room temperature.

*Reduction of 2-phenyl-3-nitrospiro(cyclopropane-1,9′-fluorene).* A mixture of 2-phenyl-3-nitrospiro(cyclopropane-1,9′-fluorene)[4] (3.82 g., 0.0122 mole) in ethanol (200 ml.), and hydrogenated Raney nickel (*ca.* 0.5 g.) was maintained at room temperature in a Parr apparatus. An excess of hydrogen (2/3 of an equivalent) was absorbed above that necessary to reduce the nitro group to the corresponding primary amine. An orange oil was obtained from the ethanol which could not be induced to crystallize. The amine was converted to a hydrochloride (m.p. 227–232° dec)., and a picrate (m.p. 240–242°).

*The hydrochloride of the amine* (m.p. 227–237° dec. from ethanol-ether).

*Anal.* Calcd. for $C_{21}H_{18}NCl$: C, 78.86; H, 5.67; N, 4.38. Calcd. for $C_{21}H_{20}NCl$: C, 78.36; H, 6.26; N, 4.35. Found: C, 77.82, 78.12, 77.98; H, 6.05, 6.36, 5.80; N, 4.23, 4.38.

*The picrate of the amine* (m.p. 227–232° from ethanol).

*Anal.* Calcd. for $C_{27}H_{20}N_4O_7$: C, 63.28; H, 3.93; N, 10.93. Calcd. for $C_{27}H_{22}N_4O_7$: C, 63.03; H, 4.31; N, 10.89. Found: C, 63.19; H, 4.54; N, 11.02.)

The composition of these derivatives and the quantity of hydrogen absorbed suggest that hydrogenolysis of the cyclopropane ring occurred. Furthermore, absorption at 1020 $cm.^{-1}$, found in the infrared spectra of the nitrocyclopropanes and assumed to be due to the presence of the cyclopropane ring,[12] was absent in the spectra of these derivatives.

*Reduction of 3-methyl-2,2-diphenyl-1-nitrocyclopropane* (XII). The reduction of XII (2.00 g., 0.0077 mole) was carried out as described for the reduction of the spirocyclopropane described above. Only 84% of the amount of hydrogen required for reduction of the nitro group to a primary amine was absorbed (90 min.). The yellow oil was chromatographed on alumina but only a yellow oily amine fraction (0.92 g.) was isolated. This compound did not form a solid picrate but did afford a solid hydrochloride (m.p. 265–267° from ethanol-ether).

*Anal.* Calcd. for $C_{16}H_{18}NCl$: C, 73.97; H, 6.98; N, 5.39. Calcd. for $C_{16}H_{20}NCl$: C, 73.40; H, 7.70; N, 5.35. Found: C 72.85; H, 6.98; N, 5.61.

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[12] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[13] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).