

and the ether was removed. The residue, when fractionated repeatedly through a short (10 × 1 cm.) column packed with glass helices, gave a distillate (1.4 g., 41%) boiling at 119–119.5° (0.15 mm.), having n_{D}^{20} 1.5866.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.07; H, 7.19.

1-[2,4-Dinitrophenyl]-3(or 5)-phenyl-5(or 3)-cyclopropyl-methylpyrazole (XVII).—This derivative of XVI crystallized from methanol in pale yellow prisms, which melted at 108–108.5°.

Anal. Calcd. for $C_{19}H_{16}O_4N_4$: C, 62.63; H, 4.43. Found: C, 62.34; H, 4.24.

The diketone XVI (1 g.) was refluxed with aqueous sodium hydroxide (10 cc., 10%). The cooled solution was extracted with ether, the extract was washed with water, dried, and the solvent was removed. The residue was separated into two fractions by distillation: A, 0.17 g., b.p. 127–130°; B, 0.1 g., b.p. 180°. The 2,4-dinitrophenylhydrazone prepared from A, after several crystallizations from ethanol, formed orange platelets or needles melting at 152.5–153°,

and analyzed for this derivative of cyclopropylacetone.

Anal. Calcd. for $C_{12}H_{14}O_4N_4$: C, 51.79; H, 5.07. Found: C, 52.18; H, 5.43.

The 2,4-dinitrophenylhydrazone prepared from B crystallized from ethyl acetate in orange-red needles which melted at 239–241°, alone or when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of acetophenone.

The aqueous alkaline layer from the above extraction was acidified and the precipitate was removed and washed with cold water. This white solid melted at 121–122°, alone or when mixed with benzoic acid. The filtrate and washings from the benzoic acid were combined and extracted thoroughly with ether. The ether was evaporated, and the liquid residue, an acid, was converted into the *p*-bromophenacyl ester. This derivative crystallized from aqueous ethanol in white platelets which melted at 82°, alone or when mixed with the *p*-bromophenacyl ester prepared from authentic cyclopropylacetic acid.

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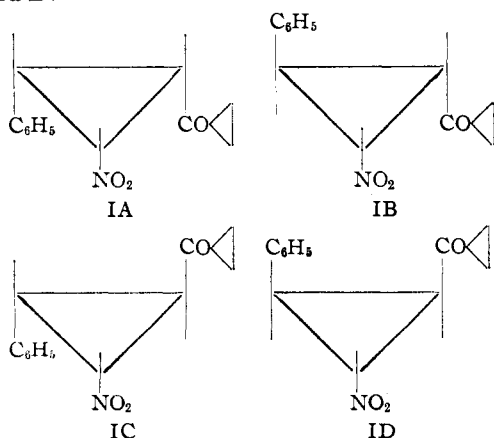
Cyclopropanes. VI.¹ The Configuration and Reduction of the Stereoisomers of Cyclopropyl 3-Phenyl-2-nitro-1-cyclopropyl Ketone

BY LEE IRVIN SMITH AND EDGAR R. ROGIER²

The two racemic forms, m.p. 63° and 75°, of the nitrocyclopropyl ketone I have been reduced, by the Meerwein-Ponndorf method, to cyclopropylcarbinols II. The 75° isomer of I gave a single carbinol, whereas the 63° isomer of I gave an unseparable mixture of two carbinols. The carbinols, in turn, were reduced over Raney nickel to aminocyclopropylcarbinols IV. It was not possible to convert either of the aminocyclopropylcarbinols IV into a crystalline cyclic derivative by a reaction involving the amino and hydroxyl groups, and thus fix the relative space relations of these two groups. Reduction of the nitrocyclopropyl ketones I over Raney nickel gave the same products from both stereoisomers of I. These products were the pyrroline V and the pyrrolidine VI.

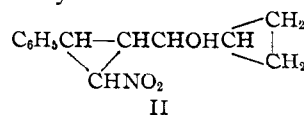
Cyclopropyl 3-phenyl-2-nitro-1-cyclopropyl ketone (I) has been prepared in two racemic forms which melt at 63° and 75°, respectively.¹ The 63° form readily forms a semicarbazone and an oxime, whereas the 75° form does not react with semicarbazide and is converted into an oxime only with difficulty. The 63° form is converted into the 75° form by action of methanolic ammonia, but this reagent is without effect upon the 75° form.

There are four possible racemic forms of I: A, B, C and D.



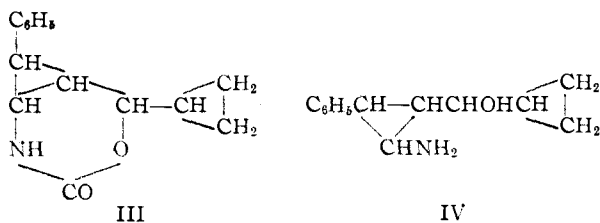
From the fact that the 63° form readily forms car-

bonyl derivatives, whereas the 75° form does not, it follows with some certainty that the 63° form does not possess configuration A, with the most hindered carbonyl group, and that the 75° form does not possess configuration C, with the least hindered carbonyl group. It is also likely that the conversion of the 63° form to the 75° form involves a change in configuration in the direction of increased stability—*i.e.*, in the direction of a "more *trans*" configuration. These assumptions lead to the conclusion that the 63° form should be represented as B, C or D, and that the 75° form should be represented by B or D. In configurations B and D, there is a *cis-trans* relationship between the nitro group and the carbonyl group; consequently, if this relationship could be established, for the 75° form, the configuration of this isomer would follow with some certainty. If the nitro group and the carbonyl group of the two stereoisomeric forms of I could be converted into functional groups capable of participating in ring closure by interaction with each other or with a reagent, the relative relationships of the two groups would be determined, for ring closure would be possible only if the two groups occupied *cis* positions with reference to each other. Thus if both the nitro group and the carbonyl group of I could be reduced, the resulting aminoalcohol II, if the two groups are *cis* to each other, might be converted into the cyclic urethan III.



(1) Paper V, Smith and Rogier, *THIS JOURNAL*, **73**, 3831 (1951).

(2) Abstracted from a thesis by Edgar R. Rogier, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, June, 1950. Allied Chemical and Dye Corporation Fellow, 1949–1950.



The literature contains only one report³ of the reduction of a nitrocyclopropyl ketone to a substance with the cyclopropane ring still intact; action of aluminum isopropoxide and isopropyl alcohol converted this nitrocyclopropyl ketone into the corresponding nitrocyclopropylcarbinol and involved no attack upon the nitro group or the cyclopropane ring.

When the 75° form of I was subjected to the conditions of the Meerwein-Ponndorf reduction, a solid was produced, from which only a pure alcohol, IIA (75%), melting at 83°, could be isolated. No other solid product could be isolated from the reaction product; hence, this reduction of the carbonyl group of the 75° form of I produced almost exclusively one of the two possible forms of the alcohol. This nitrocyclopropylcarbinol IIA was inert to the action of permanganate and of bromine in carbon tetrachloride; it gave a positive test for a nitro group with ferrous sulfate and alkali, and was readily converted into a *p*-nitrobenzoate melting at 159.5–160.5°.

In a similar manner, the 63° form of I was reduced to an alcohol IIB (71%). This alcohol was a liquid which boiled at 170–172° (0.2 mm.), and which did not solidify even after standing in a refrigerator for several weeks. This alcohol was converted into a *p*-nitrobenzoate which, even after several crystallizations, melted over the range 118–120°. The reduction of the 63° form thus led to a mixture of the two possible alcohols IIB.

The infrared absorption spectra⁴ of the nitrocyclopropylcarbinols IIA and IIB were similar, although an exact comparison was difficult because the spectrum of IIA was determined for a solution of IIA in carbon tetrachloride, whereas that of IIB was determined for the pure liquid. The spectra of both isomers show strong bands at 1360–1365 cm.⁻¹ and at 1540–1550 cm.⁻¹, which are characteristic of the nitro group. There is also a strong band at 3400–3600 cm.⁻¹ characteristic of the hydroxyl group. The strong carbonyl band at 1700 cm.⁻¹, present in the parent nitrocyclopropyl ketones I, was completely lacking in the spectra of the alcohols.

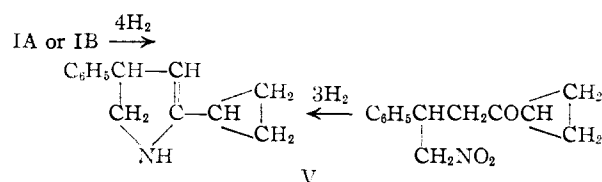
Conversion of the nitrocyclopropylcarbinols IIA and IIB into the corresponding aminocyclopropylcarbinols IVA and IVB was accomplished by catalytic reduction over Raney nickel. The alcohol IIA rapidly absorbed three moles of hydrogen over the catalyst at room temperature and atmospheric pressure, and yielded the amino alcohol IVA, a colorless viscous liquid boiling at 150–155° (0.08

mm.). When attempts were made to acetylate or benzoylate IVA, the products were gummy materials which could not be crystallized. The amino alcohol formed ether-insoluble salts with hydrogen chloride, hydrogen bromide, and oxalic acid, but all attempts to purify these salts by recrystallization from various solvents resulted in formation of uncrystallizable gums. Action of phosgene upon a benzene solution of IVA led to a gum from which only a trace of solid material could be isolated.

The nitro alcohol IIB was hydrogenated under the same conditions as those used for hydrogenation of IIA. Likewise, IIB absorbed three moles of hydrogen and produced the amino alcohol IVB, a colorless, viscous liquid boiling at 150–153° (0.3 mm.).

That IVA and IVB are aminocyclopropylcarbinols follows from their mode of formation, their composition C₁₃H₁₇ON, their reactions, and their infrared spectra,⁴ which show the strong bands at 1600–1610 cm.⁻¹ characteristic of the primary amino group, as well as five strong bands between 2870 and 3300 cm.⁻¹, the region of absorption by OH and NH.

Hydrogenation of the nitrocyclopropyl ketones IA and IB over Raney nickel at room temperature produced the same oxygen-free amine (47%) C₁₃H₁₅N (V) together with a small amount of a second amine, C₁₃H₁₇N (VI). The amine V was a colorless liquid boiling at 108–109° (0.3 mm.) which formed a hydrochloride having a neutral equivalent of 224, and an alkali-soluble benzenesulfonamide (VII) melting at 117°. The amine V was the same, whether prepared from IA or IB, as shown by the mixed melting point of the benzenesulfonamides (VII) and by the identity of the infrared absorption spectra. That the amine V was 2-cyclopropyl-4-phenyl-2(or 1)-pyrroline was shown by its synthesis, by reduction over Raney nickel, from 4-nitro-3-phenyl-1-cyclopropyl-1-butanone, a characteristic reaction of γ -nitroketones.⁵

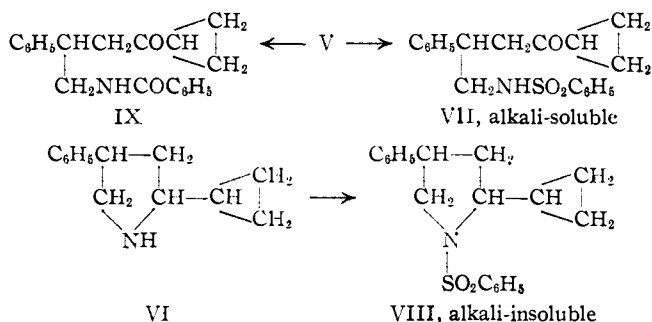


When the crude reduction product of I or of the γ -nitroketone was shaken with benzenesulfonyl chloride and alkali, there was produced an alkali-soluble benzenesulfonamide C₁₉H₂₁O₃SN (VII) melting at 117°, and an alkali-insoluble benzenesulfonamide C₁₉H₂₁O₂SN (VIII) melting at 63°. When the same amine was subjected to the action of benzoyl chloride in pyridine or aqueous alkali, a benzamide C₂₀H₂₁O₂N (IX), melting at 141–142°, was produced. These facts are consistent with the pyrroline structure V for the amine C₁₃H₁₅N, and with the pyrrolidine structure VI for the amine C₁₃H₁₇N and they reproduce the known behavior of such compounds in these reactions^{5a}; also, 2-pyrrolines are known to be readily reduced to pyrroli-

(3) Smith and Engelhardt, *THIS JOURNAL*, **71**, 2676 (1949).

(4) We wish to express our thanks to Mr. John Lancaster and to Dr. Bryce L. Crawford, Jr., of this Laboratory, for the determination of these absorption spectra and for aid in the interpretation of the curves. The complete curves may be found in the Ph.D. thesis of E. R. Rogier (ref. 2).

(5) (a) Sonn, *Ber.*, **63**, 148 (1935); (b) Rogers, *J. Chem. Soc.*, 590 (1943). On the position of the double bond in these pyrrolines, see Maginnity and Cloke, *THIS JOURNAL*, **73**, 49 (1951).



dines over Raney nickel.^{5b} It is possible that the γ -nitroketone is an intermediate in the reduction of I to V and VI; when I was reduced over Raney nickel and the reduction was interrupted after slightly less than one mole of hydrogen had been absorbed, the only pure materials isolated from the product were unchanged I and the pyrroline V. This does not, however, exclude the γ -nitroketone as an intermediate, for ring cleavage of I may be slow in comparison with reduction of the γ -nitroketone to V.

Although reduction of the nitrocyclopropyl ketones I to aminocyclopropylcarbinols II was accomplished, unfortunately the problem of assigning configurations to the stereoisomers of I could not be solved unambiguously.

Experimental Part⁶

Cyclopropyl-3-phenyl-2-nitro-1-cyclopropylcarbinol (II).

A. From the 75° Form of I.—The ketone I (m.p. 75°, 15 g.) was added to a solution of aluminum isopropoxide⁷ (13 g.) (b.p. 134–144° (11 mm.)) in dry isopropyl alcohol (65 cc.). A "partial condenser"⁸ was included in the apparatus and the mixture was refluxed at such a rate that 4–5 drops of distillate per minute was collected. When 10 cc. of distillate was collected, more isopropyl alcohol (10 cc.) was added, and this was repeated until the distillate gave a negative test for acetone⁹ (three hours; total isopropyl alcohol, 50 cc.). Most of the isopropyl alcohol was removed under reduced pressure and cold, dilute hydrochloric acid (acid 23 cc., water 115 cc.) was added to the residue. The mixture was extracted with ether, the extract was washed with water until neutral, and dried (magnesium sulfate). Removal of the solvent left a solid (14.4 g., 95%) which, after crystallization from a mixture of benzene and Skellysolve B, formed long white needles (11.4 g., 75%) melting at 81–82.5°. The analytical sample, crystallized again from the same solvent pair, melted at 83–83.5°.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$: C, 66.93; H, 6.48. Found: C, 67.20; H, 6.47.

The nitroalcohol was inert toward permanganate in acetone, and toward bromine in carbon tetrachloride. The test for nitro group with alkaline ferrous sulfate was positive. The *p*-nitrobenzoate crystallized from ethanol in long white needles melting at 159.5–160.5°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_6\text{N}_2$: C, 62.82; H, 4.74. Found: C, 62.50; H, 4.94.

B. From the 63° Form of I.—The low melting isomer of I (10 g.) was reduced as described above. The product (7.2 g., 71%), a viscous liquid, boiled at 170–172° (0.2 mm.). A center cut was taken for analysis.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$: C, 66.93; H, 6.48. Found: C, 66.79; H, 6.50.

The *p*-nitrobenzoate crystallized from ethanol in small white prisms melting at 118–120° and repeated crystal-

lization from ethanol failed to give a product with a different melting point or one with a narrower range.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_6\text{N}_2$: C, 62.82; H, 4.74. Found: C, 62.99; H, 4.98.

Cyclopropyl-3-phenyl-2-amino-1-cyclopropylcarbinol

(IV). **A. From the Solid Nitrocarbinol.**—The nitrocarbinol II (m.p. 81–83°, 4.28 g., 0.0184 mole) in ethanol (50 cc.) was shaken with hydrogen at 25° and atmospheric pressure (735 mm.) in the presence of Raney nickel catalyst.¹⁰ The uptake of hydrogen was 1485 cc. (0.058 mole) in four hours. The catalyst was removed, solvent was distilled from the filtrate, and the residue was distilled. The distillate (1.7 g., 46%) formed a clear, colorless viscous liquid which boiled at 150–155° (0.08 mm.).

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{ON}$: C, 76.80; H, 8.43. Found: C, 76.51; H, 8.90.

The substance, in dry ether, formed an insoluble hydrochloride when neutralized with hydrogen chloride. When attempts were made to recrystallize this salt from ether-methanol, ether-ethanol, ether-ethyl acetate, or dioxane, the products were gummy materials from which no crystalline substance could be obtained. The amine also formed a hydrobromide and an oxalate, but these also could not be crystallized. The amino alcohol (0.5 g.) was subjected to the action of benzoyl chloride (0.5 g.) in dry pyridine, but the only product was a gummy material. The same result was obtained when attempts were made to prepare an acetyl derivative by action of acetic anhydride upon the aminoalcohol.

A cooled (10°) solution of the aminoalcohol (0.41 g.) in benzene (20 cc.) and pyridine (5 cc.) was slowly added (1 hour) and with stirring, to a solution of phosgene (0.2 g.) in benzene (20 cc.). The solution was stirred at room temperature for four hours, then was washed successively with dilute hydrochloric acid, saturated aqueous sodium bicarbonate and water, and dried (magnesium sulfate). The solvent was removed and the residual oil was taken up in ether. Petroleum ether was added until the solution became slightly cloudy and it was then set aside in a refrigerator for several weeks. Approximately 5 mg. of solid deposited and recrystallization of this produced less than 1 mg. of material which was not investigated further.

B. From the Liquid Nitrocarbinol II.—The carbinol (5 g., 0.0215 mole) in ethanol (50 cc.) was reduced at 25° and 730 mm. for five hours as described above. Absorption of hydrogen was 1680 cc. (0.0657 mole). The product gave a distillate (1.36 g., 31%) boiling at 150–153° (0.3–0.4 mm.). This substance also formed ether-insoluble salts, but these could not be recrystallized.

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{ON}$: C, 76.80; H, 8.43. Found: C, 76.78; H, 8.71.

2-Cyclopropyl-4-phenyl-2-pyrroline (V).

A. From the 75° Form of I.—A solution of the nitroketone I (m.p. 75°) (9.24 g., 0.04 mole) in ethanol (100 cc.) was shaken with hydrogen (25°, 40 lb.) for 40 hours in the presence of Raney nickel catalyst; 0.14 mole of hydrogen was absorbed. The catalyst was removed, solvent was distilled from the filtrate, and the residue, repeatedly fractionated through a short (4 × 1 cm.) column packed with glass helices, gave a distillate (3.5 g., 47%) boiling at 108–109° (0.3 mm.) and having n_{D}^{22} 1.5521. The substance appeared to be homogeneous, but was difficult to obtain analytically pure. It was redistilled, and a center cut boiling at 104° (0.15 mm.) and having n_{D}^{22} 1.5520 was analyzed.

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{N}$: C, 84.28; H, 8.16. Found: C, 82.96; H, 8.08.

The amine formed an insoluble hydrochloride when its solution in ether was neutralized with ethereal hydrogen chloride. The solid was washed with dry ether and recrystallized from a mixture of ether and dry methanol, when it formed white platelets melting at 129.5° (capillary tube inserted in the bath at 125°; otherwise, the salt melted at about 125°).

Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{NCl}$: C, 70.41; H, 7.27; N, 6.32; neut. equiv., 222. Found: C, 70.31; H, 7.44; N, 6.51; neut. equiv., 224, 224.

The hydrobromide, prepared and recrystallized as described above, melted at 129.5°.

(6) Microanalyses by R. Amidon, J. Buckley, W. Cummings, W. Hunter, R. Kelly and H. Turner.

(7) "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 198.

(8) Arndt, *Org. Syntheses*, **20**, 27 (1940).

(9) Ref. 7, p. 200.

(10) W-G, Adkins and Billica, *This Journal*, **70**, 693 (1948).

Anal. Calcd. for $C_{13}H_{16}NBr$: C, 58.65; H, 6.06. Found: C, 58.40; H, 6.42.

The picrate crystallized from dry ethanol in flat, yellow crystals melting at 159.5–160°.

Anal. Calcd. for $C_{13}H_{18}O_7N_4$: C, 55.07; H, 4.38. Found: C, 54.76, 55.06; H, 4.23, 4.51.

Benzenesulfonamide VIII.—The above amine (0.3 g.), benzenesulfonyl chloride (0.4 g.) and aqueous sodium hydroxide (10%) were shaken together for several minutes and then warmed on the steam-bath until no further benzenesulfonyl chloride remained. The cooled reaction mixture was filtered, and the pasty solid was crystallized twice from aqueous ethanol. The white prisms melted at 62.5–63.5°.

Anal. Calcd. for $C_{13}H_{21}O_2SN$: C, 69.69; H, 6.46. Found: C, 70.42; H, 6.14.

Acidification of the alkaline mother liquor left after removal of VIII yielded a white solid which, after crystallization from ethanol, melted at 117–117.5° alone or when mixed with the benzenesulfonamide VII (see below).

Benzamide IX.—A solution of the above amine (0.3 g.) and benzoyl chloride (0.3 g.) in benzene (10 cc.) and pyridine (5 cc.) was warmed for a few minutes and then poured into water. The benzene layer was removed and extracted successively with water, aqueous sodium carbonate (5%) and water, and dried (magnesium sulfate). The solvent was removed under reduced pressure and the residue was crystallized from aqueous ethanol (Norite). The substance formed fine white needles which melted at 141–142°, alone or when mixed with IX prepared from the low melting isomer of I, or from the open-chain γ -nitroketone (see below).

B. 2-Cyclopropyl-4-phenyl-2-pyrroline (V) from the 63° Form of I.—The low melting isomer of I (3.28 g., 0.0142 mole) in ethanol (50 cc.) was reduced as described under A above; the uptake of hydrogen was 1410 cc. (0.056 mole). The product (1.2 g., 46%) boiled at 110–115° (0.7 mm.). The hydrochloride of this sample of V melted at 135°; when mixed with the hydrochloride from the amine obtained under A above (m.p. 129.5°), the substance melted at 129.5°.

Anal. Calcd. for $C_{13}H_{16}NCl$: C, 70.41; H, 7.27; neut. equiv., 222. Found: C, 70.05; H, 7.29; neut. equiv., 224.

Benzenesulfonamide VII.—The amine was subjected to the action of benzenesulfonyl chloride, as described under A

above, and the alkali-soluble benzamide was crystallized from aqueous ethanol. It melted at 117–117.5°, alone or when mixed with VII as prepared under A above.

Anal. Calcd. for $C_{13}H_{21}O_2SN$: C, 66.45; H, 6.16. Found: C, 66.61; H, 6.28.

C. Attempt to Isolate an Intermediate in the Reduction of I.—A solution of the 75° isomer of I (2 g., 0.0086 mole) in ethanol (40 cc.) was reduced at 25° and 720 mm. as described above, except that the reduction was interrupted after 200 cc. (0.0078 mole) of hydrogen was absorbed. The product, when crystallized from methanol, yielded the nitroketone I (0.72 g., 36%) melting at 74–75° alone or when mixed with an authentic specimen. The mother liquor from this product was added to a saturated solution of picric acid in methanol, and the mixture was cooled. The flat, yellow crystals melted at 159–160°, alone or when mixed with the picrate prepared directly from V.

D. Pyrroline V from 4-Nitro-4-phenyl-1-cyclopropylbutanone-1.—The γ -nitroketone (8 g., 0.00343 mole) in ethanol (75 cc.) was shaken with hydrogen (25°, 20 lb.) and Raney nickel catalyst; absorption of hydrogen (0.105 mole) was complete in three hours. The catalyst was removed, solvent was distilled from the filtrate, and the residue, repeatedly distilled through a short (4 × 1 cm.) column packed with glass helices, gave a distillate (3.8 g., 60%) boiling at 109–111° (0.1 mm.) and having n_D^{25} 1.5508. The material appeared to be homogeneous, but was difficult to obtain analytically pure. A center cut was taken for analysis.

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 82.66, 83.24; H, 8.34, 8.39.

The amine rapidly decolorized a solution of permanganate in acetone; it gave a picrate melting at 159–159.5° alone or when mixed with the picrate of V; an alkali-soluble benzenesulfonamide melting at 116.5–117°, alone or when mixed with this derivative of V; and a benzamide melting at 141.5–142.5° alone or when mixed with this derivative of V. This specimen of the benzamide IX was analyzed.

Anal. Calcd. for $C_{20}H_{21}O_2N$: C, 78.14; H, 6.89; N, 4.56. Found: C, 77.88; H, 6.96; N, 4.45.

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Cyclopropanes. VII.¹ 2-Phenylbicyclopropyl

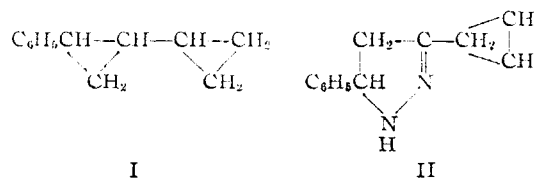
BY LEE IRVIN SMITH AND EDGAR R. ROGIER²

The first known bicyclopropyl hydrocarbon, 2-phenylbicyclopropyl (I), has been synthesized and its physical and chemical properties have been studied. The data derived from the mol. refraction, ultraviolet and infrared spectra, and reactions of I indicate that it does not exhibit any conjugative effect above that shown by phenylcyclopropane.

Cyclopropane resembles ethylene in some respects, and both systems can enter into conjugation with other unsaturated groups. A cyclopropane ring may conjugate with an ethylenic linkage,³ a carbonyl group,⁴ a phenyl group,^{3a,e} or a pyridyl group⁵; in these cases the observed shifts of absorption in the ultraviolet have been attributed to participation of the cyclopropane ring in hyperconjugation. There is also considerable chemical evi-

dence of this effect⁶; thus, certain bicyclic terpenes containing a cyclopropane ring— α -thujene, β -caradiene, etc.—undergo the Diels–Alder reaction⁷ when refluxed with maleic anhydride, although vinylcyclopropane does not undergo this reaction at 100°.^{3c}

It was of interest to determine whether or not the cyclopropane ring could enter into conjugation



(1) Paper VI, Smith and Rogier, *THIS JOURNAL*, **73**, 3837 (1951).

(2) Abstracted from a thesis by Edgar R. Rogier, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, June, 1950. Allied Chemical and Dye Corporation Fellow, 1949–1950.

(3) (a) Carr and Burt, *THIS JOURNAL*, **40**, 1590 (1918); (b) Klotz, *ibid.*, **66**, 88 (1944); (c) Van Volkenburgh, Greenlee, Derfer and Boord, *ibid.*, **71**, 172, 3595 (1949); (d) Derfer, Greenlee and Boord, *ibid.*, **71**, 175 (1949).

(4) (a) Ref. 3a; (b) ref. 3b; (c) Roberts and Green, *ibid.*, **68**, 214 (1946); (d) Fuson and Baumgartner, *ibid.*, **70**, 3255 (1948); (e) Rogers, *ibid.*, **69**, 2544 (1947).

(5) Mariella, Peterson and Ferris, *ibid.*, **70**, 1494 (1948).

(6) (a) Kohler and Conant, *ibid.*, **39**, 1404 (1917); (b) Kishner, *J. Russ. Phys.-Chem. Soc.*, **43**, 1163 (1911); (c) Allen and Boyer, *Can. J. Research*, **9**, 159 (1933); (d) Bone and Perkin, *J. Chem. Soc.*, **67**, 108 (1895).

(7) (a) Ref. 4c; (b) Gascoigne, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 359 (1941) [*C. A.*, **35**, 2876 (1941)].