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 $C_{19}H_{18}O_7N_4$: 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 $C_{19}H_{21}O_2SN$: 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 $C_{19}H_{21}O_3SN$: 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 $n^{24.5}\mathrm{D}$ 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.

MINNEAPOLIS 14, MINNESOTA

RECEIVED FEBRUARY 21, 1951

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

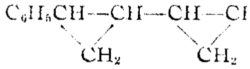
Cyclopropanes. VII.[1] 2-Phenylbicyclopropyl

BY LEE IRVIN SMITH AND EDGAR R. ROGIER[2]

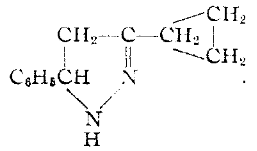
The first known bicyclopropyl hydrocarbon, 2-phenylbicyclopropyl (I), has been synthesized and its physical and chemical properties have been studied. The data derived from the mol. refraction, ultraviolet and infrared spectra, and reactions of I indicate that it does not exhibit any conjugative effect 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 group[5]; 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 evidence of this effect[6]; thus, certain bicyclic terpenes containing a cyclopropane ring—α-thujene, β-carene, etc.—undergo the Diels–Alder reaction[7] 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



I



II

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(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).

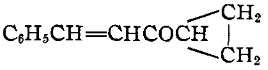
(4) (a) Ref. 3a; (b) ref. 3b; (c) Roberts and Green, *ibid.*, **68**, 214 (1946); (d) Fuson and Baumgartner, *ibid.*, **70**, 3255 (1948); (e) Rogers, *ibid.*, **69**, 2544 (1947).

(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)].

with another cyclopropane ring, and an investigation of the preparation and properties of 2-phenylbicyclopropyl (I) was undertaken. Hitherto, only two or three derivatives of the bicyclopropyl system were known—the 2,2′-dicarboxylic acid,[8] the 2,3,3,-2′,3′,3′-hexacarboxylic acid and the derived 2,3,2′,-3′-tetracarboxylic acid.[9]



$$\mathrm{C_6H_5CH{=}CHCOCH}\Big\langle\begin{array}{l}\mathrm{CH_2}\\ \vert\\ \mathrm{CH_2}\end{array}$$

III

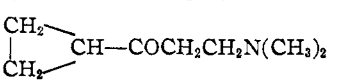
The route to I (74%) involved decomposition of the pyrazoline II[10] derived (86%) from styryl cyclopropyl ketone III.[11] The structure of the hydrocarbon $C_{12}H_{14}$ (I) follows from the method of preparation *via* a known reaction, and from the fact that it is inert toward permanganate in water or acetone, and toward bromine in carbon tetrachloride. The observed molecular refractivity of I, 51.40, is in excellent agreement with the calculated value, 51.45, and no exaltation is shown. This value, 51.45, was calculated using the value for phenylcyclopropane obtained by Rogers[4e] and the values for carbon, hydrogen and the cyclopropane ring as determined by Vogel, *et al.*[12] If the molecular refraction is calculated using the value for benzene as the starting point, the result is 51.21; still in excellent agreement with that observed, and showing little or no exaltation.

The ultraviolet absorption spectrum of I was determined; comparison of the spectrum with that of phenylcyclopropane[4e] showed the two spectra to be remarkably similar.[13] There is a peak in the spectrum of I at 2220 Å., presumably arising from the $N \rightarrow V_1$ transition in the molecule, probably corresponding with the maximum of 2455 Å. in the spectrum of styrene, with the maximum of 2060 Å. in that of ethylbenzene, and with the maximum of 2200 Å. in that of phenylcyclopropane, all of which have been attributed to the $N \rightarrow V_1$ transition from the normal to the excited states in these molecules.[14] Thus it appears that there is no conjugation in I over and above that observed in phenylcyclopropane.

The infrared absorption spectra of I and phenylcyclopropane likewise showed many similarities. In the spectra of both hydrocarbons there are strong bands at 3000 cm.$^{-1}$ (CH), 1500 and 1610 cm.$^{-1}$ (benzene ring), 1460–1465 cm.$^{-1}$ (CH_2), and, of special interest, at 1015–1020 cm.$^{-1}$, a band found by Boord, *et al.*,[15] to be characteristic of the cyclopropane ring in a number of alkyl- and alkenylcyclopropanes. There are no bands in the spectra of either hydrocarbon from 1610 to 1740 cm.$^{-1}$ characteristic of a terminal olefinic group.

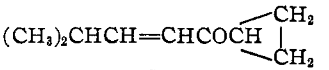
2-Phenylbicyclopropyl (I) did not react with maleic anhydride at 200°; thus both the physical and the chemical evidence indicate that there is little or no conjugative effect when two cyclopropane rings are joined directly together.

It was hoped that the parent hydrocarbon of this series, bicyclopropyl, could be prepared *via* a series of reactions similar to that used for preparation of I. However, synthesis of the necessary ketone, vinyl cyclopropyl ketone, was unsuccessful. The Mannich base IV was prepared (60%) by condensation of methyl cyclopropyl ketone, formaldehyde and dimethylamine hydrochloride, but decomposition of the base IV produced only polymeric material, and no vinyl cyclopropyl ketone could be obtained. Decomposition of the base IV was carried out in the presence of hydrazine, in the hope of obtaining a pyrazoline, but this also failed.



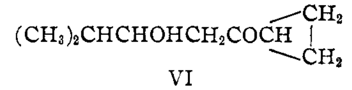
$$\begin{array}{l}\mathrm{CH_2}\\ \vert\\ \mathrm{CH_2}\end{array}\Big\rangle\mathrm{CH{-}COCH_2CH_2N(CH_3)_2}$$

IV



$$\mathrm{(CH_3)_2CHCH{=}CHCOCH}\Big\langle\begin{array}{l}\mathrm{CH_2}\\ \vert\\ \mathrm{CH_2}\end{array}$$

V



$$\mathrm{(CH_3)_2CHCHOHCH_2COCH}\Big\langle\begin{array}{l}\mathrm{CH_2}\\ \vert\\ \mathrm{CH_2}\end{array}$$

VI

As a means of obtaining starting material for conversion to an alkyl-bicyclopropyl, preparation of 5-methyl-1-cyclopropyl-2-butene-1-one (V) was investigated. Condensation of isobutyraldehyde with methyl cyclopropyl ketone at 35–40° led to a product which was a mixture of V and the related ketol VI; the ketol VI was dehydrated only with considerable difficulty, and the resulting over-all yield of ketone V was so low that synthesis of a bicyclopropyl from it in any quantity was impractical. When the condensation was carried out under more vigorous conditions, a white crystalline solid was obtained. This material had the composition $C_{18}H_{28}O_2$, was unsaturated toward permanganate and bromine in carbon tetrachloride, and reacted with two moles of 2,4-dinitrophenylhydrazine to give a derivative having the composition $C_{30}H_{36}O_8N_8$.

Experimental Part[16]

3-Cyclopropyl-5-phenyl-2-pyrazoline (II).—Styryl cyclopropyl ketone[11] (42 g., 0.245 mole) was added to a solution of aqueous hydrazine (25 cc., 0.42 mole) in ethanol (95%, 70 cc.); the mixture became warm and acquired a green color. It was allowed to stand for 45 minutes, then warmed on the steam-bath for one hour, after which excess hydrazine and solvent were removed under reduced pressure. Distillation of the residue gave a light green liquid (37.8 g., 86%) which boiled at 164° (1 mm.).

Anal. Calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58. Found: C, 77.50; H, 7.46.

The phenylthiourea derivative[17] crystallized from ethanol in colorless plates melting at 107.5–108.5°.

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[8] Müller and Roser, *J. prakt. Chem.*, **133**, 291 (1932).

[9] Farmer, *J. Chem. Soc.*, **123**, 3332 (1923).

[10] (a) Kishner, *J. Russ. Phys.-Chem. Soc.*, **44**, 165 (1912) [*C. A.*, **6**, 1431 (1912)]; (b) Davidson and Feldman, THIS JOURNAL, **66**, 488 (1944).

[11] Smith and Rogier, *ibid.*, **73**, 3831 (1951).

[12] (a) Vogel, *J. Chem. Soc.*, 133 (1946); (b) Jeffrey and Vogel, *ibid.*, 1804 (1948).

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

[14] (a) Ref. 4e; (b) Mulliken and Rieke, *Reports on Progress in Physics*, **8**, 231 (1941).

[15] Derfer, Pickett and Boord, THIS JOURNAL, **71**, 2482 (1949).

[16] Microanalyses by R. Amidon, J. Buckley, W. Cummings, W. Hunter, R. Kelly and H. Turner.

[17] Shriner and Fuson, "Systematic Identification of Organic Compounds," 3rd Ed., John Wiley & Sons, Inc., New York, N. Y., 1948, p. 179.

Anal. Calcd. for $C_{19}H_{19}N_3S$: C, 70.99; H, 5.96. Found: C, 71.08; H, 5.88.

2-Phenylbicyclopropyl (I).—Powdered potassium hydroxide (7.2 g.) and platinized asbestos (3.2 g.)[18] were placed in a 100-cc. round-bottomed flask arranged for distillation, and immersed in a metal-bath. The bath was heated to 220° (thermometer in the bath) and the pyrazoline II (37.8 g., 0.2 mole) was slowly added. After the rapid evolution of nitrogen ceased, the product was distilled from the reaction mixture; it distilled at 92–96° (0.8 mm.), and weighed 22.5 g. (74%). The products from several runs were combined and fractionated through a column (15 × 1.5 cm.) packed with glass helices. A center cut was taken for analysis. This boiled at 57° (0.12 mm.), and had n^{20}_{D} 1.5352, d^{20}_{4} 0.9587, and mol. refraction 51.40.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.97; H, 8.69.

The hydrocarbon reacted with bromine in carbon tetrachloride only upon warming; it was inert toward permanganate.

The hydrocarbon I (1.6 g.) and maleic anhydride (10 g.) were heated for five hours on the steam-bath in a stoppered flask. Distillation of the mixture yielded only maleic anhydride and unchanged I. Repetition of the experiment at 150° and 200° (refluxing maleic anhydride) led to the same result.

Cyclopropyl 2-Dimethylaminoethyl Ketone (IV).—A mixture of methyl cyclopropyl ketone (84 g.), paraformaldehyde (25 g.), dimethylamine hydrochloride (50 g.) and isopropyl alcohol (100 cc.) was refluxed for eight hours. The solvent was removed under reduced pressure, and an excess of aqueous sodium hydroxide (50%) was added to the cooled residue. The supernatant layer was removed and distilled through a column (8 × 1 cm.) packed with glass helices. The colorless liquid (51 g., 60%) boiled at 63–66° (1 mm.) and had $n^{27.6}_{D}$ 1.4545. The iodoform test was negative.

Anal. Calcd. for $C_8H_{15}ON$: C, 68.04; H, 10.71. Found: C, 68.20; H, 10.60.

The picrate of IV crystallized from ethanol in yellow needles melting at 124–124.5°.

Anal. Calcd. for $C_{14}H_{18}O_8N_4$: C, 45.41; H, 4.90. Found: C, 45.71; H, 5.09.

The base IV (10 g.) was suspended in diphenyl ether (20 cc.) and an equivalent amount of hydrogen chloride was added. This suspension was added, with stirring, to diphenyl ether (10 cc.) at 160°. No reaction was apparent. The temperature was raised to 220°, and although the mixture became dark, nothing distilled from it. Removal of diphenyl ether by decantation from the cooled mixture left a residue of hard, glassy material.

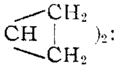
The base IV (14.1 g.) and hydrazine hydrate (17.2 cc., 85%) were heated on the steam-bath for four hours. Vigorous evolution of dimethylamine (phenylthiourea derivative, m.p. 133–134°) occurred. Excess hydrazine was removed under reduced pressure; distillation of the residue yielded less than 1 g. of material boiling at 39–96° (20 mm.). The remainder was a dark tar.

Condensation of isobutyraldehyde with methyl cyclopropyl ketone was effected following a modification of the procedure of Powell.[19] The ketone (117 g.) and ethanolic potassium hydroxide (1 *N*, 26.6 cc., 95% ethanol) were stirred while the aldehyde (38.7 g., b.p. 62.5°, freshly distilled) was slowly (one hour) added; the temperature was maintained at 35–40°. The mixture was stirred for one hour at room temperature, tartaric acid (5 g.) was added, the solid was removed and the filtrate was extracted with ether. The extract was washed and dried (magnesium sulfate), the solvent was removed, and the residue was distilled under 9 mm. through a column (10 × 1.5 cm.) packed with glass helices. Four fractions, each weighing approximately 11 g., were collected: A, b.p. 96–103°, $n^{27.2}_{D}$ 1.4617; B, b.p. 103–108°, $n^{27.2}_{D}$ 1.4594; C, b.p. 108–110°, $n^{27.2}_{D}$ 1.4596; D, b.p. 110°, $n^{27.2}_{D}$ 1.4559. Fractions B and C were combined and redistilled under 8 mm., giving E, b.p. 96–100°, $n^{27.2}_{D}$ 1.4692; F, b.p. 110–117°, $n^{27.2}_{D}$ 1.4640; G, b.p. 117–122°, $n^{27.2}_{D}$ 1.4611. Fraction G was analyzed. *Anal.* Calcd. for $C_9H_{16}O_2$ (VI): C, 69.19; H, 10.32. Found: C, 70.19; H, 10.60. It thus appeared that fraction G consisted largely of the ketol VI, with some of the ketone V. Fraction G gave a 2,4-dinitrophenylhydrazone, which crystallized from ethanol in red platelets melting at 159.5–160°. *Anal.* Calcd. for $C_{15}H_{18}O_4N_4$ (derivative of V): C, 56.59; H, 5.70. Found: C, 56.38; H, 5.72. Thus the ketol VI, when it reacts with 2,4-dinitrophenylhydrazine, gives a derivative of the ketone V.

The remainder of the ketol–ketone mixture was combined (44 g.) and distilled over iodine (0.3 g.) under atmospheric pressure, giving H, b.p. 180–194°; I, b.p. 194–200°; J, b.p. 200–204°; total, 28.7 g. Fractions I and J were combined and distilled under 0.02–0.03 mm. through a column (10 × 1.5 cm.) packed with glass helices, giving K, 7 g., b.p. 47°, n^{28}_{D} 1.4675; L, 6.3 g., b.p. 47–49°, n^{28}_{D} 1.4717; M, 7.2 g., b.p. 49–53°, n^{28}_{D} 1.4792. Fraction L was analyzed. *Anal.* Calcd. for $C_9H_{14}O$ (V): C, 78.21; H, 10.21. Found: C, 77.45; H, 10.33. It thus appeared that fraction L was largely the ketone V, but still contained some ketol VI. Fraction L gave a 2,4-dinitrophenylhydrazone melting at 159.5–160° alone or when mixed with the derivative prepared from fraction G.

Isobutylaldehyde (41 g., freshly distilled) was added slowly to a vigorously stirred solution of methyl cyclopropyl ketone (49 g.) in alcoholic potassium hydroxide (8.7 g., in water 20 cc. and ethanol to make 87 cc.). The temperature rose to 45°; stirring was continued for 23 hours at room temperature.[20] The mixture was extracted with ether, the extract was washed with saturated aqueous sodium bicarbonate and water, and dried (Drierite). The solvent was removed. From the residue there was separated by fractional distillation a product (34.7 g.) which boiled at 140–147° (1 mm.), and which crystallized after standing in a refrigerator for several days. The solid was removed and crystallized twice from methanol; it then melted at 58.5–58.7°. It was insoluble in dilute hydrochloric acid or in dilute sodium hydroxide, but dissolved in sulfuric acid to give a yellow solution. It was unsaturated toward both permanganate and bromine in carbon tetrachloride (some hydrobromic acid evolved).

Anal. Calcd. for $C_{14}H_{22}O_2$ $(CH_3)_2CHCH(CH_2CO$-



$CH\begin{matrix}\diagup CH_2\\ |\\ \diagdown CH_2\end{matrix})_2$: C, 75.63; H, 9.98. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.20; H, 10.30.

The 2,4-dinitrophenylhydrazone of this material crystallized from benzene in fine orange needles melting at 222–223° (dec.).

Anal. Calcd. for $C_{24}H_{32}O_5N_4$ (mono derivative, C_{18}): C, 63.14; H, 7.07. Calcd. for $C_{30}H_{36}O_8N_8$ (bis derivative, C_{18}): C, 56.59; H, 5.70. Found: C, 56.90; H, 5.90.

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[18] Prepared by soaking asbestos fiber in 5% solution of platinum chloride; the product was dried and reduced at 100° in a stream of hydrogen.

[19] Powell, THIS JOURNAL, **46**, 2514 (1924).

[20] Modification of a procedure of Eccot and Linstead, *J. Chem. Soc.*, 911 (1930).