idly to solutions of maleic anhydride in benzene containing 2,5-di-*t*-butylhydroquinone as inhibitor. After standing at room temperature for at least 12 hr. the residues obtained, after evaporating the solutions to dryness, were extracted with boiling hexane to remove the simple 1:1 maleic anhydride–I adduct. The hot hexane-insoluble residues were dissolved in benzene–hexane and examined for higher melting, less soluble maleic anhydride adducts such as that of 2-vinyl-1,3-butadiene. The following results are representative of typical pyrolysis experiments. From 2.5 g. of allene dimer pyrolyzed at 500° there was obtained 1.7 g. of pyrolysate which afforded 0.9 g. of adduct with maleic anhydride, m.p. 77–78°. At 600° 2.5 g. of allene dimer gave 0.9 g. of pyrolysate from which 0.16 g. of adduct m.p. 77–78° was isolated. No adduct corresponding to that of 2-vinyl-1,3-butadiene was isolated in any of the experiments.

Pyrolysis at 500° of 1.0 g. of allene dimer dissolved in 2.0 g. of glacial acetic acid gave 2.1 g. of pyrolysate from which 300 mg. of the adduct having m.p. 77–78° was obtained. In addition, some higher melting material was isolated which showed m.p. 205–207° from benzene. This was characterized as bicyclo[4,2,0]-1(6)-octene-3,4-dicarboxylic acid by a mixed m.p. determination with an authentic specimen of the acid, m.p. 206–207°.[3]

ITHACA, N. Y.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

A Simple Entry to Polycyclopropylated Molecules. Dicyclopropyl Ketone[1]

BY HAROLD HART AND OMER E. CURTIS, JR.

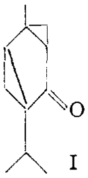
RECEIVED APRIL 22, 1955

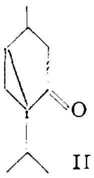
Dicyclopropyl ketone has been synthesized from γ-butyrolactone in about 50% over-all yield. The three steps, which include base-catalyzed condensation of the lactone to dibutyrolactone (VIII), conversion with hydrochloric acid to 1,7-dichloro-4-heptanone (VI) and ring closure with base, can be conveniently performed in a few hours, without isolation of the intermediates. The structure of the ketone was demonstrated by Beckmann rearrangement of its oxime to N-cyclopropylcyclopropanecarboxamide, identical with an authentic sample prepared from cyclopropanecarbonyl chloride and cyclopropylamine. Dicyclopropylcarbinol, dicyclopropylmethane and dicyclopropylketazine, a molecule with four cyclopropane rings, are described. The absorption spectra of polycyclopropylated compounds are discussed.

This paper describes a convenient, simple synthesis of dicyclopropyl ketone. Included also are a few of its reactions, and a brief discussion of the influence of the cyclopropane ring on molecular spectra.

Our interest in polycyclopropylated compounds is threefold. Firstly, recent studies on cyclopropylcarbinyl derivatives, particularly by Roberts and his co-workers,[2] have helped to make more explicit our knowledge of carbonium ion structure, and we thought that a study of reactions in which a positive charge might be generated on a carbon with two (or three) cyclopropyl groups attached to it would be significant. Dicyclopropyl ketone might be expected to serve as a good starting point for preparing such compounds.

Secondly, the unsaturated character of the cyclopropane ring is well established. Conjugation of the cyclopropane ring with the ethylenic double bond,[3a–d] carbonyl,[3a,b,e–g] phenyl[3a,g] and pyridyl[3h] groups has been demonstrated. Indeed, the interconversion of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl compounds may be looked upon as a result of the cyclopropane ring conjugating with the unsaturation of a carbonium ion. Recently, the question of whether the cyclopropane ring can conduct a chain of conjugation was raised. Smith and Rogier[4] found 2-phenylbicyclopropyl incapable of transmitting the conjugative effect of the second cyclopropane ring, its spectrum being nearly identical with that of phenylcyclopropane. Eastman,[5] in comparing the spectrum of 1-methyl-4-isopropyltricyclo[4,1,$0^{1,6}0^{2,4}$]heptanon-5 (I) with that of β-dihydroumbellulone (II), found that


I


II

instead of establishing a chain of conjugation, each cyclopropane ring conjugated separately with the carbonyl. It seemed of interest to examine the spectrum of dicyclopropyl ketone, a flexible model compound of I and spectra of related polycyclopropyl compounds.

Finally, dicyclopropyl ketone, if readily available, would offer an excellent synthetic entry into numerous molecules with two or more cyclopropane rings. Only a small number of simple molecules of this type have been reported. Among them are spiropentane,[6] dicyclopropyl[7] and 2-phenylbicyclopropyl.[4] Dicyclopropyl ketone itself was reported[8] to form in small amounts from the decarboxylation of cyclopropanecarboxylic acid over thoria, but there is some uncertainty whether

---

[1] Taken from part of a thesis submitted by Omer E. Curtis, Jr., to Michigan State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955.

[2] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509, 3542 (1951); C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952); S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948).

[3] (a) E. P. Carr and C. P. Burt, *ibid.*, **40**, 1590 (1918); (b) I. M. Klotz, *ibid.*, **66**, 88 (1944); (c) R. W. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **71**, 172, 3595 (1949); (d) J. M. Derfer, K. W. Greenlee and C. E. Boord, *ibid.*, **71**, 175 (1949); (e) R. C. Fuson and F. N. Baumgartner, *ibid.*, **70**, 3255 (1948); (f) J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946); (g) M. T. Rogers, *ibid.*, **69**, 2544 (1947); (h) R. P. Mariella, L. F. A. Peterson and R. C. Ferris, *ibid.*, **70**, 1494 (1948).

[4] L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).

[5] R. H. Eastman, *ibid.*, **76**, 4115 (1954).

[6] M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944); V. A. Slabey, *ibid.*, **68**, 1335 (1946).

[7] V. A. Slabey, *ibid.*, **74**, 4928 (1952).

[8] (a) L. Michiels, *Bull. soc. chim., Belg.*, **24**, 396 (1910); see also (b) L. Michiels, *Bull. sci. acad. roy. Belg.*, 10 (1912), for a description of cyclopropyl cyclopropylmethyl ketone and the corresponding carbinol.

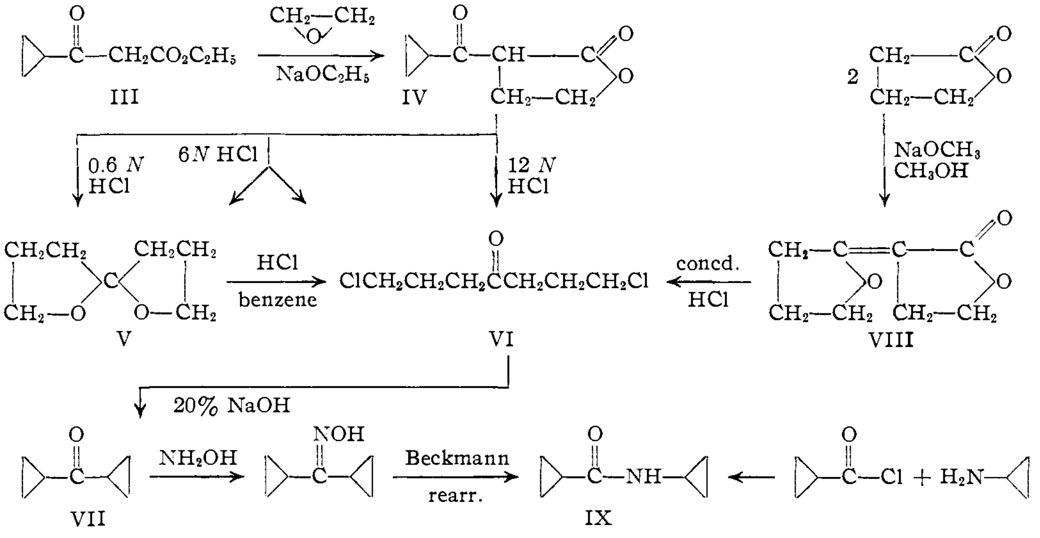
Michiels actually had the compound claimed.[9] Smith[10] has described some cyclopropyl nitrocyclopropyl ketones.

In all these cases, either the dicyclopropyl compound was obtained only with difficulty and in low over-all yield from a readily available source material, or the product did not lend itself to further syntheses of simple polycyclopropylated molecules. The procedure described in the present paper avoids these difficulties.

Results and Discussion

Synthesis.—Except for an approach which will be described in a separate paper,[11] our first attempt to prepare dicyclopropyl ketone was along rather prosaic lines, patterned after the well-known synthesis of methyl cyclopropyl ketone from α-acetyl-γ-butyrolactone.[12] Ethyl 3-cyclopropyl-3-ketopropanoate (III) was prepared from methyl cyclopropyl ketone and diethyl carbonate according to the procedure of Jackman, Bergman and Archer.[13] When treated with ethylene oxide and sodium ethoxide, α-cyclopropanecarbonyl-γ-butyrolactone (IV) was produced in 69% yield (see flow sheet). With 6 *N* hydrochloric acid, IV gave two products, neither of which was the desired cyclopropyl γ-chloropropyl ketone. The lower boiling product proved to be oxetone (1,4;4,7-dioxidoheptane) (V), the bicyclic ketal of heptan-1,7-diol-4-one. The higher boiling product contained chlorine, and its analysis, infrared spectrum and subsequent reactions are consistent with the structure 1,7-dichloro-4-heptanone (VI), formed, presumably, by cleavage of both the lactone and the cyclopropane rings.[14] IV with dilute acid gave principally V (58%), whereas with concentrated acid only VI (88%) was produced. Finally, V was converted to VI (79%) by treatment of a benzene solution of V with anhydrous hydrogen chloride at room temperature. Cyclodehydrohalogenation of VI, when refluxed with 20% aqueous sodium hydroxide, gave a 70% yield of the desired dicyclopropyl ketone (VII).

It now became apparent that a simple and direct route to dicyclopropyl ketone was at hand, from a readily available, inexpensive starting material. It had been reported[15] that oxetones resulted from the decarboxylation of the base-catalyzed condensation products of γ-lactones. Accordingly, γ-butyrolactone was refluxed with sodium methoxide in methanol for three hours, and the solvent was removed *in vacuo*, until a sirupy mass remained. This presumably was dibutyrolactone (VIII), although we did not attempt to isolate it in the crystalline state.[16] Instead of stopping at the oxetone stage, we proceeded directly to VI by refluxing the residue (VIII) with concentrated hydrochloric acid. The over-all yield of VI from γ-butyrolactone was 66%. VI was then cyclized to dicyclopropyl ketone as described above. Alternatively, it was possible to proceed directly from γ-butyrolactone to dicyclopropyl ketone without isolating any intermediates.[17] The over-all yield of dicyclopropyl ketone from γ-butyrolactone varied from 50–60%.


FLOW SHEET FOR THE PREPARATION AND STRUCTURE PROOF OF DICYCLOPROPYL KETONE

The exact sequence of events in proceeding from

---

[9] The semicarbazone was reported by Michiels to melt at 85–86°, but unfortunately he had an insufficient amount either of the ketone or its semicarbazone to analyze. We obtained a melting point of 159–160.5° for authentic semicarbazone. In a later paper Michiels[8b] reported an index of refraction n^{20}_{D} 1.4515 for his ketone, a value appreciably lower than ours.

[10] L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 3831, 3837 (1951).

[11] H. Hart and Omer E. Curtis, Jr., unpublished results.

[12] G. W. Cannon, R. C. Ellis and J. R. Leal, *Org. Syntheses*, **31**, 74 (1951).

[13] M. Jackman, A. J. Bergman and S. Archer, THIS JOURNAL, **70**, 497 (1948).

[14] E. P. Kohler and J. B. Conant, *ibid.*, **39**, 1404 (1917).

[15] R. Fittig, *Ann.*, **256**, 50 (1889); J. Volhard, *ibid.*, **267**, 78 (1892); R. Fittig and K. Strom, *ibid.*, **267**, 191 (1892).

[16] The condensation of γ-butyrolactone to VIII has been investigated in some detail by E. Y. Spencer and G. F. Wright, THIS JOURNAL, **63**, 1281 (1941), who report VIII to be a crystalline solid, m.p. 86–87°. Their yields of crystalline product were 40% or less, and the reaction was shown to be reversible. It is therefore imperative to remove all of the alcohol, or a good yield will not be obtained. The yield of crude VIII is appreciably higher than 40%. Spencer and Wright obtained oxetonecarboxylic acid from VIII and aqueous alkali.

[17] We are indebted to Joseph M. Sandri for working out the details of this modification.

dibutyrolactone to 1,7-dichloro-4-heptanone was not established. The reaction involves hydrolytic cleavage of the vinyl ether and lactone linkages, ketonization and decarboxylation of the β-keto acid. If the reaction is stopped at the dichloroketone stage, one has ready access from γ-butyrolactone to a trifunctional molecule of some synthetic interest. Some of the reactions of VI are now under investigation.

Proof of Structure.—The infrared spectrum (Table I) of VII, in addition to showing the characteristic carbonyl and cyclopropane[18] bands, contained no peaks which could be assigned to olefinic double bonds. When the oxime of VII was treated in aqueous dioxane with sodium bicarbonate and benzenesulfonyl chloride,[19] an amide (IX) was obtained in 65% yield which was identical with that prepared from cyclopropylamine and cyclopropanecarbonyl chloride.

TABLE I

THE PRINCIPAL INFRARED BANDS FOR CERTAIN POLYCYCLOPROPYL COMPOUNDS[a]

Dicyclopropyl ketone

3110(m), 3035(s), 2905(w), 1694(s), 1453(s), 1407(s), 1353(m), 1220(s), 1186(s), 1096(s),* 1068(s), 1033(s), 1017(s), 985(m), 921(m), 910(m), 877(m), 849(s), 820(s), 793(m), 733(w)

Dicyclopropylcarbinol

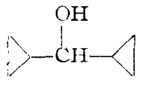
3650(m), 3500(m, broad), 3110(s), 3040(s), 2890(s), 1470(m), 1437(s), 1385(m), 1350(w), 1288(m), 1260(m), 1194(m), 1172(m), 1137(s), 1107(s), 1040(s), 1021(s),* 997(s), 970(m), 931(s), 909(m), 853(m)

Dicyclopropylmethane

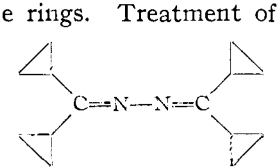
3080(s), 3020(s), 2905(s), 2855(m), 1463(m), 1444(m), 1431(s), 1390(w), 1367(w), 1287(s), 1170(w), 1105(w), 1043(s), 1012(s),* 991(s), 972(m), 928(s)

[a] The spectra were determined in carbon tetrachloride, 1 part in 50 by volume, using 0.5-mm. NaCl cells; (s), (m) and (w) indicate > 60%, 30–60% and <30% of the absorption of the most intense band which in each case is designated by an asterisk.

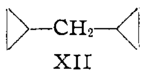
Reactions and Spectra.—Reduction of the ketone with lithium aluminum hydride in the customary manner gave dicyclopropylcarbinol (X) in 89% yield.[20] With hydrazine, VII gave a liquid hydrazone and a crystalline azine (XI), a molecule with four cyclopropane rings. Treatment of the hydrazone with base, or direct reduction of the ketone[21] gave dicyclopropylmethane (XII).



X



XI



XII

The infrared spectrum of dicyclopropyl ketone, when compared with that of diisopropyl ketone, showed a shift of the carbonyl absorption from 1722 to 1694 cm.$^{-1}$, less than the amount usually associated with double bond conjugation, but nevertheless a significant shift.[22,23] The shift in isopropyl cyclopropyl ketone was to 1702 cm.$^{-1}$.

The infrared spectra in the region of 3000 cm.$^{-1}$ (C–H stretching vibrations) of the cyclopropyl derivatives are also informative. These compounds show C–H absorption at shorter wave lengths than most other saturated organic molecules. Thus, the C–H absorption is easily resolved into four distinct bands for dicyclopropylmethane, at 3080, 3020, 2905 and 2855 cm.$^{-1}$. For dicyclopropyl ketone, bands at 3110, 3035 and 2905 cm.$^{-1}$ appear. Dicyclopropylcarbinol has very sharp bands at 3110, 3040 and 2890 cm.$^{-1}$. On the other hand, although diisopropyl ketone has the three lower frequency bands at 2990, 2950 and 2890 cm.$^{-1}$, it shows no band near 3100 cm.$^{-1}$. These resolutions were obtained with ordinary NaCl cells using no special resolving techniques. It would seem particularly that the 3100 cm.$^{-1}$ band is associated with the cyclopropane ring. Wiberley and Bunce[24] have called attention to this absorption previously and it would appear that the occurrence of bands both at 3100 and 1020 cm.$^{-1}$ can be taken as strong evidence for the presence of a cyclopropane ring. Often an unusual amount of structure also appears in the 1420–1470 cm.$^{-1}$ region, three sharp bands being frequently evident.

The ultraviolet absorption spectra (Table II) show that the second cyclopropane ring in dicyclopropyl ketone has almost no effect on the position of the short wave length band, isopropyl cyclopropyl ketone and dicyclopropyl ketone having nearly identical spectra below 220 mμ. This is analogous to the relationship between the spectra of α,β-unsaturated and α,β,α′,β′-di-unsaturated ketones.[25] Our results are in agreement with those of Rogers.[3g,26]

TABLE II

THE ULTRAVIOLET MAXIMA OF CERTAIN KETONES, mμ

	Short wave length absorption		Longer wave length absorption	
Ketone	λmax, mμ	log ε	λmax, mμ	log ε
Diisopropyl	<200	>3.0	285	1.45
Isopropyl cyclopropyl	<208	>3.0	276	1.54
Dicyclopropyl	<208	>3.1	266	1.55
Isopropenyl cyclopropyl	215	4.0	305	1.59

The chemistry and spectra of polycyclopropyl

---

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 27.

(19) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 3176 (1951).

(20) The infrared spectrum in CCl_4 showed the hydroxyl (3650 cm.$^{-1}$ sharp and 3550–3200 cm.$^{-1}$ broad) and cyclopropane (1021 cm.$^{-1}$) bands; di-*n*-propyl carbinol and *n*-propyl cyclopropyl carbinol, possible products of the reduction, have much lower refractive indices and sufficiently different percentage compositions than the actual product, so that they can be eliminated as possible structures.

(21) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(22) N. Fuson, M. L. Josien and E. M. Shelton, *ibid.*, **76**, 2526 (1954).

(23) See reference 18, p. 117.

(24) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952); see also V. A. Slabey, THIS JOURNAL, **76**, 3604 (1954).

(25) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 815 (1941); E. A. Braude, *Ann. Repts. Chem. Soc., London*, 115 (1945).

(26) Attention should be called to the unusual hypsochromic shift of the low intensity longer wave length band when cyclopropyl groups replace alkyl groups (Table II). R. H. Eastman (private communication) observed several similar cases, and the effect deserves systematic study.

compounds are being investigated further, and will be the subject of future communications.

Experimental[27]

α-Cyclopropanecarbonyl-γ-butyrolactone (IV).[28]—Ethyl 3-cyclopropyl-3-ketopropanoate[13] (III) (355 g., 2.27 moles) was added slowly to a solution of 52 g. (2.26 moles) of sodium in one liter of absolute alcohol, cooled in an ice-bath. This was followed by 130 g. (2.95 moles) of ethylene oxide. After coming to room temperature and stirring for 22 hours, the alcohol was removed *in vacuo* and the residue dissolved in 200 ml. of water. After neutralization (acetic acid) the solution was extracted with benzene. Upon drying and removal of the benzene, there was obtained 36 g. of recovered III (b.p. 92–105° at 4 mm.) and 217 g. (69%) of α-cyclopropanecarbonyl-γ-butyrolactone (IV), b.p. 122° at 3 mm., $n^{25}\text{D}$ 1.4844.

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.3; H, 6.5. Found: C, 62.2; H, 6.43.

The 2,4-dinitrophenylhydrazone, after recrystallization from methanol, melted at 175–176°.

Anal. Calcd. for $C_{14}H_{14}N_4O_6$: C, 50.26; H, 4.19; N, 16.75. Found: C, 50.62; H, 4.39; N, 16.41.

In addition to the major product, there were obtained 39 g. of lower boiling products (47–57° at 22 mm.). Refractionation gave two cuts, b.p. 59° at 32 mm., $n^{25}\text{D}$ 1.4058, and b.p. 73° at 31 mm., $n^{25}\text{D}$, 1.4027. The first fraction showed strong hydroxyl and weak carbonyl absorption in the infrared; the second, a strong ester carbonyl, and weak hydroxyl band. These products were not investigated further.

Oxetone (1,4;4,7-Dioxidoheptane) (V).—A mixture of 200 ml. of water, 10 ml. of concentrated hydrochloric acid and 47 g. (0.31 mole) of α-cyclopropanecarbonyl-γ-butyrolactone (IV) was refluxed for 45 minutes, then steam distilled until the distillate was clear. After saturation of the distillate with potassium carbonate the upper layer was separated and dried over anhydrous potassium carbonate. During the first distillation (70–170° at 30 mm.) water was formed. The distillate was again dried, and there was obtained, upon redistillation, 23 g. (58%) of oxetone (V), b.p. 49° at 10 mm.,[15] $n^{25}\text{D}$ 1.4464.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.88; H, 9.36.

1,7-Dichloro-4-heptanone (VI). (a) **From IV.**—A mixture of 200 ml. of concentrated hydrochloric acid and 76 g. (0.493 mole) of α-cyclopropanecarbonyl-γ-butyrolactone (IV) was stirred until foaming ceased, then heated to boiling. After cooling, the mixture was saturated with ammonium chloride and extracted with ether. The combined ether extracts were dried at 0° over anhydrous sodium sulfate. After removal of the solvent, there was obtained 80 g. (88%) of 1,7-dichloro-4-heptanone (VI), b.p. 106–110° at 4 mm., $n^{25}\text{D}$ 1.4734. The compound decomposed on standing, even when stored in the refrigerator, and was converted to its 2,4-dinitrophenylhydrazone, m.p. 74–75° (methanol), for analysis.

Anal. Calcd. for $C_{13}H_{16}N_4O_4Cl_2$: C, 42.79; H, 4.44; N, 15.43; Cl, 19.52. Found: C, 43.02; H, 4.43; N, 15.25; Cl, 19.44.

(b) **From V.**—Anhydrous hydrogen chloride was passed through a solution of 22 g. (0.172 mole) of oxetone (V) in 20 ml. of benzene for 90 minutes at room temperature. After washing and removal of the benzene, there was obtained 3 g. of unreacted V and 21 g. (79%) of 1,7-dichloro-4-heptanone (VI).

(c) **From γ-Butyrolactone.**—To a solution of 23 g. (1.0 mole) of sodium in 400 ml. of absolute methanol there was added 172 g. (2 moles) of γ-butyrolactone, and the resulting solution was refluxed for three hours. The solvent was removed *in vacuo*. To the thick sirupy residue there was slowly added, with cooling and vigorous stirring, 500 ml. of concentrated hydrochloric acid. The mixture was refluxed for 15 minutes, then extracted with ether. The ether extracts were dried over potassium carbonate, and, after removal of the solvent, there was obtained 119 g. (66%) of 1,7-dichloro-4-heptanone (VI).

Dicyclopropyl Ketone (VII). (a) **From 1,7-Dichloro-4-heptanone (VI).**—A mixture of 600 ml. of 20% sodium hydroxide and 165 g. (0.90 mole) of 1,7-dichloro-4-heptanone (VI) was refluxed, with vigorous stirring, for 30 minutes, then steam distilled until the characteristic odor of the ketone was absent from the distillate. The latter was then saturated with potassium carbonate, the upper layer separated and the water layer extracted with ether. After drying (potassium carbonate) and removal of the solvent, there was obtained 69 g. (70%) of dicyclopropyl ketone (VII), b.p. 69° at 20 mm., $n^{25}\text{D}$ 1.4654. It distilled without decomposition at atmospheric pressure, b.p. 162.5–163.0°.

Anal. Calcd. for $C_7H_{10}O$: C, 76.4; H, 9.1. Found: C, 76.18; H, 9.13.

The 2,4-dinitrophenylhydrazone melted (methanol) at 191.5–192.0°. *Anal.* Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.84; H, 5.04; N, 18.82.

The semicarbazone melted (water) at 159–160.5°. *Anal.* Calcd. for $C_8H_{13}N_3O$: C, 57.4; H, 7.84; N, 25.1. Found: C, 57.43; H, 7.40; N, 23.93.

(b) **Directly from γ-Butyrolactone.**—Procedure c for the preparation of 1,7-dichloro-4-heptanone (VI) was followed through refluxing with concentrated hydrochloric acid. Then 480 g. of 50% aqueous sodium hydroxide was added, with cooling. The salt which precipitated did not interfere with the reaction. The mixture was refluxed for 30 minutes, then steam distilled and worked up as in the procedure immediately above. The over-all yield of dicyclopropyl ketone (VII) varied from 50–60%.

Structure Proof for VII. (a) **Dicyclopropylketoxime.**—Dicyclopropyl ketone (VII) (21 g., 0.19 mole), 20 g. of hydroxylamine hydrochloride, 17 g. of sodium bicarbonate and 60 ml. of water, when heated together on a steam-bath for six hours gave 15 g. (62%) of dicyclopropylketoxime m.p. 76–77° (petroleum ether).

Anal. Calcd. for $C_7H_{11}NO$: C, 67.2; H, 8.8; N, 11.2. Found: C, 67.22; H, 8.97; N, 10.85.

(b) **Beckmann Rearrangement.**—A mixture of 10 g. of dicyclopropylketoxime, 16 g. of sodium bicarbonate, 65 ml. of water and 40 ml. of dioxane was treated, at the boiling point, over a period of ten minutes, with 16 g. of benzenesulfonyl chloride. After evaporation to dryness on a steam-bath, the solid residue was extracted for four hours with ether in a Soxhlet extractor. After removal of the ether, there remained 6.5 g. (65%) of N-cyclopropyl-cyclopropanecarboxamide (IX). The solid was easily sublimed, or could be recrystallized from cyclohexane, m.p. 110–111°.

Anal. Calcd. for $C_7H_{11}NO$: C, 67.2; H, 8.8; N, 11.2. Found: C, 67.78; H, 8.83; N, 10.94.

(c) **N-Cyclopropyl-cyclopropanecarboxamide (IX).**—From 10 g. of cyclopropanecarbonyl chloride and 5.0 g. of cyclopropylamine[29] in 20 ml. of cold pyridine, there was obtained 4.0 g. (36.5%) of N-cyclopropyl-cyclopropanecarboxamide (IX), m.p. 110–111°, identical with the sample prepared by rearrangement of dicyclopropylketoxime.

Dicyclopropylcarbinol (X).—Dicyclopropyl ketone (44 g., 0.4 mole) was added dropwise over a period of 30 minutes to a suspension of 6 g. of lithium aluminum hydride in 250 ml. of ether. After refluxing for one hour, the mixture was worked up in the usual manner,[30] using sodium hydroxide to dissolve the aluminum hydroxide, to give 40 g. (89%) of dicyclopropylcarbinol (X), b.p. 48° at 3 mm., $n^{25}\text{D}$ 1.4620.

Anal. Calcd. for $C_7H_{12}O$: C, 74.94; H, 10.78. Found: C, 75.02; H, 10.75.

The Hydrazone and Azine (XI) of Dicyclopropyl Ketone (VII).—A mixture of 40 g. (0.364 mole) of dicyclopropyl ketone, 40 g. of 85% hydrazine hydrate, 2 ml. of acetic acid and 100 ml. of ethanol was heated at 90° for 30 minutes. After removal of the alcohol by distillation, the residue was heated for three hours at 120°, then distilled. There was obtained 25 g. (55%) of the hydrazone, b.p. 100–115° at 6 mm., and 17 g. (43%) of the azine XI, b.p. 127–134° at 2 mm. The latter solidified on cooling and, after recrystallization from methanol, melted at 92–93°.

---

[27] Analyses were by the Clark Microanalytical Laboratory, Urbana, Ill. Melting points are uncorrected.

[28] The procedure was adapted from that used by R. M. Adams and C. A. VanderWerf, This Journal, **72**, 4368 (1950), to prepare α-acetyl-γ-valerolactone.

[29] P. Lipp, J. Buchkremer and H. Seeles, *Ann.*, **499**, 1 (1932).

[30] W. G. Brown in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. 6, 1951, p. 469.

Anal. Calcd. for $C_{14}H_{20}N_2$: C, 77.8; H, 9.3; N, 12.95. Found: C, 77.70; H, 9.55; N, 12.24.

The hydrazone was not purified further, but used directly to prepared dicyclopropylmethane (XII).

Dicyclopropylmethane (XII). (a) **From the Hydrazone.**—Sodium (2 g.) was dissolved in 100 ml. of diethylene glycol, and to this solution there was added 25 g. (0.2 mole) of dicyclopropyl ketone hydrazone. The solution was heated to 190–210° for 45 minutes and the product distilled as formed (4.2 liters of nitrogen were evolved). After drying (potassium carbonate) and redistillation there was obtained 9.0 g. (47%) of dicyclopropylmethane, b.p. 102° at atmospheric pressure, $n^{25}\text{D}$ 1.4228.

Anal. Calcd. for C_7H_{12}: C, 87.4; H, 12.6. Found: C, 87.72; H, 12.43.

(b) **From the Ketone.**—A mixture of 35 g. (0.32 mole) of dicyclopropyl ketone, 300 ml. of diethylene glycol, 40 g. of potassium hydroxide and 40 ml. of 85% hydrazine hydrate was heated for one hour at 130°. The excess hydrazine and water were removed until the pot temperature reached 180°, where it was maintained until all the product had distilled. The distillate was extracted with ether and, after drying (potassium carbonate) and removal of the solvent, there was obtained 19 g. (63%) of dicyclopropylmethane.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Reactions of Sodium Metal with Aromatic Hydrocarbons[1,2]

BY DONALD E. PAUL, DAVID LIPKIN AND S. I. WEISSMAN

RECEIVED MAY 9, 1955

The stoichiometry, optical absorption spectra and electrical conductivity of the products of the reaction of metallic sodium with aromatic hydrocarbons in tetrahydrofuran solution were studied. The results indicate that products containing one mole of sodium per mole of hydrocarbon are formed, in agreement with the conclusions arrived at by paramagnetic resonance absorption measurements. A relationship was found between the absorption spectra of reaction products and their parent hydrocarbons. The absorption spectra also were used as an analytical tool for the study of equilibria involving pairs of aromatic hydrocarbons and their corresponding negative ions. The results of these measurements give the following order of increasing electron affinities: benzene $\ll$ phenanthrene $<$ naphthalene $<$ anthracene, naphthacene. A mechanism is proposed for the reaction of a negative ion hydrocarbon free radical with various reactants (*i.e.*, carbon dioxide, water).

A brief description has been given of a reaction of sodium metal with aromatic hydrocarbons in the presence of solvents such as 1,2-dimethoxyethane and tetrahydrofuran.[3] In this paper we report the results of a more detailed study of some of the properties of the reaction products. Recently Holmes-Walker and Ubbelohde[4] described the results of an investigation of the solid reaction products obtained from the same kinds of reactants in different solvents.

In preparing solutions containing the products of the alkali metal–hydrocarbon reactions, high vacuum techniques were used similar to those employed by Kraus in his classical studies of the metal–ammonia systems and by Lewis, Lipkin and Magel[5] in their studies of triarylmethyls.[6]

The experiments were performed with tetrahydrofuran (THF) and, to a lesser extent, 1,2-dimethoxyethane as solvents. These solvents were both purified in the same way. The ether was first distilled from a mixture of activated alumina and sodium hydroxide pellets. The distillate, which was collected in a receiver containing sodium chips and anthracene, was redistilled into a solvent storage bulb on the vacuum line after standing in contact with the sodium and anthracene for at least one hour. The storage bulb contained a sphere of liquid sodium–potassium alloy and anthracene.

All the aromatic hydrocarbons used in this work, with the exception of triphenylene,[7] were Eastman Kodak Co. "white label" materials. Purification by recrystallization yielded samples with melting points in good agreement with values reported in the literature.

Composition of the Reaction Products

Scott, Walker and Hansley[8] have reported that the reaction between sodium metal and naphthalene in 1,2-dimethoxyethane, under an atmosphere of nitrogen, yields an intense green product in which the molar ratio of sodium to naphthalene is one. The data of Chu and Yu[9] for a number of aromatic hydrocarbons also indicate the formation of reaction products containing one mole of sodium per mole of hydrocarbon.

We have measured the molar ratio for the reaction between sodium metal and anthracene in THF under high vacuum conditions. The measurements were made as follows: a known volume (containing approximately 1.5×10^{-3} to 5.5×10^{-3} mole of solute) of a standard solution of anthracene in cyclohexane or benzene and a capillary containing a large excess of sodium metal were introduced into a dumper on the vacuum line. After evaporation of the solvent, anthracene was carefully sublimed from one portion of the dumper to another and the sodium then was volatilized from the capillary to form a mirror on the walls. THF from the storage bulb was distilled into the dumper and the resulting blue solution, after sufficient time for complete reaction of the hydrocarbon had elapsed, was either decanted or poured through a glass wool filter into a receiver. Solvent was distilled back into the dumper and any product remaining there poured into the receiver. The receiver was sealed off, broken open and a few drops of water immediately added to its contents. The mixture was quantitatively transferred, with enough carbon dioxide-free water to reduce the concentration of THF below

---

[1] Taken in part from a thesis submitted by Donald E. Paul to the Graduate Board of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This research was supported, in part, by a Universal Match Company Fellowship, by the joint program of the United States Atomic Energy Commission and the Office of Naval Research, and by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[3] D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

[4] W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.*, 720 (1954).

[5] G. N. Lewis, D. Lipkin and T. T. Magel, THIS JOURNAL, **66**, 1579 (1944).

[6] Holmes-Walker and Ubbelohde[4] did not use high vacuum techniques and it is possible that their results were complicated by the products resulting from decomposition of the metal-anthracene complex. In our experiments sodium metal films remained bright indefinitely, even in the presence of solvent. Furthermore, solutions of our reaction products have remained unchanged for almost a year.

[7] We wish to thank Mr. Wm. E. Emerson for the preparation of the sample of triphenylene.

[8] N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

[9] T. L. Chu and S. C. Yu, *ibid.*, **76**, 3367 (1954).