Interaction of Ketonic Mannich Bases with Nitroparaffins.—Four slightly different procedures (I–IV) were used. **Procedure** I consisted essentially of refluxing a solution of the Mannich base derived from dimethylamine in excess of the primary or secondary nitroparaffin (which must have been freshly redistilled) in presence of solid sodium hydroxide (1 mole) in an atmosphere of nitrogen. A heavy white precipitate of the sodium salt of the nitroparaffin formed rapidly and dimethylamine was evolved. When this evolution ceased (1.5–7.5 hours) the cooled reaction mixture was acidified with 10% acetic acid and ether-extracted. The extract was washed several times with water, dried, shaken with Norit, filtered and the solvent and excess nitroparaffin distilled off under reduced pressure. The crystalline residue was drained on a porous tile and recrystallized, usually from methanol.

Procedure II, applied to Mannich bases derived from such secondary bases as morpholine, was essentially the same as procedure I except that volatile secondary base was not lost from the reaction mixture and refluxing was maintained for 4–7.5 hours.

Procedure III was almost identical with that described by Reichert and Posemann[12] for the condensation of Mannich bases with nitromethane.

Procedure IV was essentially the same as Procedure I except that sodium hydroxide was omitted from the reaction mixture. The results obtained are set out in Table III.

TABLE IV

SEMICARBAZONES OF NITROKETONES

Ketone	Formula	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
XI	$C_{13}H_{18}N_4O_3$	136	20.2	19.8
XII	$C_{14}H_{20}N_4O_3$	154.5	19.2	18.8
XIII	$C_{11}H_{20}N_4O_3$	178	21.9	21.8
XIV	$C_8H_{16}N_4O_3$	193	25.9	25.9
XV	$C_{11}H_{20}N_4O_3$	138	21.9	21.6
XVI	$C_{13}H_{18}N_4O_3$	163	20.2	19.9
XIX	$C_{18}H_{20}N_4O_3$	138.5	16.5	16.4

1,6-Diphenyl-4-ethyl-4-nitro-octan-1,7-dione.—Sodium (0.23 g.) was dissolved in anhydrous methanol (5 ml.) and XVI (2.21 g.) in anhydrous methanol (10 ml.) added. A solution of G (2.33 g.) in anhydrous methanol (5 ml.) was then added and the solution refluxed gently for 3 hours. The product (2.5 g., 70%) crystallized on cooling, and after recrystallization from ethanol formed fine white needles, m.p. 163.5°.

Anal. Calcd. for $C_{22}H_{25}NO_4$: C, 71.9; H, 6.8; N, 3.8. Found: C, 72.0; H, 6.9; N, 3.7.

SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS, LEWIS FLIGHT PROPULSION LABORATORY]

Reaction of Cyclopropyl Chloride with Lithium. Isolation of Dicyclopropyl

BY VERNON A. SLABEY

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The reaction of cyclopropyl chloride with lithium in ether was investigated. Cyclopropane was the principal product of the reaction; however, 10 to 12% yields of a liquid hydrocarbon product were also obtained. The physical and chemical properties of a hydrocarbon isolated from the liquid product support the opinion that the hydrocarbon is dicyclopropyl. M.p., b.p., n^{20}D, d^{20} and the infrared spectrum are presented for the hydrocarbon, and for cyclopropyl chloride, 1,1-dichlorocyclopropane and *trans*-1,2-dichlorocyclopropane. The cyclopropyl halides were prepared by the photochlorination of cyclopropane.

Dicyclopropyl, the smallest of the dicyclic hydrocarbons, was desired for an investigation of the effects of structure on combustion characteristics and other properties pertinent to the research at the Lewis laboratory on aircraft propulsion systems. Several methods are known for the preparation of hydrocarbons which contain one cyclopropyl ring, but a search of the literature when the present work was begun did not reveal any previous attempts to prepare a hydrocarbon which contained two cyclopropyl rings.[1] The reaction of cyclopropyl chloride with lithium was investigated as a possible approach to the synthesis of dicyclopropyl. The properties of a hydrocarbon isolated from the reaction products support the opinion that the hydrocarbon is dicyclopropyl.

Cyclopropane was the principal product of the reaction of cyclopropyl chloride with lithium in ether; however, 10 to 12% yields of a liquid hydrocarbon product, boiling from 70–75°, were also obtained.[2] Unsaturated constituents, traces of which were disclosed by infrared spectra, were removed from the liquid product by extractions with aqueous silver nitrate.[3] The extracted hydrocarbon was then passed through silica gel and, finally, fractionated azeotropically with ethanol through a column at better than 150 theoretical plate efficiency. The physical properties of the purified hydrocarbon, determined by methods previously referenced,[4] are given in Table I.

The composition of the purified hydrocarbon corresponded well to that calculated for C_6H_{10}. Unsaturated structures were ruled out since the hydrocarbon was inert toward both bromine in carbon tetrachloride and potassium permanganate in acetone. The strong absorption in the infrared spectrum (Fig. 1(d)) at 9.82 μ was interpreted to be convincing evidence that the hydrocarbon contained at least one cyclopropyl group, since absorption attributed to the cyclopropyl ring has previously been observed in this region in over 40 hydrocarbon and non-hydrocarbon derivatives of cyclopropane.[5] A comparison of the molecular refractivity of the hydrocarbon with the refractivities of several monoalkylcyclopropanes (Table II) showed the hydrocarbon had twice the exaltation of the structures which contained only one cyclopropyl ring. The method of preparation and these

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(1) Recently, L. I. Smith and E. R. Rogier (THIS JOURNAL, 73, 3840 (1951)) reported the synthesis of 2-phenylbicyclopropyl. They were unable to prepare the necessary intermediate for the synthesis of dicyclopropyl by the same method.

(2) When methylcyclohexane was used in place of ether, no reaction occurred. When sodium was used in place of lithium in ether, the products were the same, but the yield of liquid product was reduced.

(3) M. Murray and E. Stevenson, THIS JOURNAL, 66, 812 (1944).

(4) I. A. Goodman and P. H. Wise, *ibid.*, 72, 3076 (1950).

(5) Unpublished work from this Laboratory and J. M. Derfer, E. E. Pickett and C. B. Boord, *ibid.*, 71, 2482 (1949).

physical and chemical properties support the proposed dicyclopropyl structure for the hydrocarbon.

TABLE I

PHYSICAL PROPERTIES OF DICYCLOPROPYL AND CHLORINATED CYCLOPROPANES

Compound	M.p., °C.	B.p., °C. at 760 mm.	n^{20}D	d^{20}, g./ml.
Dicyclopropyl[a]	−82.62	76.10	1.4239	0.78979
Cyclopropyl	−97.68[b]	43.43	1.4108	.9962
chloride[6]	...	43	1.4079[c]	.9899[c]
1,1-Dichlorocyclo-	−37.47[b]	75.55	1.4400	1.2159
propane[7]	...	75.0	1.4377[c]	1.2178[c]
trans-1,2-Dichloro-	−18.74	87.94	1.4526	1.2459
cyclopropane[7]	−19.5	87.2	1.4502[c]	1.2492[c]

[a] Net heat of combn., 885 kcal./mole. [b] F.p., °C. [c] 25°.

TABLE II

MOLECULAR REFRACTIONS OF CYCLOPROPANES

Compound	Obsd.	Calcd.[b]	Exal.
Dicyclopropyl	26.53	25.83	0.70
Ethylcyclopropane[a]	23.66	23.24	.42
2-Cyclopropylpropane	28.33	27.88	.45
2-Cyclopropylbutane	32.85	32.53	.32
2-Cyclopropylpentane	37.51	37.18	.33
2-Cyclopropylhexane	42.14	41.82	.32
2-Cyclopropyl-3-methylbutane	37.39	37.18	.21
Av. exal. for monoalkylcyclopropanes			0.34

[a] Observed value taken from data of C. E. Boord, 11th Annual Report, APRIRP 45, Columbus, Ohio, June, 1949. Other observed values from unpublished data of Lewis laboratory. [b] Calculated values determined by summing only the required number of carbon and hydrogen atomic refractivities. The atomic refractivities of A. I. Vogel (*J. Chem. Soc.*, 1833 (1948)) were used.

The character of the unsaturated impurities in the liquid reaction product was also investigated. A portion of the crude product was fractionated through silica gel in order to concentrate the unsaturated constituents. The infrared absorption of the impurities (Fig. 1(e)) matched the absorption of 1-hexyne at 3, 4.8, 8 and 14.5 to 15.5 μ. The boiling range of the liquid product (70–75°) supported this identification. Infrared bands at 6.1 and 10.2 μ indicated that a constituent with a terminal olefinic linkage was also present, and from the strong absorption at 9.8 μ, it was inferred that this olefinic constituent was a cyclopropylalkene. Only two structures, 2-cyclopropylpropene and 3-cyclopropylpropene, fitted the interpretation of the infrared spectrum, since the narrow boiling range of the liquid product supported the assumption that the hydrocarbons in the liquid product were isomeric. The former structure was eliminated when its spectrum was compared with Fig. 1(e); the spectrum of the latter was not available, so the identity of the olefinic constituent of the liquid product was not definitely proved.

The physical properties and infrared spectra of cyclopropyl chloride, 1,1-dichlorocyclopropane and *trans*-1,2-dichlorocyclopropane are given in Table I and Fig. 1, respectively. The three halides were found to be present in the products of the chlorination of cyclopropane to the following extent: cyclopropyl chloride, 52 wt. %; 1,1-dichloro, 24% and *trans*-1,2-dichloro, 2%.

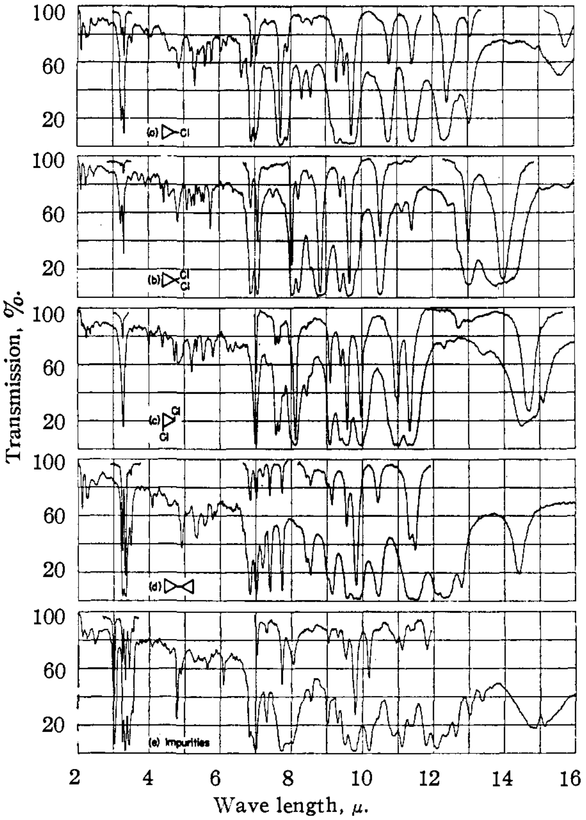

Fig. 1.—Infrared spectra: (a), (b) and (c) undiluted and 1:10 CS_2; (d) and (e) undiluted and 1:10 CCl_4; cell width, 0.1 mm.

Experimental

Chlorination of Cyclopropane.—The apparatus was essentially that of Roberts and Dirstine[8] with elimination of the recycling system. The reaction chamber consisted of 470 cm. of 0.7 cm. Pyrex tubing bent to form a planar grid which was illuminated by two G.E. RS sun lamps. Gas flows of the reactants were regulated to approximately 0.12 mole cyclopropane/min. and 0.046 mole chlorine/min. At the end of a 6-hour reaction period the amount of cyclopropane used was 1866 g. (44.4 moles) and the amount of chlorine 1148 g. (16.2 moles). Fractionation of the products gave 352 g. (4.6 moles) of cyclopropyl chloride and 394 g. of higher-boiling halides. Refractionation of the higher-boiling halides from several experiments (4711 g.) gave 377 g. of additional cyclopropyl chloride, 2071 g. of 1,1-dichlorocyclopropane, 101 g. of *trans*-1,2-dichlorocyclopropane, and 190 g. of a product, which from its physical properties (m.p. −58.98°, b.p. 145.55° at 760 mm., n^{20}D 1.4718, d^{20} 1.35557 g./ml.) was believed to be 1,1,3-trichloropropane. No other pure products could be isolated from the remaining complex mixture of polyhalides.

Reaction of Cyclopropyl Chloride with Lithium.—Twenty moles (1531 g.) of cyclopropyl chloride, n^{20}D 1.4108, was added with stirring to a 5-liter flask containing 20 g. atoms (138 g.) of lithium sand covered with 1 liter of dry ether. A vigorous reaction occurred with the addition of the first 10 ml. of halide, and a flocculent white precipitate appeared. The color of the reaction mixture gradually changed from milky to reddish-brown as the remainder of the halide was added. Evolution of cyclopropane occurred simultaneously with the color change and became so vigorous that external cooling with solid CO_2 was necessary to keep the reaction under control. When the vigorous reaction had subsided, the reaction mixture was permitted to warm, and stirring was continued at room temperature for 10 days.

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(6) M. T. Rogers and John D. Roberts, THIS JOURNAL, 68, 843 (1946).

(7) P. G. Stevens, *ibid.*, 68, 620 (1946).

(8) J. D. Roberts and P. H. Dirstine, *ibid.*, 67, 1281 (1945).

The mixture was then hydrolyzed by the cautious addition of water. The volatile products were removed by steam distillation, dried over Drierite, and then fractionated through a 22-mm. by 7-ft. column which was packed with $^1/_8$-inch glass helices. The distillate after the ether was removed consisted of 321 g. of unreacted cyclopropyl chloride, 110 g. of hydrocarbon, b.p. 70–75°, $n^{20}\mathrm{D}$ 1.4225–1.4242 (98 g., b.p. 74–75°, $n^{20}\mathrm{D}$ 1.4237–1.4239), and 100 g. of tar. In addition to these products, a total of 272 g. of cyclopropane was collected during the course of the reaction, and another 86 g. during hydrolysis of the reaction mixture.

The disposition of the cyclopropyl chloride was calculated to be 21% recovered, 32% used in the formation of cyclopropane during the reaction and 10% during the hydrolysis, and 14% used in the formation of liquid products; the remaining 23% was presumed to have been lost through volatilization and polymer and tar formation.

Purification of the Hydrocarbon.—A quantity of the hydrocarbon (93 g., $n^{20}\mathrm{D}$ 1.4237–1.4239) was chilled to 0° and extracted in a separatory funnel first with six 80-ml. portions of an ice-cold saturated solution of silver nitrate and then with two 100-ml. portions of distilled water. Loss of hydrocarbon during the extraction process was 4 g. The extracted hydrocarbon was dried over calcium chloride and the physical properties then determined: m.p. −82.74°, b.p. 76.07° at 760 mm., $n^{20}\mathrm{D}$ 1.4340, d^{20} 0.78969 g./ml. This material plus additional hydrocarbon treated in the same manner (total quantity, 167 g.) was passed through a 6-ft. water-cooled column of "through 200 mesh" silica gel to obtain 155 g. of constant $n^{20}\mathrm{D}$ fractions. Azeotropic fractionation of 144 g. of the constant index hydrocarbon with ethanol through a 6-ft. Podbielniak column gave the following *hydrocarbon* fractions: first fraction, $n^{20}\mathrm{D}$ 1.4235 (5.5 g.), next eight fractions, $n^{20}\mathrm{D}$ 1.4239 (106 g.), last fraction, $n^{20}\mathrm{D}$ 1.4246 (9.0 g.). The six middle fractions were combined for determination of physical properties (Table I). The purified hydrocarbon did not decolorize one drop of either 5% bromine in carbon tetrachloride or 2% potassium permanganate in acetone.[9]

Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found: C, 87.65; H, 12.32.

Separation of Impurities with Silica Gel.—A 50-g. sample of the crude liquid reaction product was absorbed in a water-cooled column (ASTM designation D-936-49T) of "through 200 mesh" silica gel. Ethanol was used to elutriate the hydrocarbon from the gel, and the hydrocarbon was collected in 20 fractions: the first fraction (2.2 g.), $n^{20}\mathrm{D}$ 1.4235; the next 13 fractions (35.6 g.), $n^{20}\mathrm{D}$ 1.4239; two fractions (4.4 g.), $n^{20}\mathrm{D}$ 1.4227 and 1.4214, respectively; two fractions (1.2 g.), $n^{20}\mathrm{D}$ 1.4246; and the last two fractions (1 g. each), $n^{20}\mathrm{D}$ 1.4250 and 1.4258, respectively. Infrared spectra were determined for all fractions; the first 14 were essentially identical and showed all the bands of the major constituent of the reaction product, and no absorption at 3 μ (C≡C) or at 6.1 μ (C=C), while the last 6 showed acetylenic and olefinic impurities were present. The olefinic impurity appeared in higher concentration in the last 6 fractions with each successive fraction, while the acetylenic impurity remained at approximately the same concentration. The infrared spectrum of fraction 19 (Fig. 1(e)) shows the major absorption bands of the impurities, and is presented to substantiate their proposed identification.

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(9) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 36, 38.

CLEVELAND 11, OHIO

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Dehydration of Methylcyclopropylcarbinol over Alumina. A Synthesis of Vinylcyclopropane

BY VERNON A. SLABEY

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The dehydration of methylcyclopropylcarbinol over alumina at temperatures between 265 and 300° gave vinylcyclopropane in yields as high as 54%. Other identified products of the reaction were propene, isoprene, 1,3-pentadienes and 2-methyltetrahydrofuran. Vinylcyclopropane of high purity (99.9 mole %) was obtained by fractionating the hydrocarbon azeotropically with ethanol. Some physical properties of vinylcyclopropane (m.p., b.p., $n^{20}\mathrm{D}$, d^{20}, heat of combustion and $\Delta T_{\mathrm{m.p.}}$/mole % impurity) were measured and the liquid phase infrared spectrum of the hydrocarbon was determined.

The preparation of several cyclopropylalkenes by the dehydration of tertiary alkylcyclopropylcarbinols over alumina[1] suggested that vinylcyclopropane could be prepared from methylcyclopropylcarbinol in the same way, although Dojarenko[2] had already investigated the reaction at temperatures varying from 240 to 365° and had concluded that the products were propene, divinylmethane, piperylene and methylcyclobutene. The results of the previous work were questioned, because (1) only very small quantities of carbinol were used in the investigation, (2) the identification of products by reaction with bromine would obscure the presence of cyclopropane derivatives, and (3) vinylcyclopropane was apparently not considered to be a possible product of the reaction. Recently, Van Volkenburgh, *et al.*,[3] reported that methylcyclopropylcarbinol was dehydrated very slowly by sulfuric acid to give a mixture which contained approximately equal amounts of vinylcyclopropane and other unsaturated hydrocarbons (presumably isoprene, 1,4-pentadiene and 1,3-pentadienes); the yield of vinylcyclopropane was 39%. Vinylcyclopropane has also been prepared by the exhaustive methylation of methylcyclopropylcarbinylamine.[4]

Contrary to the previous report,[2] vinylcyclopropane has now been found to be the principal product when methylcyclopropylcarbinol, dissolved in toluene, is passed over an alumina catalyst at temperatures from 265 to 300°. Other distillable products of the reaction were propene, isoprene, 1,3-pentadienes and 2-methyltetrahydrofuran. The process was less time consuming than previously reported methods of preparing vinylcyclopropane, and is convenient for preparations on either large or small scale.

The effect of temperature, over the limited range investigated (265–300°), on the yield of vinylcyclopropane was not so nearly pronounced as

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(1) V. A. Slabey and P. H. Wise, THIS JOURNAL, **74**, 1473 (1952).

(2) M. Dojarenko, *Ber.*, **60B**, 1536 (1927).

(3) R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 3595 (1949).

(4) N. J. Demjanov and M. Dojarenko, *Ber.*, **55B**, 2718 (1922).