Hexahydroindolo-(2,3-a)-quinolizine (II).—1-Ketoquinolizidine (3.06 g., 0.02 mole) and phenylhydrazine (2.4 g., 0.022 mole) were heated together on a steam-bath for 30 minutes. The liberated water was removed under reduced pressure, and the residual material was taken up in 85 ml. of absolute ethanol. The solution was saturated with dry hydrogen chloride, and then refluxed for 3.5 hours. The solution was resaturated with hydrogen chloride after it had stood overnight, and it was then refluxed for an additional hour. The alcohol was removed *in vacuo*, the residue was made basic with potassium carbonate solution, and was extracted with ether and benzene. The organic extracts were combined, washed with water and evaporated in air. Hexane was added and the solid collected on a filter. The product was dried, purified by sublimation at 150° (0.01 mm.), and was obtained as a pale yellow solid (2.1 g., 46%), m.p. 144–149°. The analytical sample was recrystallized twice from hexane, m.p. 148–151°. *Anal.* Calcd. for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02. ·Found: C, 79.54; H, 8.39.

The picrate was obtained from ethanol, m.p. 228–230°. *Anal.* Calcd. for $C_{21}H_{21}N_5O_7$: C, 55.38; H, 4.65. Found: C, 55.30; H, 4.63.

The Methiodide (IIIa).—The indolo-(2,3-a)-quinolizidine (0.567 g., 0.0025 mole) and an excess of methyl iodide were added to 25 ml. of ethyl acetate. The mixture was allowed to stand at room temperature for an hour, and the light tan precipitate was collected. The crude product (m.p. 150–160°) was taken up in 20 ml. of methanol, treated with decolorizing charcoal, concentrated to a few ml., and the product precipitated by adding ether. After three such treatments, 0.570 g. (62%) of nearly colorless amorphous material was obtained, m.p. 160–162°. *Anal.* Calcd for $C_{16}H_{21}IN_2 \cdot {}^1/_2H_2O$: C, 50.94; H, 5.84. Found: C, 50.60; H, 5.77.

The Benzyl Quaternary Salt (IIIb).—Sixty-six mg. of the indoloquinolizidine (II) was dissolved in 20 ml. of absolute ethanol. To this was added 2 ml. of benzyl chloride, and the solution was refluxed for 30 minutes. The solution was then concentrated to 10 ml., ether was added, and the solution was placed in the refrigerator for three days. The solid was collected and sublimed to give 64 mg. (60%) of pale yellow solid sintering about 190° and resolidifying to give tiny white prisms, m.p. 265° (dec.). It was recrystallized from alcohol–ether and showed the same melting point behavior. *Anal.* Calcd. for $C_{22}H_{25}ClN_2 \cdot H_2O$: C, 67.87; H, 7.50. Found: C, 67.86; H, 7.36.

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Dimethyleneketene: An Attempted Synthesis

BY HARRY M. WALBORSKY

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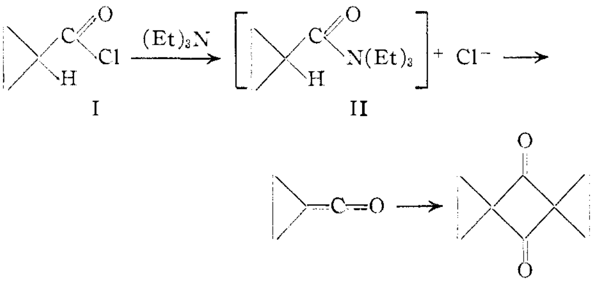
An elegant procedure for the preparation of ketoketene dimers is the reaction of an acid chloride with a tertiary amine yielding a ketoketene, which dimerizes to a 1,3-cyclobutanedione derivative. This method has been used successfully for the preparation of dimers from cyclohexanecarbonyl chloride,[1] cyclopentanecarbonyl chloride[2] and cyclobutanecarbonyl chloride.[3] In spite of the apparent generality of this method, attempts to prepare dimethyleneketene and subsequent dimer from cyclopropanecarbonyl chloride were abortive. An earlier attempt[4] to prepare this ketene by the mixed anhydride method also was futile.

When the acid chloride was added to triethylamine an immediate reaction occurs. The solid precipitate which was formed was undoubtedly the acyl quaternary ammonium salt[5] (II). When a sample of II was placed in aniline the anilide of I was formed. However, II did not eliminate triethylamine hydrochloride under the usual conditions to yield dimethyleneketene (III). A change to higher boiling solvents (benzene and xylene) did not effect elimination. In one run, sodium hydride was added to the reaction mixture in the hope that it would remove the α-hydrogen atom and thus promote the reaction, but this also failed.



The failure to obtain III is an excellent example of I-strain.[6] An exocyclic double bond in III would necessitate the conversion of the cyclopropyl carbon from a tetrahedral to a trigonal configuration. The bond angle in cyclopropane (60°) already imposes a certain amount of strain on the tetrahedral form (60 to 109°) but this strain is greatly increased in going to the trigonal form (60 to 120°). Energy considerations would then account for the failure to obtain III under these conditions.

The above considerations are in direct correlation with the facts that cyclopropanone[7] exists only as the hydrate and that nitrocyclopropane[8] is insoluble in bases.

Experimental

In a three-necked flask equipped with stirrer, dropping funnel and condenser were placed 10 g. (0.1 mole) of I and 50 cc. of dry ether. To this mixture, with stirring, was slowly added 12 g. (0.12 mole) of triethylamine. An immediate precipitate was obtained and the mixture was refluxed for 48 hours.

A sample of the mixture was removed and added to aniline. The resultant anilide gave a m.p. and mixed m.p. 111–112°[9] identical with cyclopropanecarboxanilide. To assure the fact that this was a reaction of **II** with aniline, 0.4 g. of the acid chloride was mixed with 1 cc. of triethylamine and all excess reagent removed *in vacuo*. The dry solid was washed with ether, dried, and reacted with aniline to yield 0.3 g. of anilide, m.p. and mixed m.p. 111–112°.

The remainder of the mixture was poured into ice-cold 50% sulfuric acid and extracted with ether. The ether extract was dried, stripped and residual oil was distilled *in vacuo* to yield 6.8 g. (0.081 mole, 81%) of cyclopropanecarboxylic acid, b.p. 101–102° (41 mm.). The residue did not contain any ketonic material.

The above experiment was modified by changing the solvent to benzene and xylene and placing a Dry Ice trap in the system to collect the ketene as it was formed. No material was found in the trap and only the acid was isolated from the

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[1] C. M. Hill, Ph.D. Thesis, Cornell University, 1941.

[2] Unpublished results.

[3] H. M. Walborsky and E. R. Buchman, A.C.S. Meeting, April, 1950.

[4] A. Staudinger, H. Schneider, P. Shotz and P. M. Strong, *Helv. Chim. Acta*, **6**, 294 (1923).

[5] H. Adkins and Q. E. Thompson, THIS JOURNAL, **71**, 2242 (1949).

[6] H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

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

[8] Private communication from Dr. H. Shechter, The Ohio State University.

[9] W. Autenrieth, *Ber.*, **38**, 2549 (1905).

reaction mixture. The addition of an equivalent of sodium hydride had no effect on the course of the reaction.

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Synthesis and Purification of 2-Cyclopropyl-3-methyl-1-butene and 2-Cyclopropyl-3-methylbutane

BY VERNON A. SLABEY

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The preparation of a series of cyclopropylalkenes[1] and cyclopropylalkanes,[2] in which the cyclopropyl ring was located in the 2-position of C_3, C_4, C_5 and C_6 straight chains, was recently reported. Similar reactions are described herein for the preparation of a cyclopropylalkene and a cyclopropylalkane in which the cyclopropyl ring was located in the 2-position of a branched C_4 chain.

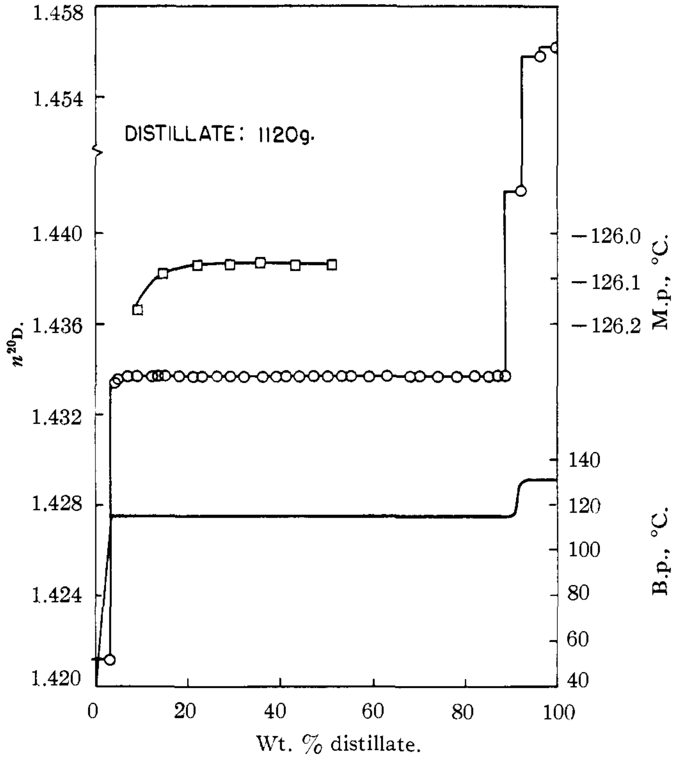

Fig. 1.—Distillation of products from the dehydration of methyl isopropylcyclopropylcarbinol over alumina.

The Grignard reagent of isopropyl bromide reacted with methyl cyclopropyl ketone to give methylisopropylcyclopropylcarbinol. The purified carbinol was dehydrated over alumina at 200–250°. Fractionation of the products (Fig. 1) gave principally 2-cyclopropyl-3-methyl-1-butene. A small amount of product which boiled considerably higher than anticipated for the other position isomer, 2-cyclopropyl-3-methyl-2-butene, and a large amount of viscous residue were also obtained.

The formation of 2-cyclopropyl-3-methyl-1-butene in high yield from the dehydration reaction was unexpected. If the formation of either of the position isomers were to be favored, removal of the tertiary hydrogen adjacent to the hydroxyl group was expected to predominate with 2-cyclopropyl-3-methyl-2-butene the resultant product. Although the 2-butene may have been produced in the dehydration reaction and subsequently polymerized during the fractionation process to give the viscous residue, the high yield of 2-cyclopropyl-3-methyl-1-butene (64%) indicated that the removal of primary hydrogen was favored in the dehydration process.

The hydrogenation of 2-cyclopropyl-3-methyl-1-butene in the presence of a barium-promoted copper chromite catalyst gave principally 2-cyclopropyl-3-methylbutane. Although the hydrogenation product was fractionated through a 6-ft. Podbielniak column at better than 150-plate efficiency, all the distillate had the same refractive index and none of the fractions could be crystallized. Small changes in density from fraction to fraction indicated that the distillate contained an impurity boiling too close to the cyclopropane hydrocarbon to be separated. From the results of previous hydrogenations of other 2-cyclopropyl-1-alkenes,[2] the hydrogenation of 2-cyclopropyl-3-methyl-1-butene was expected to give small amounts (<2% of the product) of 2,3-dimethylhexane. Since azeotropic fractionations had previously proved useful in separating close-boiling paraffin–cyclopropane mixtures,[2] the distillate was refractionated azeotropically with propanol. Although the hydrocarbon purified in this way still could not be crystallized, the densities of successive fractions of the hydrocarbon portion of the distillate from the points of 20 to 80% distilled (Fig. 2) were identical within the limits of the accuracy of measurement (0.00005 unit). While the purity of the hydrocarbon could not be established, it was believed to be near that of the other 2-cyclopropylalkanes already reported,[2] *i.e.*, better than 99 mole %.

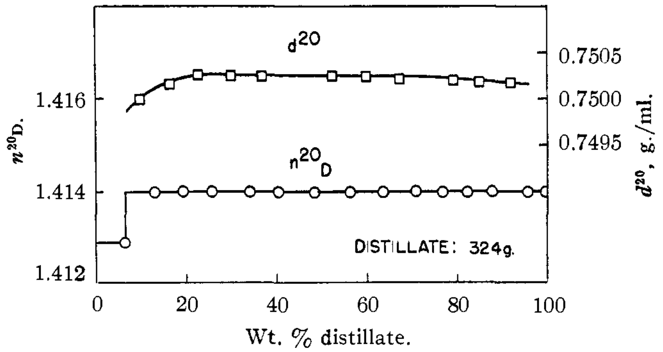

Fig. 2.—2-Cyclopropyl-3-methylbutane from azeotropic distillation with propanol.

The physical properties of the hydrocarbons, determined by methods previously referenced,[3] are presented in Table I. The author is indebted to

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

[2] V. A. Slabey and P. H. Wise, *ibid.*, **74**, 3887 (1952).

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