[CONTRIBUTION FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Addition of Dichlorocarbene to Olefins

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The reaction of chloroform with cyclohexene in the presence of potassium *t*-butoxide gives an excellent yield of a product, $C_7H_{10}Cl_2$, which contains the bicyclo[4.1.0]heptane (norcarane) skeleton and most probably is 7,7-dichlorobicyclo[4.1.0]-heptane. This reaction represents the first structural evidence for the formation of CCl_2 (dichlorocarbene) from chloroform. Dichlorocarbene can be added easily to a variety of olefins, including isobutylene, 2-methylbutene-2, hexene-1, 4-vinylcyclohexene and the pinenes. Bromoform similarly reacts with cyclohexene to give 7,7-dibromobicyclo[4.1.0]heptane and there is indication that iodoform undergoes a similar reaction.

Along with the resurgence of interest in the organic chemical reactions of carbenes (divalent carbon intermediates),[1,2] there has been a renewed effort[3] to substantiate the original suggestion of Geuther[4] that dichlorocarbene is involved in the alkaline hydrolysis of chloroform.[5] In an ingenious experiment, Hine[3] used kinetic analysis of the competition of hydroxide ion and thiophenolate ion to exclude bimolecular displacement as the mechanism of formation of phenyl orthothioformate. Although his results were quite consistent with dichlorocarbene being the intermediate,[9] the structure of the product could be accommodated by a variety of mechanisms. In order to support the hypothesis more forcefully it appeared desirable to find a reaction of chloroform in the presence of base that would give reliable indication by its structural outcome that dichlorocarbene had been an intermediate.

Among the unique and characteristic reactions of carbenes, addition to olefins to form cyclopropane derivatives[10] seemed promising, certainly more so than the addition to benzenes[2b,f] or to the saturated carbon–hydrogen bond.[2c]

The initial experiment was carried out in the following way. A mixture of cyclohexene and an essentially saturated solution of potassium *t*-butoxide in *t*-butyl alcohol was cooled and treated dropwise with chloroform. The vigorously exothermic reaction was accompanied by immediate precipitation of potassium chloride. From the neutral reaction mixture, a product, $C_7H_{10}Cl_2$, was isolated in 40% of the theoretical yield based on potassium *t*-butoxide. When alcohol-free potassium *t*-butoxide was used in order to minimize reaction of chloroform with the alcohol,[11] the yield was improved (59%). A similar, considerably less exothermic reaction occurred with bromoform leading to $C_7H_{10}Br_2$ in 75% of theory.

Both molecules are saturated to bromine and acid or alkaline permanganate, and show no absorption between 6–6.5 μ. These properties are consistent with the absence of a double bond. The halogens are remarkably inert in displacement reactions. There is no precipitation with alcoholic silver nitrate at room temperature; the dichloride is inert to silver oxide in boiling water and loses no chloride ion on refluxing in 50% potassium hydroxide–ethylene glycol for a few minutes. This inertness is similar to that reported for 1,1-dichlorocyclopropane by Gustavson[12a] who found no reaction with metallic sodium at 140°. Petrenko-Kritschenko, Opotsky, *et al.*,[13] report, however, some reaction with potassium hydroxide although there is no indication of the purity of their starting material. It is pertinent that both cyclopropyl derivatives[12b,14] and the *gem*-dichloride, methylene chloride,[3] are considerably less reactive than normal halides.

Catalytic hydrogenation of $C_7H_{10}Cl_2$ with Raney nickel removed chlorine and gave methylcyclohexane. Reduction of $C_7H_{10}Br_2$ with sodium in alcohol afforded bicyclo[4.1.0]heptane (norcarane) identical with an authentic sample.[10] These results can be considered together since both the dichloride and the dibromide appear to be structurally related. They are formed under the same conditions, have properties in common and have infrared spectra (Fig. 1) showing many similarities. The results of the reductions indicate a norcarane structure for the halides. The additional carbon atom has therefore reacted to saturate the double bond by forming a three-membered ring.

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[1] (a) H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942); (b) W. von E. Doering and L. H. Knox, THIS JOURNAL, **72**, 2305 (1950); (c) W. von E. Doering and L. H. Knox, "Abstracts of Papers," 119th Meeting, American Chemical Society, Boston, Mass., April 1, 1951, p. 2 M; (d) G. F. Hennion and D. E. Maloney, THIS JOURNAL, **73**, 4735 (1951); (e) W. H. Urry and J. R. Eizner, *ibid.*, **73**, 2977 (1951); (f) W. von E. Doering and L. H. Knox, *ibid.*, **75**, 297 (1953).

[2] The term "carbene"[1c] bears the same relationship to "methylene" as does the term "carbinol" to "methanol" and is to be employed in the same way as "carbinol."

[3] J. Hine, THIS JOURNAL, **72**, 2438 (1950).

[4] A. Geuther, *Ann.*, **123**, 121 (1862).

[5] This explanation was prompted by Geuther's finding that carbon monoxide was formed along with formate ion,[4] an observation that had been made earlier by Hermann using bromoform[6] and later by Sherman and Bernstein on bromodichloromethane and chlorodibromomethane.[7] The formation of isonitriles from chloroform, alkali and primary amines was considered to involve dichlorocarbene[8] as was the Reimer–Tiemann reaction[8] and the conversion of pyrrole to β-chloropyridine.[8]

[6] M. Hermann, *Ann.*, **95**, 211 (1855).

[7] R. H. Sherman and R. B. Bernstein, THIS JOURNAL, **73**, 1376 (1951).

[8] J. U. Nef, *Ann.*, **298**, 202 (1897).

[9] The reaction of thiophenolate ion with chloroform was much slower than the second-order hydrolysis by hydroxide and could be markedly accelerated by adding hydroxide ion, the product meanwhile remaining phenyl orthothioformate.

[10] W. von E. Doering and L. H. Knox, unpublished work, have obtained pure norcarane (b.p. 116°, $n^{25}\mathrm{D}$ 1.4550) from the photochemical decomposition of diazomethane in cyclohexene. We thank Dr. L. H. Knox, Hickrill Chemical Research Foundation, for a sample of this material.

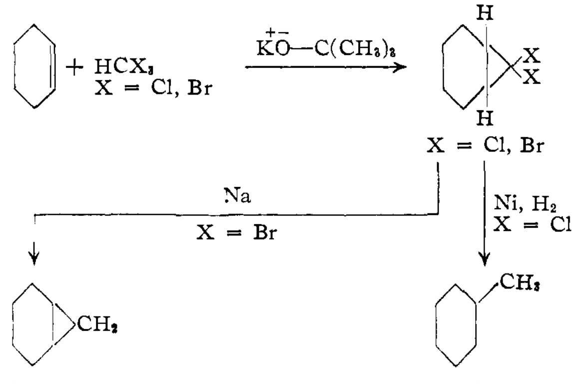
[11] J. Hine, E. L. Pollitzer and H. Wagner, THIS JOURNAL, **75**, 5607 (1953).

[12] (a) G. Gustavson, *J. prakt. Chem.*, [2] **42**, 496 (1890); (b) [2] **43**, 396 (1891).

[13] P. Petrenko-Kritschenko, V. Opotsky, M. Diakowa and A. Losowoy, *Ber.*, **62**, 581 (1929).

[14] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951).

The facts are consistent with the assignment of 7,7-dichloro- and 7,7-dibromobicyclo[4.1.0]heptane to the products. The only point of doubt concerns the position of the halogen atoms. The assigned positions are consistent with the inertness of the halogen atoms and represent the only mechanistically feasible structure. It is most difficult to imagine the elements of carbon and two chlorine atoms derived from chloroform forming a cyclopropane ring by addition to a double bond without having the two chlorine atoms retain their original attachment to the single adding carbon atom.



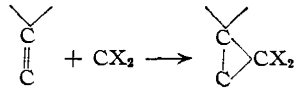
This striking new reaction of chloroform and bromoform can be accommodated by assuming the intermediate formation of dichloro- and dibromocarbene. Indeed the only analogies for the formation of cyclopropane derivatives by the *direct* addition to a double bond are in the addition of methylene to cyclohexene to form norcarane,[10] in the formation of tropilidene derivatives by the addition of methylene to benzene and its derivatives[1b,f] and in the additions of carbethoxycarbene from the photochemical decomposition of ethyl diazoacetate to aromatic compounds.[15,16]

The first step of the mechanism is the removal of a proton from haloform to produce the trihalomethide ion. This reaction is abundantly established by deuterium exchange in alkali[7,17,18] and by a number of other reactions, such as the addition of haloform to carbonyl compounds[19] and the reaction of chloroform with sodium hypobromite to give bromotrichloromethane.[20]

In the second step trihalomethide ion loses halide ion to give the neutral dihalocarbene which adds to the olefin. The alternative hypothesis that the trihalomethide ion adds to the olefin to give a carbanion which displaces halide ion forming the product is inconsistent with the failure of bases to add to olefins and with the failure to isolate the product of the reaction of the intermediate carbanion with a proton.

$$HCX_3 + {}^-OR \rightleftharpoons HOR + {}^-CX_3$$

$$CX_3^- \rightleftharpoons X^- + CX_2$$



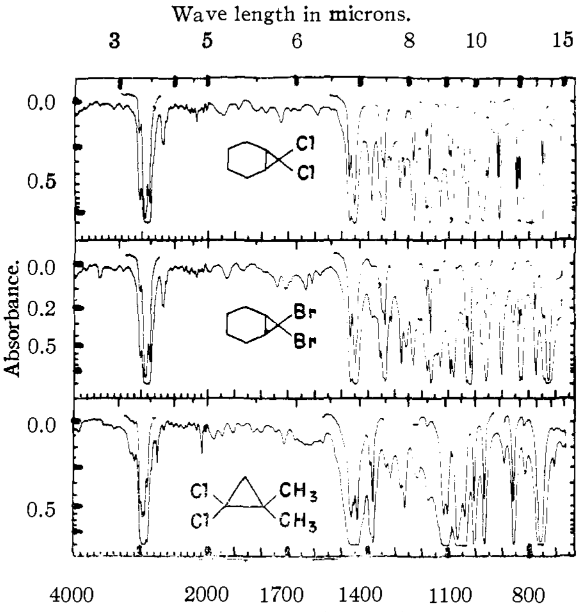


Fig. 1.—Infrared spectra of 7,7-dichlorobicyclo[4.1.0]-heptane (upper), 7,7-dibromobicyclo[4.1.0]heptane (middle) and of 1,1-dichloro-2,2-dimethylcyclopropane (lower) taken with a Perkin-Elmer model 21 infrared spectrophotometer with sodium chloride optics, samples neat of 0.100 mm. and 0.024 mm. thickness.

The new reaction has been extended to other olefins. Thus isobutylene reacts with chloroform to give 1,1-dichloro-2,2-dimethylcyclopropane. This compound also can be obtained in small amount from the decomposition of chloroform in *t*-butyl alcohol along with potassium *t*-butoxide. This result is not surprising in view of the recent observation of Hine, Pollitzer and Wagner[11] that isobutylene is produced under these conditions. The more and less highly substituted olefins, 2-methylbutene-2 and hexene-1, also react smoothly with chloroform. 4-Vinylcyclohexene-1 reacts to give a mixture of monoaddition product. α-Pinene leads to unstable, unsaturated products, whereas β-pinene appears to afford the typical adduct.

An attempt to carry out the reaction of iodoform with cyclohexene was apparently successful, but the product could not be purified by distillation and was therefore not characterized.

The investigation is being extended to other haloforms and halogen derivatives as well as to the chemistry of the dihalocyclopropanes. Their use for the introduction of methyl groups and for the preparation of cyclopropanes appears to be quite promising.

Experimental[21]

7,7-Dichlorobicyclo[4.1.0]heptane (Dichloronorcarane).—The reaction of potassium metal (60 g., 1.5 moles) and 1.5 l.

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[15] G. O. Schenk and H. Ziegler, *Naturwissenschaften*, **38**, 356 (1951).

[16] W. von E. Doering and L. H. Knox, unpublished work.

[17] J. Horiuti and Y. Sakamoto, *Bull. Chem. Soc. Japan*, **11**, 627 (1936).

[18] J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

[19] E. D. Bergmann, D. Ginsburg and D. Lavie, *ibid.*, **72**, 5012 (1950).

[20] W. M. Dehn, *ibid.*, **31**, 1220 (1909).

[21] Boiling points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside 17, N. Y.

of dried (distilled from aluminum *t*-butoxide) *t*-butyl alcohol was carried out with stirring at the boiling point in a 2-l., three-necked flask equipped with a reflux condenser and an Ascarite drying-tube. After the potassium had reacted, the stirred solution was concentrated by distillation and finally dried at 150–160° at 1–2 mm. for 1.5 hr. The white powder was covered with 1 l. of dried and distilled cyclohexene and cooled in an ice-bath. Chloroform (120 ml., 1.5 moles) was then added with stirring in portions of 10–20 ml. each. After 20 ml. of chloroform had been added, the contents became gelatinous and difficult to stir and were diluted with 250 cc. of pentane. With continued stirring the rest of the chloroform was added. The dark brown mixture was then stirred 0.5 hr. longer at room temperature and poured into water. The cyclohexene layer was separated, combined with a pentane extract of the aqueous layer and dried over magnesium sulfate. Concentration by distillation left a residue which was fractionally distilled *in vacuo* to give 143 g. (59% based on chloroform) of dichloronorcarane, b.p. 78–79° at 15 mm., n^{23}_{D} 1.5014, d^{23}_{4} 1.2115; M_{D} calcd.[22] 40.6, M_{D} found 40.1.

Anal. Calcd. for $C_7H_{10}Cl_2$: C, 50.9; H, 6.1; Cl, 43.0. Found: C, 51.1; H, 6.2; Cl, 43.0.

When this preparation is carried out without prior removal of the *t*-butyl alcohol the yield is 40%.

The synthesis also was attempted in aqueous medium. A mixture of 560 g. of potassium hydroxide in 500 ml. of water and 870 g. of cyclohexene was placed in a 3-l. Morton flask equipped with a Morton Hi-Speed Stirring Assembly. Chloroform (370 g.) was added with stirring and cooling. The reaction was quite exothermic and required ice-cooling. When all the chloroform had been added, an additional 243 g. of potassium hydroxide in 200 ml. of water was added, followed by 150 g. of additional chloroform. Stirring of the heavy slurry was continued overnight at 2700 r.p.m. After pouring the reaction mixture into water, drying the cyclohexene layer, and evaporating solvent, distillation afforded 2 g. (0.55%) of product (b.p. 78° at 15 mm., n^{26}_{D} 1.5008) and 1 g. of forerun (b.p. 76–82° at 22 mm., n^{26}_{D} 1.4999).

Dichloronorcarane does not react with aqueous silver nitrate and is recovered largely unchanged after refluxing several hours with alcohol and silver oxide. It is unchanged by refluxing 12 hr. with lithium aluminum hydride in tetrahydrofuran and by refluxing for 5 min. with 50% potassium hydroxide in ethylene glycol. It is recovered in 62% yield from treatment with sodium amide in hexane at 60–70° for 7 days. Dichloronorcarane fails to react with bromine in carbon tetrachloride and with alkaline or acid permanganate in the cold.

Hydrogenolysis of 7,7-Dichlorobicyclo[4.1.0]heptane.—Dichloronorcarane (50 g.) was dissolved in a solution of 40 g. of potassium hydroxide in 80 ml. of ethanol and 10 ml. of water. The reduction was effected at 50 lb. in a Parr hydrogenation apparatus with 30 g. of freshly prepared Raney nickel W-7 catalyst.[23] After 8 days, 48% of the calculated amount of hydrogen for removing two chlorine atoms had been absorbed. As the addition of fresh catalyst effected no further absorption of hydrogen in the next 24 hr., the hydrogenation was discontinued. The mixture of catalyst and potassium chloride, removed from the ethanolic solution by centrifugation and decantation, was washed with water and extracted with pentane. The ethanolic solution was poured into twice its volume of water, and extracted with three 100-ml. portions of pentane. The combined pentane extracts were washed once with 100 ml. of water and dried over magnesium sulfate. After slow evaporation of the pentane at a bath temperature of 45–50°, the residue was fractionally distilled, yielding four fractions of which the first (3 g., b.p. 90–130°) was subjected to careful refractionation using a concentric tube column. Nine fractions boiling over a range of 93.5 to 113° were collected. Fractions 2–6 boiled from 96–100.5° and fraction 6, b.p. 100–100.5°, had an infrared spectrum identical with that of methylcyclohexane.

7,7-Dibromobicyclo[4.1.0]heptane (Dibromonorcarane).—Potassium (40 g., 1 mole) reacted with 1.2 l. of *t*-butyl alcohol to give a solution to which 950 ml. of cyclohexene was added followed by the slow addition of 304 g. (1.2 moles) of bromoform with stirring and ice-cooling. After being stirred 15 min. following the addition of the bromoform, the reaction mixture was poured into water and extracted with pentane. The pentane extracts were combined with the cyclohexene layer, washed with 6 l. of cold water and dried over magnesium sulfate. After removal of the solvent, the residue was distilled to give 189.4 g. (75%) of dibromonorcarane, b.p. 100° at 8 mm., n^{22}_{D} 1.5578, d^{22}_{4} 1.7637; M_{D} calcd.[22] 46.5, M_{D} found 47.2.

Anal. Calcd. for $C_7H_{10}Br_2$: C, 33.1; H, 4.0; Br, 62.9. Found: C, 33.3; H, 4.2; Br, 62.7.

Dibromonorcarane is unaffected by aqueous silver nitrate at room temperature, is decomposed rapidly by aluminum chloride in pentane with evolution of hydrogen bromide and reacts vigorously with magnesium in ether.

Reduction of 7,7-Dibromobicyclo[4.1.0]heptane with Sodium and Alcohol.—Dibromonorcarane (50 g., 0.2 mole was dissolved in 200 ml. of ether in a 2-l., three-necked flask cooled in ice and equipped with a stirrer, Dry Ice condenser and dropping funnel. Metallic sodium (70 g., 3 g. atom) was added in roughly 2-cc. pieces during the course of the reduction. At the same time, wet methanol (10 ml. water–300 ml. methanol) was added dropwise with rapid stirring. Reaction of the sodium required 2.5 hr. An additional 23 g. (1 g. atom) of sodium and 200 ml. of wet methanol were added at the end of this time. After the reaction was complete, 300 ml. of water was added, the ether solution was separated and the aqueous layer was extracted three times with ether. The combined ether layers were dried over magnesium sulfate and fractionally distilled. Fraction e (a, 1.4 g., b.p. 65–85°; b, 2.0 g., b.p. 85–103°; c, 0.8 g., b.p. 103–112°; d, 7.0 g., b.p. 112–116°; e, 2.5 g., b.p. 116°, n^{25}_{D} 1.4552; f, 0.4 g., b.p. 116–117°) was cooled in Dry Ice and treated with bromine until saturated. A pentane solution of the reaction mixture was washed with 0.2 *N* sodium hydroxide, dried over sodium carbonate and fractionally distilled. Fraction c (a, b.p. 112–115°; b, b.p. 115–116°; c, b.p. 116°, n^{25}_{D} 1.4550; d, b.p. 116–117°) had an infrared spectrum identical with that of an authentic sample of bicyclo[4.1.0]heptane (norcarane).[10]

Reaction of 7,7-Dibromobicyclo[4.1.0]heptane with Zinc Bromide.—Dibromonorcarane (34.8 g.) and anhydrous zinc bromide (10 mg.) were placed in a 50-ml. distilling flask. No reaction occurring at room temperature, the mixture was heated over an open flame. Hydrogen bromide was evolved copiously accompanied by a light yellow distillate. The crude distillate (14.5 g.) was washed with water, dried and distilled. Hydrogen bromide was again evolved and distillation was continued till the vapor temperature reached 140°. The distillate was dissolved in ether and washed with 0.2 *N* sodium hydroxide. Concentration of the ether solution and distillation afforded 5 g. (40%) of toluene, b.p. 111–112°, having an infrared spectrum identical with that of authentic toluene.

Reaction of Iodoform, Cyclohexene and Potassium *t*-Butoxide.—To a solution of potassium *t*-butoxide (from 40 g. of potassium) in 1.2 l. of *t*-butyl alcohol and 1 l. of cyclohexene, there was added 400 g. of powdered iodoform from a flask connected by Gooch tubing. The reaction was stirred for 3 hr. and poured into 4 l. of water. The cyclohexene layer was washed with 2 l. of water, combined with the pentane extract of the aqueous layer and dried. After removal of half of the solvent *in vacuo*, filtration removed 54 g. of recovered iodoform. The remaining solvent was then removed leaving a good yield of a dark, heavy oil which could not be evaporatively distilled without decomposition.

1,1,-Dichloro-2,2-dimethylcyclopropane.—Potassium metal (40 g., 1 mole) was dissolved in 1200 ml. of *t*-butyl alcohol in a flask equipped with a reflux condenser and stirrer. The flask was cooled to −10° in an ice–salt-bath with stirring and the reflux condenser was replaced by a vertical Dry Ice condenser. Liquid isobutylene (500 ml. at −80°) was then boiled through a sodium hydroxide drying tower into the flask containing the potassium *t*-butoxide. Chloroform (150 g., 1.25 moles) was then added with stirring in 10-ml. portions. There was a slow deposition of potassium chloride and gentle refluxing of the isobutylene. Following this addition, another 75 g. (0.63 mole) portion of chloroform was added. After 15 minutes stirring at −10°, the reaction mixture was warmed slowly to room temperature and diluted with 2 l. of cold water. After most of the isobutylene had boiled away, the chloroform layer was washed thoroughly with 6 l. of water, dried over magnesium sulfate and distilled to give 33 g., b.p. 119–120°. The fore-

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[22] Using the values given by A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 514 (1952).

[23] H. Adkins and H. R. Billica, This Journal, **70**, 695 (1948).

run was again washed with two 1-l. portions of water, dried and redistilled affording an additional 29 g. of product. Refractionation of the forerun, b.p. 100–118°, gave 28 g. of product, b.p. 118–120°. The total yield of 1,1-dichloro-2,2-dimethylcyclopropane was 90 g. (65%), b.p. 118–120°, $n^{20}\text{D}$ 1.4461, d^{22}_4 1.0854.

Anal. Calcd. for $C_5H_8Cl_2$: C, 43.2; H, 5.8; Cl, 51.0. Found: C, 43.4; H, 6.0; Cl, 51.3.

Reaction of Chloroform with Potassium *t*-Butoxide.—Chloroform (75 g., 0.63 mole) was added with shaking to a solution of 20 g. (0.51 g. atom) of potassium in 500 ml. of *t*-butyl alcohol. The reaction mixture, after the chloroform had been added, was poured into water and the mixture was extracted with pentane. Distillation gave 5 g. of material, b.p. 119.5–120°, $n^{26}\text{D}$ 1.4454, having an infrared spectrum identical with that of 1,1-dichloro-2,2-dimethylcyclopropane.

Reaction of Chloroform with 4-Vinylcyclohexene.—A solution of chloroform (200 ml.. 2.5 moles) in an equal volume of 4-vinylcyclohexene was added slowly to a stirred, ice-cooled solution of 89 g. (2.2 g. atoms) of potassium metal in 1200 ml. of *t*-butyl alcohol containing 600 ml. of 4-vinylcyclohexene. Following the addition of the chloroform, the reaction mixture was stirred for 1 hr., after which it was poured into water. The olefin layer was separated, dried and concentrated by distillation to a residue which was fractionally distilled *in vacuo*, to yield the following fractions: a, 3 g., b.p. 68–81° at 8 mm.; b, 8 g., b.p. 81–90° at 8 mm.; c, 10 g., b.p. 90–95° at 8 mm.; d, 19 g., b.p. 95–96° at 8 mm.; e, 17 g., b.p. 96° at 8 mm.; f, 25 g., 96–96.5° at 8 mm.

Fraction e was ozonized by the procedure of Wilms,[24] forming an oil which was converted to its S-benzylisothiouranium salt, m.p. 135.5–136°.

Anal. Calcd. for $C_{16}H_{20}O_2N_2Cl_2S$: C, 51.2; H, 5.4; Cl, 18.9. Found: C, 50.9; H, 5.2; Cl, 18.2.

Reaction of Chloroform with β-Pinene.—Analcoholic potassium *t*-butoxide stirred with 350 ml. of pentane and 500 g. of β-pinene was allowed to react with 120 ml. (1.5 moles) of chloroform with ice-cooling. After the chloroform had been added, the reaction mixture was stirred for 5 min. and poured into 2 l. of water. The pentane extract of the water layer was combined with the pinene layer and dried over magnesium sulfate. The pentane and pinene was removed by distillation *in vacuo*. The residue was fractionally distilled *in vacuo* yielding 164 g. (50%) of product having a b.p. of 70–71° at 0.5 mm., $n^{25}\text{D}$ 1.5070, d^{26}_4 1.1402.

Anal. Calcd. for $C_{11}H_{16}Cl_2$: C, 60.3; H, 7.4; Cl, 32.4. Found: C, 60.6; H, 7.2; Cl, 32.1.

Reaction of Chloroform with α-Pinene.—Chloroform (158 ml., 2 moles) was added dropwise to an iced solution of 70 g. of potassium in 1.2 l. of *t*-butyl alcohol containing 1 l. of α-pinene (b.p. 155–156°). After completion of the addition of chloroform, the ice-bath was removed and stirring was continued for 0.5 hr. The reaction mixture diluted with 500 ml. of pentane was poured into 4 l. of water and thoroughly washed with additional portions of water. Distillation of the pentane and α-pinene *in vacuo* yielded a residue which was fractionally distilled. Four fractions were obtained: a, 3 g., b.p. 68–77° at 2 mm.; b, 13 g., b.p. 77–79° at 2 mm.; c, 26 g., b.p. 79–82° at 2 mm.; d, 13 g., b.p. 82–84° at 2 mm. Each of these fractions showed unsaturation to bromine in carbon tetrachloride solution and darkened and became viscous on standing.

1,1-Dichloro-2,2,3-trimethylcyclopropane.—Analcoholic potassium *t*-butoxide prepared from 60 g. (1.5 g. atoms) of potassium and 1.2 l. of *t*-butyl alcohol was stirred with 450 g. of 2-methylbutene-2 in an ice-bath. Chloroform (180 g., 1.5 mole) was added dropwise with stirring. After the addition of chloroform was completed, the reaction mixture was stirred for 5 min. and poured into 1 l. of water. The butene layer was separated, and the water layer was washed with two 50-ml. portions of pentane. The pentane and butene layers were combined and dried over sodium sulfate. The pentane and olefin was removed by distillation and the residue fractionally distilled *in vacuo*. Two fractions were collected; a, 14.6 g., b.p. 68° at 55 mm.; and b, 152 g. (66%), b.p. 69–70° at 55 mm., $n^{25}\text{D}$ 1.4555, d^{26}_4 1.0927. At 760 mm. the b.p. is 144° with some decomposition and evolution of a small amount of hydrogen chloride.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 47.3; H, 7.0; Cl, 46.6.

1-Butyl-2,2-dichlorocyclopropane.—Sodium *t*-amylate was prepared from 46 g. (2 g. atoms) of sodium dissolved in 1.8 l. of refluxing *t*-amyl alcohol with stirring. Removal of the *t*-amyl alcohol by distillation followed by heating at 160–170° at 1 mm. for 2 hr. afforded analcoholic sodium *t*-amylate. The sodium amylate was stirred with 450 g. of hexene-1 in an ice-bath, while 240 g. (2 mole) of chloroform was added dropwise. The reaction was considerably more vigorous than the reactions of potassium *t*-butoxide, olefin and chloroform. After half the chloroform had been added, the reaction mixture was diluted with 200 ml. of pentane. After the addition of chloroform was completed, the reaction mixture was washed well with three 1-l. portions of water, dried and fractionally distilled to give 54 g. (16%) of product having a b.p. of 75–76° at 25 mm., $n^{25}\text{D}$ 1.4501, d^{26}_4 1.0522.

Anal. Calcd. for $C_7H_{12}Cl_2$: C, 50.3; H, 7.2; Cl, 42.4. Found: C, 50.5; H, 7.1; Cl, 42.1.

New Haven, Conn.

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[24] H. Wilms, *Ann.*, **567**, 96 (1950).

[Contribution from the Department of Chemistry, Oregon State College]

Ortho–Para Migration in the *Para*-Claisen Rearrangement[1]

By Elliot N. Marvell and Roy Teranishi

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The Hurd–Pollack mechanism for the *para*-Claisen rearrangement postulates a dienone intermediate. If the two groups *ortho* to the keto function are both of allylic nature either could migrate further to the *para* position. Rearrangement of γ-phenylallyl 2,6-diallylphenyl ether gives a product in which 2,6-diallyl-4-(γ-phenylallyl)-phenol was identified. However, identical treatment of allyl 2-allyl-6-(α-phenylallyl)-phenyl ether gives at least two products, both 2,4-diallyl-6-(α-phenylallyl)-phenol and 2,6-diallyl-4-(γ-phenylallyl)-phenol being identified. This evidence supports the Hurd–Pollack mechanism for it indicates the equivalence of the ether and the *ortho*-allyl groups during the migration process, and it shows that migration from the *ortho* to the *para* position proceeds with inversion.

Recent studies on the *para*-Claisen rearrangement[2] have revived interest in the Hurd–Pollack[3] mechanism for the rearrangement. One requirement of that mechanism is that a dienone intermediate I should be formed. It is reasonable to conclude that if both A and B in I are of allylic nature either may migrate further to the *para* position. To test this conclusion two new ethers, γ-phenylallyl 2,6-diallylphenyl ether and allyl 2-allyl-6-(α-phenylallyl)-phenyl ether, have been prepared and rearranged. While this material was being prepared for publication results of similar studies

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[3] C. D. Hurd and H. Pollack, *J. Org. Chem.*, **3**, 550 (1939).