Esterifications. The esters were prepared from the pure acids with the appropriate diazolkane. The procedure below is representative.

A solution of diazoethane in methylene chloride was prepared from 20 g. of *N*-nitrosoethylurea in the usual way.[17] To this solution was added in small portions 2.0 g. of *cis*-1,3-cyclohexanedicarboxylic acid. The solvent was evaporated and the residue was distilled at 1.5 mm. The distillate was collected in three fractions, the last two of which were shown by vapor phase chromatography to be quite pure. Experiments with known mixtures showed that the *cis* and *trans* isomers were easily separable by vapor phase chromatography. A silicone on firebrick column was used for the separation with a column temperature of 200°. The retention times were on the order of 20 min., and no equilibration occurred on the column under these conditions. The physical constants of the esters are listed in Table I.

Equilibration. cis-Diethyl 1,3-cyclohexanedicarboxylate, 2.8 g., was dissolved in 100 ml. of absolute ethanol containing 2.0 g. of sodium. The resulting solution was heated under reflux for 2 hr., cooled, and poured onto a mixture of ice and 6*N* hydrochloric acid. The resulting cold acid solution was extracted with ether, and the combined ether solutions were washed with a dilute bicarbonate solution. After drying the ether solution with anhydrous magnesium sulfate, the solvent was evaporated and the residue was distilled at 1.5 mm. The distillate was analyzed by vapor phase chromatography, and was found to contain 71 ± 4% *cis* and 29 ± 4% *trans* ester. A sample of this material was again treated under equilibration conditions, and the product was isolated and analyzed as before. The composition was unchanged, indicating that equilibrium had been reached. The dimethyl esters were equilibrated in a similar manner, using methanol as the solvent and sodium methoxide as the base. The equilibrium mixture was found to contain 70 ± 4% *cis* and 30 ± 4% *trans* ester in this case.

Acknowledgment. The authors are indebted to Professor E. L. Eliel for helpful discussion concerning the present work.

DEPARTMENT OF CHEMISTRY
WAYNE STATE UNIVERSITY
DETROIT 2, MICH.

---

(17) W. E. Bachmann and W. S. Struve, *Org. Reactions,* **1**, 50 (1942).

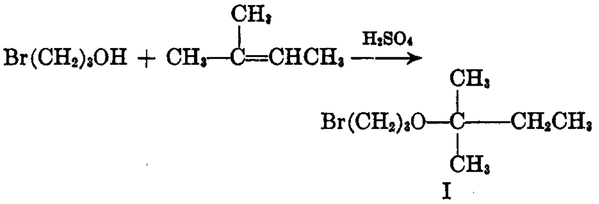
Synthesis of Substituted Tetrahydrofurans. An Application of the Grignard Reagent from 3-Bromo-1-(1,1-dimethylpropoxy)-propane[1]

W. B. RENFROW, DEREK OAKES, CAROL LAUER, AND T. A. WALTER

Received May 13, 1960

t-Butyl ester have been shown to be useful in certain syntheses involving malonic[2] and acetoacetic[3] esters because the ester groups can be cleaved by heating with a strong acid to produce a hydroxyl group and 2-methylpropene. Similarly, we have prepared the *t*-amyl ether of 3-bromo-1-propanol, converted the bromo ether to a Grignard reagent and examined some synthetic applications of this reagent resulting from cleavage of the ether grouping.

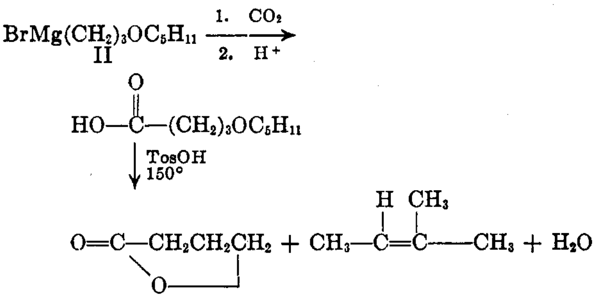
The method of Evans and Edlund[4] was adapted to the preparation of 3-bromo-1-(1,1-dimethylpropoxy)propane (I) from 3-bromopropanol and 2-methyl-2-butene.



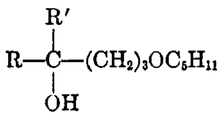
$$Br(CH_2)_3OH + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3 \xrightarrow{H_2SO_4} Br(CH_2)_3O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$$

I

The bromo ether (I) formed a Grignard reagent (II) in about 80% yield as estimated by titration of an aliquot with standard acid. The structure of II was confirmed by carbonation. The resulting acid showed the expected analytical values and was converted to γ-butyrolactone by heating with a catalytic amount of *p*-toluenesulfonic acid.

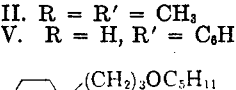


The Grignard reagent (II) reacted normally with acetone, benzaldehyde and cyclohexanone to produce hydroxy ethers III, IV and V. These were converted to substituted tetrahydrofurans (VI, VII, VIII), water, and isoamylene by heating with *p*-toluenesulfonic acid.

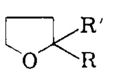


$$R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R'}{|}}{C}}-(CH_2)_3OC_5H_{11}$$

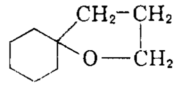
III. $R = R' = CH_3$
IV. $R = H, R' = C_6H_5$



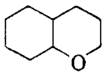
V



VI. $R = R' = CH_3$
VII. $R = H, R' = C_6H_5$



VIII



IX

---

[1] Supported by a grant from Research Corporation.

[2] D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1286 (1944).

[3] W. B. Renfrow and G. B. Walker, *J. Am. Chem. Soc.*, **70**, 3957 (1948).

[4] T. W. Evans and K. R. Edlund, *Ind. and Eng. Chem.*, **28**, 1186 (1936).

The physical properties of VI agreed well with reported values for 2,2-dimethyltetrahydrofuran and were considerably different from reported[5] values for the isomeric 3-methyltetrahydropyran which is the only other likely product. The structure of VII was confirmed by catalytic hydrogenolysis to 4-phenyl-1-butanol and characterization of the alcohol as the phenylurethan. The cyclic ether prepared from cyclohexanone appears to be pure spiran (VIII), free of the isomeric hexahydrochroman (IX). The infrared spectra of VIII and of IX (prepared by a known method[6] from coumarin) were distinctly different in the 7–9 and 10–13μ regions. The geometrical isomers of IX have not been characterized but it is unlikely that the compound isolated is the unknown isomer of IX.

EXPERIMENTAL

3-Bromo-1-(1,1-dimethylpropoxy)propane (I). 3-Bromopropanol[7] (139 g., 1 mole) and 2-methyl-2-butene[8] (250 ml., 2.4 moles) were stirred and refluxed from a water bath maintained at 40–45°. Concentrated sulfuric acid (about 0.8 ml.) was dropped in until a small lower phase was apparent. Stirring and heating were continued for 4 hr. with occasional addition of sulfuric acid (about 3 ml., total) to maintain two phases. The lower layer was drawn off and discarded, the solution washed with water, 25% potassium hydroxide solution, sodium bicarbonate solution, and dried (potassium carbonate). Fractional distillation produced about 50 g. of low-boiling material, an intermediate fraction (about 20 g.) boiling up to 70° (10 mm.) and a main fraction (65 g.) boiling at 70–75° (10 mm.). Analysis[9] revealed 0.2 mequiv. per ml. of impurity which reacted with methylmagnesium iodide.

The main fraction was treated with 15 ml. of 2*N* *n*-butylmagnesium bromide in ether and distilled at 10 mm. pressure. There was obtained a small forerun boiling up to 70° and 155 g. (74%) of 3-bromo-1-(1,1-dimethylpropoxy)propane boiling mostly at 74° (10 mm.), n_D^{20} 1.4494, d_4^{20} 1.1646.

Anal. Calcd. for $C_8H_{17}OBr$: C, 45.9; H, 8.2; Br, 38.2. Found: C, 46.1; H, 8.3; Br, 38.5.

1-(1,1-Dimethylpropoxy)-3-propylmagnesium bromide (II). The Grignard reagent was prepared by dropping a 1.5 *M* solution of I in ether onto an equivalent amount of magnesium turnings in a flask fitted with a stirrer and reflux condenser.

4-(1,1-Dimethylpropoxy)butyric acid. The Grignard reagent from I (0.1 mole) was poured onto solid carbon dioxide (30 g.) and the resulting magnesium salt converted to the acid with 2*N* hydrochloric acid (50 ml.). The organic acid was dissolved in sodium bicarbonate solution, liberated with hydrochloric acid, and distilled. There was obtained 4-(1,1-dimethylpropoxy)butyric acid (9.3 g., 53%), b.p. 139–140° (10 mm.), n_D^{20} 1.4350, d_4^{20} 0.972.

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.1; H, 10.4; neut. equiv., 174.2. Found: C, 62.0; H, 10.3; neut. equiv., 174.3.

Heating 4-(1,1-dimethylpropoxy)butyric acid with 1% *p*-toluenesulfonic acid at 130–150° for 15 min. gave γ-butyrolactone, b.p. 202–205°, n_D^{20} 1.4331; further characterized[10] by conversion to the phenylhydrazide of 4-hydroxybutyric acid, m.p. 94°.

Addition of II to acetone, benzaldehyde, and cyclohexanone. The Grignard reagent from 1 mole of I was maintained under a nitrogen atmosphere, cooled in an ice bath, and stirred while 0.8 mole of the carbonyl compound in 200 ml. of ether was added. The reaction mixture was refluxed 30 min., cooled in ice, and a solution of 100 ml. of concd. hydrochloric acid in 350 ml. of water added. The ether layer was washed with water and sodium bicarbonate solution, and dried over magnesium sulfate. The products were isolated in 90% yields by vacuum distillation.

5-(1,1-Dimethylpropoxy)-2-methyl-2-pentanol (III), b.p. 101–103° (10 mm.), n_D^{20} 1.4360, d_4^{20} 0.884.

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.2; H, 12.8. Found: C, 70.0; H, 12.5.

1-[3-(1,1-Dimethylpropoxy)propyl]-1-cyclohexanol (V), b.p. 148–149° (10 mm.), n_D^{20} 1.4623, d_4^{20} 0.926.

Anal. Calcd. for $C_{14}H_{28}O_2$: C, 73.6; H, 12.4. Found: C, 73.5; H, 12.1.

4-(1,1-Dimethylpropoxy)-1-phenyl-1-butanol (IV), b.p. 170–171° (10 mm.), n_D^{20} 1.4964, d_4^{20} 0.973.

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.8; H, 10.2. Found: C, 76.6; H, 10.3.

Conversion of hydroxy ethers to tetrahydrofurans. The apparatus consisted of a 100-ml. round bottomed flask fitted with a magnetic stirrer and a short (10 cm.) packed fractionating column attached to an efficient condenser. Approximately 40 g. of hydroxy ether (III, IV, or V) and 0.3 g. of *p*-toluenesulfonic acid monohydrate was placed in the flask and heated in an oil bath at 150–165°. The tetrahydrofuran from III, along with isoamylene and water, distilled smoothly at atmospheric pressure. The tetrahydrofurans from IV and V were distilled from the reaction mixture by lowering the pressure to about 25 mm. Products were dried and distilled through a spinning band fractionating column. Active-hydrogen determinations[9] were run on samples of the distillates and when active hydrogen was found to be present the product was redistilled from a slight excess of butylmagnesium bromide. Yields were 70–90%.

2,2-Dimethyltetrahydrofuran (VI). Found: b.p. 90.8° (742 mm.), n_D^{20} 1.4071, d_4^{20} 0.840; previously reported[11]: b.p. 92.25° (760 mm.), n_D^{20} 1.4068, d_4^{20} 0.84019.

2-Phenyltetrahydrofuran (VII). Found: b.p. 107° (15 mm.), n_D^{20} 1.5299, d_4^{20} 1.032; previously reported[12]: b.p. 105° (14 mm.), d_{15} 1.037.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.0; H, 8.2. Found: C, 81.1; H, 8.0.

1-Oxaspiro[4,5]decane (VIII), b.p. 182° (742 mm.), n_D^{20} 1.4651, d_4^{20} 0.949.

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.1; H, 11.4.

Hexahydrochroman (IX) was prepared in three steps from coumarin[6] and purified by distillation from butylmagnesium bromide. Found: b.p. 189° (742 mm.), n_D^{20} 1.4738, d_4^{20} 0.962; previously reported[6]: b.p. 186–187° (760 mm.), n_D^{22} 1.4718, d_4^{22} 0.9533.

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.0; H, 11.3.

Hydrogenolysis of 2-phenyltetrahydrofuran. The tetrahydrofuran (VII, 1.48 g.), acetic acid (4 ml.), 60% perchloric acid (2 drops), and Adams' platinum oxide catalyst were shaken with hydrogen at 27° and 713 mm. until (45 min)

---

(5) E. Hanschke, *Ber.*, 88, 1052 (1955).

(6) P. L. de Benneville and R. Connor, *J. Am. Chem. Soc.*, 62, 283 (1940).

(7) 3-Bromopropanol was purchased from Distillation Products or prepared from trimethylene glycol and hydrogen bromide. See M. T. Bogert and H. R. Slocum, *J. Am. Chem. Soc.*, 46, 765 (1924).

(8) J. F. Norris and J. M. Joubert, *J. Am. Chem. Soc.*, 49, 884 (1927).

(9) G. F. Wright, *Organic Analysis*, Vol. 1, Interscience Publishers, Inc., New York, 1955, pp. 155–193.

(10) E. H. Huntress and R. S. Mulliken, *Identification of Pure Organic Compounds*, Order I, John Wiley and Sons, Inc., New York, 1941, p. 352.

(11) V. A. Slabey and P. H. Wise, *Natl. Advisory Comm. Aeronaut., Tech. Notes No. 2258*, p. 17 (1951) [*C.A.*, 47, 7532 (1951)].

(12) H. Normant, *Compt. rend.*, 226, 1734 (1948).

the calculated volume (260 ml.) of hydrogen was absorbed. Saponification of the product gave 4-phenyl-1-butanol (1.2 g.), b.p. 135–140° (14 mm.); further characterized as the phenylurethan, m.p. 50–52°. Previously reported[13] for 4-phenyl-1-butanol: b.p. 140° (14 mm.); phenylurethan, m.p. 51–52°.

DEPARTMENT OF CHEMISTRY
OBERLIN, COLLEGE
OBERLIN, OHIO

---

(13) J. von Braun, *Ber.*, **44,** 2871 (1912).

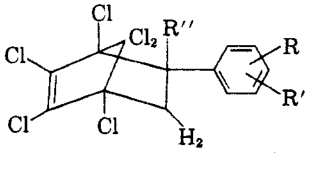
Preparation of Hexachloronorbornenes Containing Aromatic Substituents

BY E. F. JASON AND E. K. FIELDS

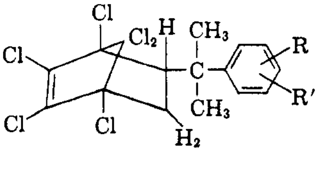
Received May 31, 1960

For studies in the 1,4,5,6,7,7-hexachloro-5-norbornene series, a variety of such hexachloronorbornenes containing aromatic rings with alkyl and hydroxyl groups were needed as intermediates. Norbornenes of this structure have not previously been reported. They were prepared in three different ways: (1) Diels-Alder condensation of hexachlorocyclopentadiene with substituted styrenes, (2) alkylation of 2-arylhexachloronorbornenes with alkyl halides and aluminum chloride, and (3) alkylation of ring-substituted aromatics with 2-isopropenylhexachloronorbornene,[1] the adduct of isoprene with hexachlorocyclopentadiene.

Ten new hexachloronorbornenes have been prepared and characterized. Four were made by the first two methods and have the structure:



Six were made by the third method and have the structure:



Physical constants and elemental analyses are listed in Table I. 2-Isopropenylhexachloronorbornene neither alkylated *p*-disubstituted benzenes nor polymerized with Lewis-acid catalysts.

EXPERIMENTAL

Hexachlorocyclopentadiene was obtained from Hooker; isoprene, from Matheson; vinyltoluene (60% *meta* and 40% *para*) and *p*-isopropyl-α-methylstyrene, from Dow; styrene, isopropyl chloride, phenol, *o*-cresol, toluene, *o*-xylene, and *m*-xylene, from Eastman; ethanesulfonic acid, from Amoco. All chemicals were used without further purification.

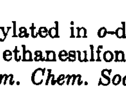
Method 1. Preparation of 1,4,5,6,7,7-hexachloro-2-tolyl-5-norbornene. To 40 ml. (0.25 mole) of hexachlorocylopentadiene at 145° was added 35 ml. (0.25 mole) of vinyltoluene in 2-ml. portions over 2 hr. After addition was complete, the reaction mixture was stirred an additional hour at 140 to 145°. Distillation of the resulting material through a 6-in. Vigreux column gave 92.5 g. of a mobile clear yellow oil, n_D^{20} 1.5857.

Method 2. Preparation of 1,4,5,6,7,7-hexachloro-2-isopropylphenyl-5-norbornene. A mixture of 37.2 g. (0.1 mole) of 1,4,5,6,7,7-hexachloro-2-phenyl-5-norbornene, 100 ml. of carbon tetrachloride, and 2 g. of aluminum chloride was stirred at about 5°, while 22.4 g. (0.3 mole) of isopropyl chloride in 50 ml. of carbon tetrachloride was added dropwise over 45 min. The mixture was then allowed to warm to room temperature and was stirred for 16 hr. It was poured into ice water, the organic layer was separated, and the aqueous solution was extracted twice with carbon tetrachloride. The organic extracts were combined and dried over anhydrous sodium sulfate. Distillation of the resulting residue, after removal of solvent, gave 32.1 g. of the product as a viscous pale yellow oil, n_D^{20} 1.5700. This oil, on standing at room temperature, slowly solidified.

Method 3. Preparation of 2-phenyl-2-(1,4,5,6,7,7-hexachloro-5-norbornenyl)propane. A mixture of 68 g. (0.20 mole) of isopropenylhexachloronorbornene,[1] 439.5 g. (5.62 moles) of benzene, and 3.6 g. of aluminum chloride was stirred and refluxed for 13 hr. The cooled reaction mixture was washed successively with water, dilute base, and water. The organic layer was separated, and the excess of benzene was removed by distillation. The residue was distilled to give 61.9 g. of the product as a pale yellow oil, n_D^{20} 1.5839. This oil solidified on standing.[2]

DISCUSSION

Although hexachlorocyclopentadiene reacts readily with a great variety of simple olefinic compounds to give hexachloronorbornenes in high yields,[3,4] Method 1 has the drawback that ring-substituted styrenes are not easily available. In Method 2, alkylation of the styrene adduct with a Friedel-Crafts catalyst again shows the amazing inertness of the chlorine atoms in hexachloronorbornene. Method 3 is the most versatile and could be used to prepare many new derivatives; the resulting quarternary connecting configuration *o*-cresol alkylated readily; *p*-cresol and *p*-xylene,



$$R-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-R'$$

---

[1] Prepared by the procedure of S. H. Herzfeld *et al.*, *Chem. Abstr.*, **47,** 8775 (1953); U. S. Patent 2,606,910.

(2) Phenols were alkylated in *o*-dichlorobenzene solution at reflux for 11 hr. with ethanesulfonic acid as catalyst.

(3) E. A. Prill, *J. Am. Chem. Soc.*, **69,** 62 (1947); E. K. Fields, *J. Am. Chem. Soc.* **76,** 2709 (1954); C. W. Roberts, *Chem. & Ind.* (*London*), 110 (1958).

(4) H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58,** 249 (1958).