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The Addition of α,β-Dichloroethyl Ethers to Isoprene

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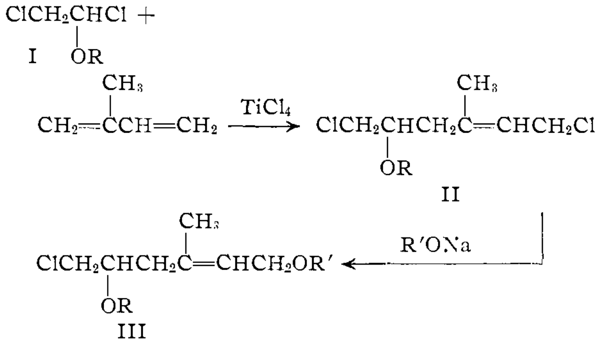
The addition of α,β-dichloroethyl ethers to isoprene has been found to furnish 1,4-adducts, namely, 1,6-dichloro-3-methyl-5-alkoxy-2-hexenes, in good yield. These compounds have a structure similar to the seven-carbon terminal grouping of the vitamin A side chain. Their transformation into structures more closely related to this grouping has been investigated. The allylic chlorine present in these compounds was readily replaced by alkoxyl or acetoxyl groups. The resulting 1,5-dialkoxy-6-chloro-2-hexenes have been subjected to reactions involving selective displacement of an alkoxyl group and to the simultaneous elimination of halogen and alkoxyl by the action of alkali metal.

The condensation of β-ionone with the appropriate seven-carbon intermediate would appear to be one of the more direct routes to derivatives of vitamin A. Syntheses of the vitamin in which such an intermediate is combined with β-ionone are reported.[1-3] However, none of these procedures seems to have found commercial application, presumably due to the formation of products in the final dehydration reaction other than the desired pentaene.[4] In the work reported here a novel reaction of α,β-dichloroethyl ethers has been used to prepare a series of seven-carbon adducts. These products have been examined primarily on the basis of their close structural relationship to the terminal portion of the vitamin A side chain.

Addition of α,β-Dichloroethyl Ethers to Isoprene.—The addition of α-chloro ethers to dienes to produce substituted allyl chlorides has been investigated previously.[5,6] A reaction of this type has been used to prepare a group of substituted heptenes (II).



$$\underset{\text{I}}{ClCH_2\underset{OR}{\underset{|}{CHCl}}} + CH_2{=}\overset{CH_3}{\overset{|}{C}}CH{=}CH_2 \xrightarrow{TiCl_4} \underset{\text{II}}{ClCH_2\underset{OR}{\underset{|}{CH}}CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2Cl}$$

$$\underset{\text{III}}{ClCH_2\underset{OR}{\underset{|}{CH}}CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_2OR'} \xleftarrow{R'ONa} \text{II}$$

Since 1,2- and 1,4-addition products are obtained when α-chloro ethers are added to butadiene, the reaction involving an α,β-dichloroethyl ether (I) and isoprene might be expected to yield a mixture of adducts. This difficulty was not encountered; the principal product of the reaction was formed by the 1,4-addition of the dichloro ether to isoprene.

The α,β-dichloroethyl ethers required in this investigation have been prepared by the addition of chlorine at low temperature to the corresponding vinyl ethers. These chloro ethers (I) are quite reactive and decompose on standing. They were purified most satisfactorily by vacuum distillation in the presence of an alkali carbonate.

The addition of the various α,β-dichloroethyl ethers (I) to isoprene was accomplished in the presence of titanium tetrachloride, but other anhydrous metal halides such as zinc chloride and ferric chloride also could be used. The reaction produced essentially one product, which was shown by elemental analysis to have the empirical formula expected for the desired adduct (II). One chlorine atom in the compound was readily replaceable; reactions of the material with sodium acetate in acetic acid or with sodium alkoxides in the corresponding alcohols yielded the respective acetate or ethers (III) in high yield. All of the compounds formed in this way (listed in Table I) retained one chlorine atom. Three α,β-dichloroethyl ethers (I), prepared from ethyl vinyl ether, isopropyl vinyl ether and benzyl vinyl ether, respectively, have been added to isoprene.

Structure Proof of the 1-Methoxy-5-ethoxy Adduct (IV).—The formation of an isoprene adduct was effected initially with α,β-dichloroethyl ethyl ether and the product obtained was studied in the form of its more stable methoxyl derivative. As a typical member of the series, this methyl ether was subjected to a proof of structure. Oxidative degradation of the compound through the use of ozone has established it as the desired 1-methoxy-3-methyl-5-ethoxy-6-chloro-2-hexene (IV). The degradation reaction produced γ-chloro-β-ethoxypropyl methyl ketone (V) in more than 80% yield. Of the several structural isomers which could have been formed by the addition of α,β-dichloroethyl ethyl ether to isoprene, only the desired adduct would be expected to yield this ketone. The ozonolysis reaction was accomplished in ethyl acetate and the resulting ozonide was reduced catalytically.[7] Besides the substituted propyl methyl ketone, the mixture of products contained glyoxal, identified by a nitric acid oxidation to oxalic acid dihydrate, and a small amount of formaldehyde, identified as its dimedon derivative. The presence of the expected methoxyacetaldehyde could not be detected in the reaction mixture. This fragment evidently was oxidized further under the conditions of the reaction to furnish glyoxal and formaldehyde.

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(1) F. B. Kipping and F. Wild, *Chemistry and Industry*, **58**, 802 (1939).

(2) O. Isler, British Patent 626,392 (July 27, 1949) and U. S. Patent 2,529,498 (November 14, 1950).

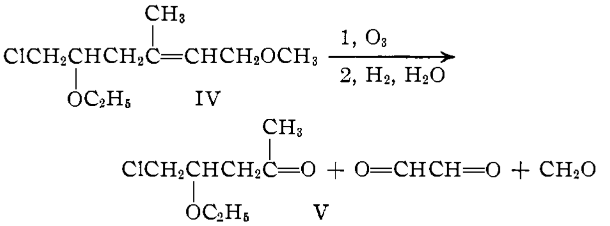
(3) M. Freed, U. S. Patent 2,587,457 (February 26, 1952).

(4) W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 295, 3807 (1952); **75**, 1050 (1953).

(5) F. Straus and W. Thiele, *Ann.*, **525**, 151 (1936).

(6) A. N. Pudovik, *Izvest. Akad. Nauk. U.S.S.R. Otdel Khim. Nauk*, 529 (1948); *C. A.*, **43**, 2158i (1949).

(7) F. G. Fischer, H. Düll and L. Ertel, *Ber.*, **65**, 1467 (1932).



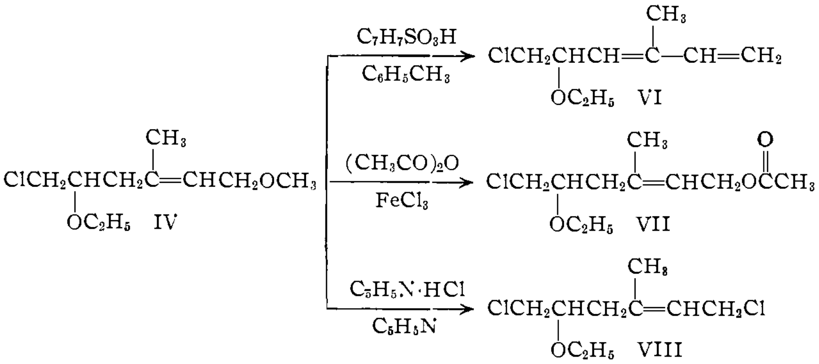
$$\mathrm{ClCH_2\underset{\underset{OC_2H_5}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2OCH_3}\ \text{IV}\ \xrightarrow[2,\ H_2,\ H_2O]{1,\ O_3}\ \mathrm{ClCH_2\underset{\underset{OC_2H_5}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}{=}O + O{=}CHCH{=}O + CH_2O}\ \text{V}$$

Abnormal ozonolysis reactions of this type have been observed previously with allyl type ethers.[8]

γ-Chloro-β-ethoxypropyl methyl ketone (V), the key intermediate in the assignment of a structure to the isoprene adduct, was characterized largely on the basis of its elemental analysis and its infrared absorption spectrum. The compound reacted with sodium hypoiodite to produce iodoform and also furnished a 2,4-dinitrophenylhydrazone, but this derivative could be crystallized only with difficulty and was not obtained in a pure state.

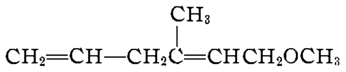
Attempts to obtain additional information concerning the structural features of 1-methoxy-3-methyl-5-ethoxy-6-chloro-2-hexene (IV), using oxidative methods other than ozonolysis, were unsuccessful. The compound resisted the action of performic and perbenzoic acids, reagents which normally convert olefins to epoxides.[9] Moreover, the corresponding glycol could not be prepared by the reaction of the 2-hexene (IV) with such reagents as aqeuous potassium permanganate or hydrogen peroxide–osmium tetroxide.[10]

Reactions of the 1-Methoxy-5-ethoxy Adduct (IV).—Various reactions of compound IV clearly demonstrate an enhanced chemical reactivity toward acidic reagents at the 1-methoxyl position. The 5-ethoxyl group was found to be relatively unreactive under these conditions. Dealcoholation of the compound, which is described in detail in the publication which follows,[11] involved the methoxyl group exclusively. In the presence of p-toluenesulfonic acid, a 1,4-elimination of the elements of methanol occurred to produce a 1,3-hexadiene (VI). In the presence of acetic anhydride and ferric chloride, the corresponding 1-acetoxyl derivative (VII) was formed, while pyridine hydrochloride in pyridine reacted with the adduct to regenerate the parent 1-chloro compound (VIII).



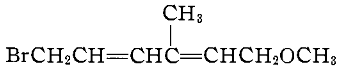
$$\mathrm{ClCH_2\underset{\underset{OC_2H_5}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2OCH_3}\ \text{IV}\ \begin{cases} \xrightarrow[C_6H_5CH_3]{C_7H_7SO_3H} \mathrm{ClCH_2\underset{\underset{OC_2H_5}{|}}{C}HCH{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2}\ \text{VI} \\ \xrightarrow[FeCl_3]{(CH_3CO)_2O} \mathrm{ClCH_2\underset{\underset{OC_2H_5}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2O\overset{\overset{O}{\|}}{C}CH_3}\ \text{VII} \\ \xrightarrow[C_5H_5N]{C_5H_5N\cdot HCl} \mathrm{ClCH_2\underset{\underset{OC_2H_5}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2Cl}\ \text{VIII} \end{cases}$$

Inasmuch as the carbon skeleton of the terminal portion of the vitamin A side chain is present in the 1-methoxy-5-ethoxy adduct (IV), the condensation of this material with β-ionone was studied. When lithium was used as the condensing agent, the only product identified was 1-methoxy-3-methyl-2,5-hexadiene (IX) formed by the removal of the 5-ethoxyl and 6-chloro groups.[12] Higher boiling products were obtained also but they were not definitely characterized. The unconjugated diene (IX) formed in this condensation also could be prepared by the action of sodium, dispersed in petrolatum, upon an ether solution of the 1-methoxy-5-ethoxy adduct (IV). Several attempts were made to transform this diene into a useful intermediate for attaching as the vitamin A side chain. Reaction with N-bromosuccinimide might be expected[13] to convert it into 1-methoxy-3-methyl-6-bromo-2,4-hexadiene (X) but this reaction was not accomplished. The preparation of a lithium alkyl (XI or XII) directly from the unconjugated diene (IX) by the action of either lithium or phenyllithium likewise was not successful.



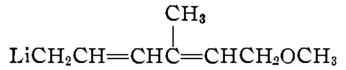
$$\mathrm{CH_2{=}CH{-}CH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2OCH_3}$$

IX



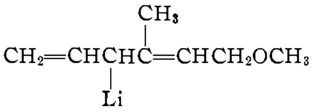
$$\mathrm{BrCH_2CH{=}CH\overset{\overset{CH_3}{|}}{C}{=}CHCH_2OCH_3}$$

X



$$\mathrm{LiCH_2CH{=}CH\overset{\overset{CH_3}{|}}{C}{=}CHCH_2OCH_3}$$

XI



$$\mathrm{CH_2{=}CH\underset{\underset{Li}{|}}{C}H\overset{\overset{CH_3}{|}}{C}{=}CHCH_2OCH_3}$$

XII

The dealcoholation of all 1,5-dialkoxy-6-chloro-2-hexenes (III) prepared has been investigated extensively. The results of this study are reported in the publication which follows.[11]

Attempted Preparation of a 5-Acetoxy Adduct.—The 1,4-addition of α,β-dichloroethyl acetate to isoprene would produce a 2-hexene containing a 5-acetoxyl group (II, R = CH_3CO). The 1-alkoxyl derivative of this compound (III, R = CH_3CO) might be expected to lose the elements of acetic acid on pyrolysis, yielding a 1-alkoxy-3-methyl-6-chloro-2,4-hexadiene. The preparation of such an acetoxyl analog was attempted with a variety of acid catalysts without success. Under the conditions used, polymerization of the isoprene was the chief reaction observed.

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[8] W. G. Young, A. G. McKinnis, I. D. Webb and J. D. Roberts, THIS JOURNAL, **68**, 293 (1946).

[9] D. Swern, *Chem. Revs.*, **45**, 1 (1949).

[10] N. A. Milas and S. Sussman, THIS JOURNAL, **59**, 2345 (1937).

[11] J. N. Coker, A. S. Bjornson, T. E. Londergan, T. F. Martens and J. R. Johnson, *ibid.*, **77**, 5546 (1955).

[12] H. B. Dykstra, J. F. Lewis and C. E. Boord, *ibid.*, **52**, 3396 (1930); B. H. Shoemaker and C. E. Boord, *ibid.*, **53**, 1505 (1931).

[13] P. Karrer and W. Ringli, *Helv. Chim. Acta*, **30**, 863, 1771 (1947).

Experimental

Preparation of α,β-Dichloroethyl Ethers (I). α,β-Dichloroethyl Alkyl Ethers.—α,β-Dichloroethyl ethyl ether and α,β-dichloroethyl isopropyl ether were prepared by identical procedures. A 3-l. r.b. flask equipped with a gas inlet tube, a stirrer and a thermometer was immersed in a trichloroethylene–Dry Ice bath and charged with 8.0 moles of the required vinyl alkyl ether. After the contents of the flask had cooled to −70°, chlorine was passed in at a rate which maintained the reaction temperature at −50 to −60°. This addition was continued until the appearance of a yellow color in the solution was noted. The crude reaction product was scrubbed free of excess chlorine and hydrogen chloride by a stream of nitrogen. During this scrubbing period, the product was allowed to warm slowly to room temperature. One hundred grams of sodium carbonate was added and the product was distilled immediately through a 3-foot vacuum-jacketed column packed with 1/8" glass helices. Using this procedure, α,β-dichloroethyl ethyl ether, b.p. 51–53° (30 mm.), n^{20}_D 1.4420, was obtained in a 48% yield.

α,β-Dichloroethyl isopropyl ether, b.p. 48–49° (14 mm.), n^{20}_D 1.4390, was isolated in a 54% yield.

Anal. Calcd. for $C_5H_{10}OCl_2$: C, 38.15; H, 6.37. Found: C, 39.14, 39.26; H, 6.51, 6.51.

Both products, though relatively stable in pure form, were stored under nitrogen at temperatures below 0°.

α,β-Dichloroethyl Benzyl Ether.—Since the benzyl ether required for the preparation of this compound is not commercially available, it was prepared by the reaction of benzyl alcohol with acetylene under pressure in the presence of aqueous potassium hydroxide.[14] The chlorination of benzyl ether was carried out in methylene chloride.

A mixture of 197 g. (1.47 moles) of benzyl vinyl ether, b.p. 70–72° (12 mm.), n^{20}_D 1.5160, and 200 g. of dry methylene chloride was cooled to −40 to −50°. Chlorine was passed in at this temperature at the rate of 3 g./minute with vigorous stirring. When 86 g. (1.21 moles) of chlorine had been added, a yellow color developed in the solution. The addition of chlorine was stopped immediately and the color was removed by purging the solution with dry nitrogen at a temperature of −30°. The solvent was removed under reduced pressure (15–20 mm.) at a temperature of 0° or lower. The cold residue was placed under a 6" × 3/4" electrically heated Vigreux column, 40 g. of dry potassium carbonate added, and the pressure of the system reduced rapidly to less than 10 mm. Only then was the charge allowed to warm to room temperature. After a pressure of 2 mm. had been attained in the system, heating was begun and the product was distilled rapidly from the reaction mixture. This product, b.p. 105–110° (5–7 mm.), n^{20}_D 1.5285, occurred as a middle cut in the distillation and was obtained in a 52% yield (152.0 g.).

Anal. Calcd. for $C_9H_{10}OCl_2$: C, 52.71; H, 4.88; Cl, 34.61. Found: C, 53.17, 53.25; H, 4.65, 4.88; Cl, 34.36, 34.29.

It was found necessary throughout the distillation of α,β-dichloroethyl benzyl ether to supply heat to the Vigreux column.

Addition of α,β-Dichloroethyl Alkyl Ethers (I) to Isoprene.—The addition of α,β-dichloroethyl ethyl ether and α,β-dichloroethyl isopropyl ether to isoprene was accomplished by the following procedure. To a 3-l., r.b. flask, equipped with a thermometer, a Dry Ice condenser, a dropping funnel and a stirrer, 3.5 moles of α,β-dichloroethyl alkyl ether, 800 ml. of methylene chloride and 20 g. (0.125 mole) of anhydrous titanium tetrachloride were added. To the stirred solution, 252 g. (3.7 moles) of isoprene was introduced dropwise over a period of 0.5 hour, the temperature of the reaction mixture being maintained below 40° during this addition. Stirring was continued for an additional 2.5 hours. The reaction catalyst was removed by washing the reaction mixture with four 1000-ml. portions of water. These aqueous washings were extracted with methylene chloride. After the methylene chloride extracts were combined with the solution of product, the mixture was passed through a column packed with anhydrous sodium carbonate. The effluent obtained was dried over anhydrous sodium sulfate. The solvent was stripped under reduced pressure and the residue subjected to a vacuum fractional distillation using a 36" × 1" vacuum-jacketed column packed with 1/8" glass helices. 1,6-Dichloro-3-methyl-5-ethoxy-2-hexene, b.p. 75–78° (0.15 mm.), n^{20}_D 1.4772, was isolated in a 50–60% yield. This compound could be distilled without decomposition only at pressures below 15 mm.

Anal. Calcd. for $C_9H_{16}OCl_2$: C, 51.13; H, 7.59. Found: C, 51.15; H, 7.50.

1,6-Dichloro-3-methyl-5-isopropoxy-2-hexene, b.p. 80–82° (1.0 mm.), was obtained in a 55% yield and was comparable in stability to the corresponding 5-ethoxyl adduct.

Anal. Calcd. for $C_{10}H_{18}OCl_2$: C, 53.34; H, 7.99; Cl, 31.57. Found: C, 53.35, 53.14; H, 8.04, 7.96; Cl, 31.37.

Replacement of the 1-Chloro Group in 1,6-Dichloro-3-methyl-5-alkoxy-2-hexenes.[15] Reaction with Sodium Acetate.—In a 500-ml. r.b. flask equipped with an efficient stirrer, 20.5 g. (0.21 mole) of potassium acetate was dissolved in 100 ml. of glacial acetic acid. To this solution was added 0.21 mole of the 1,6-dichloro adduct. The mixture was stirred vigorously under reflux for one hour. After cooling, the potassium chloride was filtered and the filtrate diluted with 500 ml. of water. The organic layer was removed, washed several times with water, and dried over anhydrous sodium sulfate. The crude product was fractionally distilled under vacuum to give approximately a 70% yield of the corresponding 1-acetoxy-3-methyl-5-alkoxy-6-chloro-2-hexene.

Reaction with Sodium Alkoxides.—Thirteen grams (0.56 mole) of sodium was added in small portions to 250 ml. of the required alcohol. When all the metal had reacted, 0.5 mole of the 1,6-dichloro adduct was added over a period of 20 minutes with vigorous stirring. The mixture was refluxed gently with stirring for an additional 1.5 hours. The precipitated sodium chloride was filtered and the filtrate concentrated *in vacuo* until about two-thirds of the initial volume had been distilled. After the residue had been washed with several portions of water, it was dried over sodium sulfate. Fractional distillation under reduced pressure yielded the desired 1,5-dialkoxy-3-methyl-6-chloro-2-hexene in pure form.

This procedure was used to prepare methoxyl, *n*-butoxyl, *n*-pentoxyl and benzyloxyl derivatives.

Ozonolysis of the 1-Methoxy-5-ethoxy Adduct (IV).—The ozonolysis of the 1-methoxy-5-ethoxy adduct (IV) was carried out in ethyl acetate. To 60 ml. of this solvent, containing 10.3 g. (0.05 mole) of the adduct, ozone was passed in at a temperature of −13 to −16° until a very slight excess of this reagent had been introduced. After the system had been purged free of ozone with a stream of nitrogen, 2.0 g. of palladium-on-alumina was added. The solution was allowed to warm to room temperature and hydrogen was bubbled in with stirring for 0.5 hour. At the end of this period, the solution was found to be peroxide-free. The catalyst was filtered off and the filtrate was extracted with four 25-ml. portions of water. The water extracts contained most of the formaldehyde and glyoxal formed in the reaction.

To 50 ml. of this water solution, 0.5 ml. of concentrated nitric acid was added and the resulting mixture evaporated to dryness. The white precipitate which remained was identified as oxalic acid dihydrate. It could be sublimed in the form of white needles, m.p. 100–101°, which did not depress the m.p. of an authentic sample of oxalic acid dihydrate. An aqueous solution of this product formed a precipitate with calcium ion and reduced potassium permanganate.

The remaining quantity of water extract was used to prepare the dimedon derivative of formaldehyde. To 50 ml. of this solution, 2.5 ml. of 10% ethanolic methone solution was added along with 1 ml. of glacial acetic acid. The resulting mixture was refluxed gently for 10 minutes. Cooling produced a mass of white crystals, m.p. 185–186°. This product, identified as the dimedon derivative of formaldehyde, did not depress the melting point of an authentic sample of this derivative.

γ-Chloro-β-ethoxypropyl methyl ketone (V) remained in the ethyl acetate solution, and was isolated in crude form by removing the solvent under reduced pressure. The

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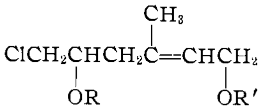
[14] M. F. Shostakowski and M. S. Burnistrova, *J. Appl. Chem.* (*U.S.S.R.*), **15**, 260 (1942); *C. A.*, **37**, 2336^3 (1943).

[15] The physical constants of the products obtained are given in Table I.

TABLE I

PHYSICAL CONSTANTS OF DERIVATIVES FORMED BY THE REPLACEMENT OF THE 1-CHLORO GROUP IN THE 1,6-DICHLORO-3-METHYL-5-ALKOXY-2-HEXENES



$\mathrm{Cl{CH_2}\underset{OR}{CH}CH_2\overset{CH_3}{C}{=}CH\underset{OR'}{CH_2}}$

R	R'	$n^{20}D$	B.p. °C.	B.p. Mm.	Empirical formula	Elemental analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found	Yield, %[a]
CH_2CH_3	CH_3	1.4578	55–57	0.07	$C_{10}H_{19}O_2Cl$	58.13	58.01	9.20	9.06	17.18	17.03	85
CH_2CH_3	n-C_4H_9	1.4564	90–92	.6	$C_{13}H_{25}O_2Cl$	62.71	62.70 62.60	10.07	10.01 9.94	14.28	14.19	83
i-C_3H_7	CH_3	1.4570	72–74	.7	$C_{11}H_{21}O_2Cl$	59.85	60.05 59.91	9.51	9.45 9.36	...	...	68
i-C_3H_7	n-C_5H_{11}	1.4545	95–98	.3	$C_{15}H_{29}O_2Cl$	65.08	65.28 65.12	10.49	10.60 10.53	12.82	13.12	60
i-C_3H_7	$CH_2C_6H_5$	1.5044	125–127	.1	$C_{17}H_{25}O_2Cl$	68.80	68.72 68.76	8.44	7.68 7.77	11.99	11.79 11.85	64
i-C_3H_7	C_6H_5	1.5117	125–126	.2	$C_{16}H_{23}O_2Cl$	67.97	68.36 68.54	8.16	8.03 8.28	12.56	12.56 12.56	55
$CH_2C_6H_5$	CH_3	1.5205	113–114	.2	$C_{15}H_{21}O_2Cl$	67.04	67.31	7.82	7.48 7.52	13.22	13.68 13.50	6
CH_2CH_3	$COCH_3$	1.4662	72–74	.1	$C_{11}H_{19}O_3Cl$	56.29	56.01 56.08	8.11	8.10 8.11	...	...	70

[a] From the corresponding 1,6-dichloro adduct.

product, b.p. 46–48° (2.0 mm.), $n^{20}D$ 1.4411, was purified by vacuum distillation.

Anal. Calcd. for $C_7H_{13}O_2Cl$: C, 51.06; H, 7.90. Found: C, 51.13, 51.26; H, 8.00, 8.12.

The ketone reacted with sodium hypoiodite to form the expected amount of iodoform, m.p. 118–119°, and with 2,4-dinitrophenylhydrazine to form an oily 2,4-dinitrophenylhydrazone.

Reaction with Sodium Phenoxide.—Only 1,6-dichloro-3-methyl-5-isopropoxy-2-hexene has been treated with this reagent. Nine and four-tenths grams (0.1 mole) of phenol was dissolved in 75 ml. of absolute ethanol. To this solution 5.4 g. (0.1 mole) of sodium methoxide was added with vigorous stirring. The solution was brought to a gentle reflux and 22 g. (0.1 mole) of 1,6-dichloro-3-methyl-5-isopropoxy-2-hexene was added in one portion. The suspension which resulted was refluxed with stirring for 1.5 hours. At the end of this period, a filtration removed the precipitated sodium chloride. The filtrate after cooling to room temperature was diluted with 50 ml. of methylene chloride. Several water washings were followed by drying over sodium sulfate and the solvent was removed under reduced pressure. Finally, a fractional distillation of the residue through a 10″ × 1/4″ platinum spiral column yielded 15.5 g. (0.55 mole) (55%) of 1-phenoxy-3-methyl-5-isopropoxy-6-chloro-2-hexene, b.p. 125–126° (0.2 mm.), $n^{20}D$ 1.5117. Characterization of this product was based on infrared analysis and on elemental analysis.

Addition of α,β-Dichloroethyl Benzyl Ether to Isoprene and Methoxylation of the Product.—The addition of α,β-dichloroethyl benzyl ether to isoprene was accomplished by the method used with other α,β-dichloroethyl ethers. However, the 1,6-dichloro adduct formed was not isolated, but was treated directly with sodium methoxide to produce the desired 1-methoxy-3-methyl-5-benzyloxy-6-chloro-2-hexene.

A mixture of 151 g. (0.74 mole) of pure α,β-dichloroethyl benzyl ether was stirred with 4.5 g. (0.023 mole) of titanium tetrachloride for 10 minutes. The temperature of the reaction mixture was maintained at 25° during this period. Stirring was continued for an additional 1.5 hours at a temperature of 25–34°. After the catalyst had been removed and the solution dried over anhydrous sodium carbonate, removal of the solvent under reduced pressure yielded 206 g. of crude product which was used directly in the next step.

Fifty grams (0.93 mole) of sodium methoxide dissolved in 250 ml. of dry methanol was added with vigorous stirring to the 206 g. of crude adduct. The resulting suspension was stirred for 1 hour at 40–55°. The precipitated sodium chloride was removed by filtration and most of the methanol separated from the filtrate under reduced pressure. After 100 ml. of methylene chloride had been added, the product was washed with several portions of water and dried over sodium sulfate. The methylene chloride was removed under reduced pressure and the residue distilled in a high vacuum in the presence of 25 g. of anhydrous sodium carbonate. The distillation yielded 55 g. of crude product, b.p. < 100° (3 mm.), which was refractionated through a 20″ × 1/4″ rotating platinum-band still, again in the presence of sodium carbonate. The second distillation yielded 14.8 g. (0.055 mole) (6%) of pure 1-methoxy-3-methyl-5-benzyloxy-6-chloro-2-hexene, b.p. 113–114° (0.2 mm.), $n^{20}D$ 1.5205. This compound was characterized by its infrared spectrum and by elemental analysis.

Preparation of 1-Methoxy-3-methyl-2,5-hexadiene (IX).—Sixty milliliters of dry diethyl ether was mixed with 9.2 g. of a 50% sodium emulsion in petrolatum. To the resulting suspension, 20.7 g. (0.1 mole) of 1-methoxy-3-methyl-5-ethoxy-6-chloro-2-hexene was added at room temperature with vigorous agitation. The reaction mixture was then refluxed gently for 3.5 hours. Twenty ml. of absolute ethanol was added and heating was continued for an additional 0.5 hour. The ether layer was washed with several 50-ml. portions of water and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue distilled in a vacuum to yield 2.5 g. of unreacted starting material, 5.2 g. (0.041 mole) of product, b.p. 53–54° (23 mm.), $n^{20}D$ 1.4410 and 2.8 g. of residue. The yield of 1-methoxy-3-methyl-2,5-hexadiene amounted to 47%. It was identified by its infrared absorption spectrum and by elemental analysis.

Anal. Calcd. for $C_8H_{14}O$: C, 76.21; H, 11.10. Found: C, 75.96; H, 11.11, 10.89.

This compound also was prepared in a comparable yield by the reaction of dispersed sodium with 1-methoxy-3-methyl-5-isopropoxy-6-chloro-2-hexene.

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