Preparation of S-methyl O-3-heptyl xanthate. Two-tenths mole of 3-heptanol was added to 0.2 g.-atom of sodium in 150 ml. of dry *p*-xylene and the mixture was stirred and refluxed for 3 hr. The mixture was cooled, then 150 ml. of dry ether and 30.5 g. of carbon disulfide was added and refluxed for 2 hr. Then 57 g. of methyl iodide was added and the mixture refluxed for twelve more hours. The mixture was cooled, filtered, low boiling material taken off below 80° at 20 mm., then a 52% yield of the product was collected at 105° at 5 mm.; n_D^{20} 1.5103.

Anal. Calcd. for $C_9H_{18}OS_2$: S, 31.1. Found: S, 28.3.

Decomposition of the esters. The acetates were passed through a 25-cm. heated zone (450–520°) with a slow stream of nitrogen. The collected material was washed with 5% sodium bicarbonate and water, then dried and distilled. The alkyl hydrogen phthalates were distilled in a micro-distillation apparatus under partial reflux until the vapor temperature reached 200°; the distillate was washed, dried, and distilled. The xanthate was heated in the same apparatus until distillation ceased; the distillate was washed with 20% sodium hydroxide, then twice with sodium plumbite, and finally water, then dried and distilled.

3-Dimethylaminoheptane. A mixture of 3-heptanone, dimethylamine, and platinum oxide in ethanol was loaded into an Aminco high pressure reaction vessel under 1100 p.s.i. of hydrogen, then heated to 260° and allowed to cool slowly overnight. Low boiling material was removed, then the desired amine was taken up in dilute hydrochloric acid, washed with ether, then liberated with sodium hydroxide. A 22% yield of 3-dimethylaminoheptane was obtained, boiling at 159–160°, n_D^{20} 1.4225. Neutral equivalent, calcd. for $C_9H_{21}N$, 143, Found: 143.

Preparation and pyrolysis of dimethyl-3-heptylamine oxide. 3-Dimethylaminoheptane was stirred for 30 hr. with an excess of 24% hydrogen peroxide, then another equivalent was added and the mixture heated to just below boiling for 40 min. The mixture was cooled and the excess hydrogen peroxide was destroyed with beef liver catalase. The mixture was filtered and the water removed under aspirator pressure. The residue was subjected to 2 mm. pressure and heated until decomposition of the amine oxide was complete. The distillate was washed with 10% hydrochloric acid, then with 10% sodium hydroxide, then with water, dried, and distilled.

Trimethyl-3-hepthylammonium iodide. 3-Dimethylaminoheptane in benzene was refluxed with an excess of methyl iodide for 20 min., then cooled and filtered. A 95% yield of the salt, melting 182–184°, was obtained.

Anal. Calcd. for $C_{10}H_{24}NI$: I, 44.5. Found: I, 42.5.

Preparation and pyrolysis of trimethyl-3-heptylammonium hydroxide. The iodide was dissolved in water, then shaken with silver oxide for 2 hr. The filtrate was transferred to a micro-distillation apparatus, and the water distilled; decomposition began as the rate of heating was increased and continued until no more distillate was collected. The distillate was washed with 5% hydrochloric acid, then with water, then dried and distilled.

Analysis of olefin mixtures. Olefin mixtures were analyzed by gas chromatography using a column of 6 ft. of benzyl ether and 6 ft. of *o*-nitrophenyl ether on firebrick. Reference samples were a commercial 2-heptene, 3-heptene from the pyrolysis of 4-heptyl hydrogen phthalate, and 2,4-dimethyl-2-hexene from dehydration of 2,4-dimethyl-2-hexanol with phosphoric acid. The heptenes were resolved into four distinct peaks, apparently in order of boiling point. The product of reaction of 2,4-dimethyl-3-chlorohexane with base was a mixture of only the two isomeric olefins expected, and was used to identify 2,4-dimethyl-3-hexene. The analysis of the 2,5-dimethylhexenes was performed on a column of 8 ft. of benzyl ether on firebrick at a later date, after a separation according to boiling point had been demonstrated for olefins on the column. Three peaks, corresponding to *cis*- and *trans*-diisopropylethylene and 2,5-dimethyl-2-hexene were obtained.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION, PITTSBURGH PLATE GLASS COMPANY]

Reaction of Cyclopentadiene with Hemiacetal Chlorides

ROSTYSLAW DOWBENKO

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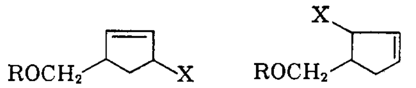
Cyclopentadiene reacts with hemiacetal chlorides to give alkoxymethyl-3-chlorocyclopentenes (I). Various transformations of I are described.

The reaction of olefins with hemiacetal chlorides which, in the simplest case, may be exemplified by the reaction of ethylene with chloromethyl ether,[1a] is well known in the literature.[1] Such reactions of cyclopentadiene, however, are unknown, except for one instance of its reaction with α-methoxybenzyl chloride reported by Straus and Thiel.[1c] It has now been shown that cyclopentadiene reacts smoothly with hemiacetal chlorides in the presence of tin tetrachloride to give chloro compounds I which are believed to be composed of either 5-alkoxymethyl-3-chlorocyclopentenes (Ia) or 4-alkoxymethyl-3-chlorocyclopentenes (Ib), or both. The chlorides I are unstable and, in the course of hours at room temperature or days in the cold, evolve hydrogen chloride and become discolored. Acids seem to accelerate the decomposi-

$$CH_2{=}CH_2 + ClCH_2OCH_3 \longrightarrow CH_3OCH_2CH_2CH_2Cl$$



Ia and/or Ib. R = CH_3, CH_3CH_2, $(CH_3)_2CH$, butyl, allyl; X = Cl

IIa and/or IIb. R = $CH_3CH_2CH_2$, $(CH_3)_2CH$, butyl, allyl; X = $OCOCH_3$

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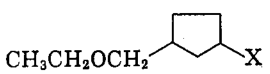
[1] (a) British Patent **423,520**, February 4, 1935; (b) N. D. Scott, U. S. Patent **2,024,749**, December 17, 1935; (c) F. Straus and W. Thiel, *Ann.*, **525**, 151 (1936); (d) C. D. Nenitzescu and V. Przemetzki, *Ber.*, **69**, 2706 (1936); (e) C. D. Hurd, U. S. Patent **2,805,259**, September 3, 1957; (f) E. W. Lane, U. S. Patent **2,829,174**, April 1, 1958; (g) B. A. Vovsi and A. A. Petrov, *Zhur. obschechei khim.*, **28**, 1426 (1958).

tion, but bases inhibit it sufficiently so that in some instances the chloro compounds I could be distilled in the presence of potassium hydroxide.

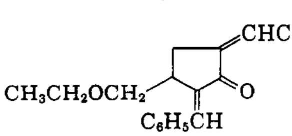
In all probability the structure of the chloro compounds I is as shown with Ia predominating in analogy to the predominant 1,4-addition of bromine to cyclopentadiene[2] and also because of the results obtained on acetolysis and further transformations of the products to be described presently, although nonhomogeneity of II ($R = CH_3CH_2$;$X = OCOCH_3$) in vapor phase chromatography (on Apiezon L) indicated the possibility of the presence of the *cis-trans* isomers of both IIa and IIb. Because of the instability of I, no attempt was made to analyze them by the same method. The alcohol IV, obtained by hydrogenation and saponification of the acetate IIIa (or by hydrolysis of the chloride to the alcohol IIIb and subsequent hydrogenation), was oxidized with chromic acid to the corresponding ketone V. The latter, when treated with benzaldehyde in the presence of a base, gave as the only isolable compound the dibenzylidene derivative which is formulated as VI.[3] From this it is concluded that the ketone and, therefore, the intermediates leading to it have the structures IIa ($R = CH_3CH_2$), IV, V, and VI. However, since the yield of the dibenzylidene compound VI was low, the presence of 2-(ethoxymethyl)cyclopentanone (which could arise from 1,2-addition of hemiacetal chlorides to cyclopentadiene or allylic rearrangement of Ia on treatment with sodium acetate in acetic acid) could have escaped the detection. The formation of IIa ($R = CH_3CH_2$) may have come about from Ia or Ib, but it is likely that 1,4-addition is the predominant reaction of cyclopentadiene with chloromethoxy compounds, and that Ia is the main product.

$CH_3CH_2OCH_2C_5H_6X$

IIIa. $X = OCOCH_3$
IIIb. $X = OH$
IIIc. $X = OCOC(CH_3){=}CH_2$
IIId. $X = OC_6H_5$
IIIe. $X = Cl$
IIIf. $X = CH_3$
IIIg. $X = C_6H_5$
IIIh. $X = OCH_3$



IV, X=OH
V, X=O



VI

The chlorides I obtained from addition of hemiacetal chlorides to cyclopentadiene were converted to the actetates II by sodium (or potassium) acetate in acetic acid, and the results are summarized in Table I. In a similar manner the chloride IIIe was converted to the methacryloxy compound IIIc by sodium methacrylate in dimethylformamide. With phenol in the presence of potassium carbonate the chloride IIIe gave the phenoxy compound IIId, while with methanolic potassium hydroxide the chloride IIIe (ethyl replaced by butyl) yielded the methyl ether IIIh (ethyl replaced by butyl).

An attempt was made to separate the alcohol IIIb obtained from hydrolysis of the corresponding chloride into individual isomers if any. Careful fractionation gave fractions which showed different refractive indices and boiling points but nearly indistinguishable infrared spectra. No crystalline α-naphthylurethan could be prepared from one of such fractions, a fact which could possibly indicate that the alcohol is a mixture of isomers. The other material that was separated from the crude reaction mixture was a higher boiling fraction which appeared to be 4-ethoxymethyl-2-cyclopentenyl ether.[4]

Although attempted hydrogenation of IIIe in the usual manner did not lead to absorption of hydrogen, its hydrogenation in the presence of triethylamine gave (ethoxymethyl)cyclopentane. The effect of triethylamine on this reaction is also shown by the fact that it can promote dehydrochlorination of IIIe. From dehydrochlorination of IIIe with triethylamine there was obtained, in addition to some (ethoxymethyl)cyclopentadiene, as a predominant product a higher boiling material which apparently was a dimer of (ethoxymethyl)cyclopentadiene. This material was extremely reactive with atmospheric oxygen so that after twenty-four hours at room temperature (or one hour at 100°) it became solid and showed very strong new bands at 2.9 and 5.85 μ in the infrared.

While a Grignard reagent could not be prepared from IIIe under the conditions used, and most of the chloride could be recovered even after prolonged refluxing with magnesium in ether containing some iodine, the chloride IIIe reacted with methylmagnesium iodide and phenylmagnesium bromide to give compounds which are formulated as 5-ethoxymethyl-3-methylcyclopentene (IIIf) and 5-ethoxymethyl-3-phenylcyclopentene (IIIg), respectively.

EXPERIMENTAL[5]

The starting hemiacetal chlorides were prepared from the appropriate alcohol, paraformaldehyde, and hydrogen

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[2] W. G. Young, H. K. Hall, Jr., and S. Winstein, *J. Am. Chem. Soc.*, **78**, 4338 (1956).

[3] For a reaction of benzaldehyde with 2- and 3-methylcyclopentanones, *cf.* N. Speranski, *J. Russ. Phys.-Chem. Soc.*, **34**, 10 (1902); *Chem. Centralblatt*, **73**, I, 1221 (1902) and O. Wallach, *Nachr. Königl. Ges. Wiss. Göttingen*, 399 (1907); *Chem. Centralblatt*, **79**, I, 637 (1908), respectively.

[4] *Cf.* S. David, G. Dupont, and C. Paquot, *Bull. soc. chim.*, **11**, 561 (1944) and A. W. Carlson, U. S. Patent 2,739,161, March 20, 1956, for the formation of 2-cyclopentenyl ether.

[5] All melting and boiling points are uncorrected. Analyses by Galbraith Laboratories, Knoxville, Tenn.

TABLE I

4-ALKOXYMETHYL-2-CYCLOPENTENYL ACETATES (II)

Alkyl	B.P. (Mm.)	n_D^t[a]	% Yield of Pure Cpd.[b]	Formula	Calcd. C	Calcd. H	Found C	Found H
Methyl	84 (4.5)	1.4519	28	$C_9H_{14}O_3$	63.51	8.29	63.86 64.06	8.49 8.60
Ethyl	91 (4.25)	1.4491	39	$C_{10}H_{16}O_3$	65.19	8.76	65.11 65.29	8.60 8.64
Isopropyl	89 (2.75)	1.4463	42	$C_{11}H_{18}O_3$	66.64	9.15	66.33 66.41	8.99 9.02
Butyl	101 (6.0)	1.4493	42	$C_{12}H_{20}O_3$	67.89	9.50	68.03 68.19	9.53 9.42
Allyl	108–112 (3.5)	1.4601	21	$C_{11}H_{16}O_3$	67.32	8.22	66.72 66.79	8.00 8.07

[a] 23°, 23°, 24°, 30°, respectively. [b] Based on cyclopentadiene.

chloride as described in the literature,[1b] except that all but the methyl compound were distilled at reduced instead of atmospheric pressure. In this manner were obtained *methyl chloromethyl ether*, b.p. 58–59°, n_D^{21} 1.3968; *ethyl chloromethyl ether*, b.p. 58–59°, n_D^{21} 1.3968; *ethyl chloromethyl ether*, b.p. 40° (160 mm.) to 44° (158 mm.), n_D^{25} 1.4005; *isopropyl chloromethyl ether*, b.p. 51–54° (147 mm.), n_D^{24} 1.4059; *butyl chloromethyl ether*, b.p. 56° (51 mm.) to 58° (54 mm.), n_D^{24} 1.4171. *Allyl chloromethyl ether*[6] was prepared similarly, b.p. 98–110°, n_D^{25} 1.4316. *Cyclopentadiene* was obtained by cracking of its dimer[7] and was redistilled freshly before use either at atmospheric pressure or under reduced pressure with receiver cooled in Dry Ice.

Reaction of hemiacetal chlorides with cyclopentadiene: A general method. To a solution of 1.0 mole of hemiacetal chloride in 100 ml. of ether, petroleum pentane or carbon tetrachloride containing 2 ml. of a solution of tin tetrachloride (5 g. of stannic chloride in 100 ml. of carbon tetrachloride) there was added dropwise with cooling and stirring a cold solution of 1.1 moles of cyclopentadiene in 100 ml. of the same solvent, while the temperature was kept between 0° and 3°. Addition of the cyclopentadiene took about 1 hr., and the reaction mixture was stirred at 0–3° for an additional 1.5 to 2.5 hr., after which 0.5 ml. of triethylamine was added. The solvent was evaporated *in vacuo* at room temperature, and the residue was used immediately in the subsequent reactions without distillation, unless stated to the contrary.

In some instances the product was distilled. Thus, 5-ethoxymethyl-3-chlorocyclopentene (IIIe) was obtained as a colorless liquid, b.p. 40–50° (0.03 mm.) n_D^{23} 1.4672, on distillation of the crude reaction product to which few pellets of potassium hydroxide have been added.

Reaction of (alkoxymethyl)cyclopentenyl chlorides (I) *with sodium or potassium acetates: (alkoxymethyl)cyclopentenyl acetates* (II). To a solution of 4.0 moles of sodium or potassium acetate in 1200 ml. of acetic acid at 60° there was added slowly in one portion the crude I from a 2.0-mole run. After heating at 80° for 20–24 hr., the mixture was poured into water and extracted with ether. The extract was washed with a sodium bicarbonate solution and with water, then dried. The solvent was removed and the residue fractionated *in vacuo* to obtain the products shown in Table I.

Hydrolysis of 5-ethoxymethyl-3-chlorocyclopentene (IIIe). To a solution of 320 g. (3.0 moles) of sodium carbonate in 2 l. of water there was added 553 g. of crude IIIe (from a 3.0-mole run). A mild exothermic reaction occurred and the temperature remained constant at 32° for 45 min. The mixture was then heated at 75° for 4.5 hr., then cooled and extracted with ether. Fractionation gave 223 g. (52%) of a liquid, b.p. 72–85° (3.0 mm.), n_D^{23} 1.4639, showing strong absorption at 2.98 μ (hydroxyl) and 9.0 μ (ether) in the infrared. Fraction, b.p. 90° (5 mm.), was analyzed.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.55; H, 9.92. Found: C, 67.70, 67.83; H, 9.61, 9.76.

In addition to the fraction above there was obtained 34.5 g. of a fraction, b.p. 68–106° (0.2 mm.) (mostly at 105°), n_D^{24} 1.4916, apparently impure 4-ethoxymethyl-2-cyclopentenyl ether.

Alternatively, when 884 g. of crude IIIe (from a 5.0-mole run) was hydrolyzed with a solution of 690 g. (5.0 moles) of potassium carbonate in 2 l. of water there was obtained after a usual work-up the following fractions: (1) low-boiling forefraction containing unchanged chloride IIIe; (2) 321 g. of a yellow liquid, b.p. 71° (5 mm.) to 90° (3 mm.); (3) 190 g. of a yellow liquid, b.p. 87° (1 mm.) to 190° (0.6 mm.) and about 50 g. of a dark residue. When an attempt was made to fractionate fraction 2 on a 25-in. column packed with helices there were obtained 6 fractions, b.p. 83° to 95° (4–5 mm.), whose refractive indices varied from 1.4632 to 1.4650 and whose infrared spectra were nearly indistinguishable. An attempt at preparation of a crystalline α-naphthylurethan of one of these fractions failed.

3-(Ethoxymethyl)cyclopentanol (IV). A solution of 28.4 g. (0.20 mole) of the alcohol IIIb, b.p. 72–82° (2.5 mm.), n_D^{24} 1.4639, in 150 ml. of methanol was hydrogenated in the presence of 1 ml. of Raney nickel, whereupon it absorbed 100% of the theoretical amount of hydrogen in about 15 min. Distillation gave 28.8 g. (100%) of a colorless oil, b.p. 83–93° (4.5 mm.), n_D^{25} 1.4507. It was chiefly IV and showed a strong hydroxyl band at 2.97 μ, but there was a weak ketone band at 5.78 μ that evidently was cuased by isomerization of the alcohol during hydrogenation.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.19. Found: C, 66.76; 66.95; H, 11.07, 11.03.

3-(Ethoxymethyl)cyclopentyl acetate. A mixture of 36.8 g. (0.20 mole) of the acetate IIIa, b.p. 89–92° at 4 mm., 150 ml. of ethyl acetate, and 1 ml. of Raney nickel was shaken with hydrogen at an initial pressure of *ca.* 50 p.s.i. After 2.5 hr. there occurred a drop of pressure equivalent to the uptake of 103% of the theoretical amount of hydrogen. Filtration and distillation of the filtrate gave 36 g. of a colorless liquid, b.p. 76–78° (0.8 mm.). A middle fraction, b.p. 77° (0.8 mm.), n_D^{22} 1.4393, was analyzed.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 65.35, 65.58; H, 10.22, 10.10.

Saponification of 3-(ethoxymethyl)cyclopentyl acetate. A mixture of 27 g. (0.145 mole) of the acetate, b.p. 76–78° at 0.8 mm., 22 g. of potassium hydroxide, 150 ml. of methanol, and 20 ml. of water was refluxed for 4 hr. Most of the solvent was removed *in vacuo*, the residue poured into water and extracted with ether. The ether extract gave on distillation 13 g. of a liquid which was redistilled to obtain 11 g. (53%) of a colorless liquid, b.p. 90–94° (6 mm.), n_D^{23} 1.4535, showing a hydroxyl band at 2.97 μ but no carbonyl in the infrared.

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(6) C. D. Hurd, U. S. Patent 2,847,456, August 12, 1958.

(7) Technical Bulletin No. 12, Enjay Co., Inc.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.19. Found: C, 66.84; 66.96; H, 11.01, 11.34.

3-(Ethoxymethyl)cyclopentanone (V). To a solution of 10 g. (0.070 mole) of the alcohol IV, b.p. 88° at 5.5 to 95° at 4.5 mm., in 30 ml. of acetic acid, there was added dropwise over a period of 75 min. a solution of 5.0 g. (0.050 mole) of chromic acid in 5 ml. water and 15 ml. of acetic acid, the temperature being regulated and kept at 30–40° by the rate of addition. After all the chromic acid solution was added, the mixture was stirred for 1 hr. at room temperature and 3.5 hr. at 40°. It was then diluted with water, neutralized with solid sodium bicarbonate, and extracted with ether. The extract was washed with aqueous sodium bicarbonate and water and dried. Distillation gave 7.0 g. of a colorless liquid, b.p. 90–97° (19 mm.), which showed strong carbonyl (5.77 μ) and a weak hydroxyl (2.9 μ) absorption in the infrared. Redistillation gave 4.5 g. of V as a colorless liquid, b.p. 85° (7 mm.) to 89° (9 mm.), n_D^{23} 1.4428.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.22. Found: C, 67.57, 67.78; H, 9.89, 10.01.

The *2,4-dinitrophenylhydrazone* of V melted at 81–82° (methanol) with softening at 75°.

Anal. Calcd. for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63; N, 17.37. Found: C, 51.99; 52.01; H, 5.32, 5.10; N, 18.18, 18.37.

3-Ethoxymethyl-2,5-dibenzylidenecyclopentanone (VI). To a cooled solution of 3.55 g. (0.025 mole) of V and 5.40 g. (0.051 mole) of benzaldehyde in 10 ml. of methanol there was added 0.3 g. of sodium methoxide and the mixture allowed to come slowly to room temperature. After a few hours the mixture crystallized to a yellow solid. More methanol was added and the solid was recrystallized to obtain 6.5 g. of a greenish-yellow solid, m.p. 101–104°, and some greenish oil in the filtrate. Two more recrystallizations from methanol gave 4.0 g. of a yellow solid, m.p. 104–118°. Four more recrystallizations gave 2.5 g. of yellow crystalline VI, m.p. 121–122°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.91; H, 6.97. Found: C, 82.87, 83.04; H, 7.04; 6.84.

Reaction of 5-ethoxymethyl-3-chlorocyclopentene (IIIe) *with sodium methacrylate.* A mixture of 97 g. (0.5 mole) of a crude chloride, 54 g. (0.50 mole) of sodium methacrylate, 1 g. of hydroquinone, and 200 ml. of dimethylformamide was heated at 100° for 20 hr. After cooling, the mixture was poured into water and extracted with ether. The extract was washed with water and sodium bicarbonate solution and dried. After removing the solvent the residue was distilled to obtain 61 g. of a yellow liquid, b.p. 45–147° (0.3 mm.). Fractionation gave 33 g. (31% based on cyclopentadiene) of a colorless liquid, b.p. 92–101° (0.8 mm.) (mostly 98–100°), n_D^{25} 1.4628, which showed a band at 5.81 μ and a weaker one at 6.11 μ (unsaturation) in the infrared.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63, Found: C, 68.48, 68.65; H, 8.26, 8.55.

Reaction of 5-butoxymethyl-3-chlorocyclopentene with methanolic potassium hydroxide. To a solution of 42 g. (0.75 mole) of potassium hydroxide in 750 ml. of methanol there was added the crude chloride (from an 0.5-mole run) whereupon the temperature rose to 42°. The mixture was refluxed for 5 hr., then poured into water and extracted with a mixture of ether and benzene. The extract was evaporated and distilled to obtain 72 g. of a yellow liquid, b.p. 55° (7 mm.) to 140° (4 mm.). This was fractionated to give 39 g. of a colorless liquid, b.p. 91–92° (5 mm.), apparently 5-butoxymethyl-3-methoxycyclopentene. A middle fraction, b.p. 91.5° (5 mm.), n_D^{23} 1.4461, was analyzed.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.87, 71.91; H, 10.99, 11.09.

Reaction of 5-ethoxymethyl-3-chlorocyclopentene (IIIe) *with phenol.* To a mixture of 47 g. (0.50 mole) of phenol, 70.5 g. (0.51 mole) of potassium carbonate, and 300 ml. of acetone there was added dropwise over a period of 1 hr. a solution of 0.50 mole of crude chloride dissolved in 100 ml. of ether. The mixture was refluxed (50°) for 22 hr., cooled, and poured into water and extracted with ether. The extract was washed with dilute aqueous sodium hydroxide then evaporated to obtain a yellow liquid. Fractionation gave, in addition to the unchanged chloride and residue, 33.5 g. (31% of the theory based on cyclopentadiene) of a colorless liquid, b.p. 118–132° (1.2 mm.), n_D^{24} 1.5201, showing no hydroxyl or carbonyl in the infrared, apparently 5-ethoxymethyl-3-phenoxycyclopentene (IIId).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.03; 77.23; H, 8.16, 8.38.

Hydrogenation of 5-ethoxymethyl-3-chlorocyclopentene (IIIe). A mixture of 48.3 g. (0.30 mole) of IIIe, b.p. 43° (0.02 mm.) to 54° (0.08 mm.), n_D^{24} 1.4667, 35 g. (0.36 mole) of triethylamine, 100 ml. of ethyl acetate, and 7 ml. of Raney nickel was shaken with hydrogen whereupon, after 5.5 hr., the mixture absorbed 0.58 mole of hydrogen. The mixture was poured into water and extracted with ether. The extract was successively washed with acetic acid, sodium bicarbonate solution, and water and dried. Two fractional distillations gave, in addition to a forefraction and a residue, 15.9 g. (41.5%) of a colorless liquid, apparently ethoxymethylcyclopentane. A middle fraction, b.p. 145–146°, n_D^{24} 1.4256, was analyzed.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58, Found: C, 74.85, 75.02; H, 13.04, 12.85.

Dehydrochlorination of 5-ethoxymethyl-3-chlorocyclopentene (IIIe). A mixture of the crude chloride (from 1.5-mole run) and 300 g. of triethylamine was refluxed (82°) fo 23 hr. The excess amine was distilled and the residue was dissolved in petroleum pentane and cooled. Filtration gave 122 g. of a white solid, apparently triethylamine hydrochloride. The filtrate was washed well with dilute acetic acid, then sodium bicarbonate solution, and then dried. Removal of solvent gave 93.6 g. of a residue which was distilled to obtain 84 g. of a yellowish liquid, b.p. 54° (17 mm.) to 165° (0.7 mm.). Fractionation gave fractions which were reactive with maleic anhydride and higher boiling ones which reacted with silver nitrate and a main fraction, 47 g. of a yellowish liquid, b.p. 93° (1.1 mm.) to 120° (1.5 mm.). Repeated fractionations gave 35 g. of a colorless liquid, b.p. 100–135° (1.5 mm.), n_D^{22} 1.4928, which did not react with maleic anhydride and showed a negative chloride test, apparently a dimer of (ethoxymethyl)cyclopentadiene.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 78.40, 78.65; H, 9.92, 9.69.

From a low-boiling fraction, b.p. 44° (4.5 mm.) to 48° (0.3 mm.) an adduct with maleic anhydride was prepared by allowing the reagents to react at room temperature, then at steam bath temperature to obtain a white solid, m.p. 122–126°.

A similar reaction of IIIe with trimethylpyridine at 50° for 8 hr. gave after customary separation and purification a colorless liquid, b.p. 95–115° (0.2 mm.), n_D^{23} 1.4928, which showed an identical spectrum with that of the liquid obtained by triethylamine dehydrochlorination.

Hydrogenation of a 12.5-g. sample of this compound gave, after absorption of 0.061 mole of hydrogen, 10 g. of a colorless liquid, b.p. 75° at 0.02 mm. to 110° at 0.05 mm., n_D^{24} 1.4842. This product showed a different spectrum from that of the starting compound.

The dimer, on standing in the air, rapidly absorbed oxygen and yielded materials which liberated iodine from a potassium iodide solution and which gave color with diphenylpicrylhydrazyl. When exposed as a thin film, it dried after 24 hr. at room temperature or after 1 hr. at 100°, developing very strong bands at 2.9 and 5.85 μ in the infrared.

When IIIe was heated with solid potassium hydroxide at 85° in such a manner that the volatile materials could be distilled, the distillate contained no materials reactive toward maleic anhydride and was essentially the unchanged chloride. Heating the chloride with potassium hydroxide and diethylene glycol dimethyl ether at 137° also failed and no (ethoxymethyl)cyclopentadiene could be obtained.

Attempted preparation of a Grignard reagent from IIIe. The reaction of the chloride with magnesium in ether even in the presence of iodine was slow. The mixture was refluxed for 8 hr., then cooled and poured onto a mixture of ether and powdered Dry Ice. Customary separation gave an acidic and a neutral fraction. The former gave a trace of a residue, while the latter, on distillation, gave a liquid b.p. 64° (1.0 mm.) to 140° (0.15 mm.), giving a precipitate with aqueous silver nitrate, apparently unreacted starting material.

Reaction of IIIe *with methylmagnesium iodide.* To the Grignard solution, prepared from 0.50 mole of each magnesium and methyl iodide in a total of 300 ml. of ether, there was added dropwise 175 ml. a cold ether solution of the above chloro compound (from a 0.50-mole run). The reaction was very exothermic and addition took 1.5 hr. After all the chloride was added, the mixture was refluxed 45 min. during which time it became intensely green-colored and a green oil precipitated. After allowing to stand at room temperature for 0.5 hr., the mixture was decomposed with a saturated ammonium chloride solution and extracted with ether. After removal of the solvent the residue was distilled to obtain 25 g. of a dark orange liquid, b.p. 44° (11 mm.) to 45° (10 mm.). This was washed with a sodium sulfite solution and redistilled to obtain 23 g. (33%) of a nearly colorless liquid, b.p. 68–69° (34 mm.), n_D^{23} 1.4357, which decolorized bromine in carbon tetrachloride and exhibited an infrared spectrum which contained no hydroxyl or carbonyl absorption.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.08, 77.28; H, 11.35, 11.36.

Reaction of IIIe *with phenylmagnesium bromide.* To a Grignard solution prepared from 1.0 mole of reagents in 400 ml. of ether there was added with stirring over a period of 1.5 hr. a solution of 0.54 mole of the chloro compound in 100 ml. of benzene. The reaction was exothermic and a solid precipitated at the end of addition. The resulting mixture was refluxed for 16 hr., then was cooled and decomposed with an excess of a saturated ammonium chloride solution and extracted with petroleum pentane (b.p. 30–60°). Distillation gave 106 g. (96%) of a yellowish liquid, b.p. 35° (0.2 mm.) to 105° (0.03 mm.). This was fractionated twice to obtain 82.8 g. (76%) of a colorless liquid, b.p. 87–99° (0.1 mm.). A middle fraction, b.p. 95–96° (0.1 mm.), n_D^{24} 1.5219, was analyzed.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 84.23; 84.55; H, 8.44, 8.62.

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The Chemistry of α,β-Unsaturated Ethers. IV. Addition of Methanol to 1-Methoxy-1,3-butadiene[1]

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Methanol adds 1,4 to 1-methoxy-1,3-butadiene in the presence of acid catalysts. The product, 1,1-dimethoxy-2-butene, also adds 1,4 to 1-methoxy-1,3-butadiene with sulfuric acid as a catalyst at 20° to 60° to yield 1,1,5-trimethoxy-2,6-octadiene. Below 20° with sulfuric acid as the catalyst or at 40° with hydrochloric acid as the catalyst no 1,1,5-trimethoxy-2,6-octadiene is formed. 1,1,5-Trimethoxy-2,6-octadiene has been converted to 1,1,5-trimethoxyoctane, 5-methoxyoctanal, 5-methoxyoctanol, 2,4,6-octatrienal, and 1-octanol.

There is a paucity of information concerning the addition of various reagents to 1-alkoxy-1,3-butadienes. Flaig[3] has reported that the bromination of 1-ethoxy-1,3-butadiene is a 1,4-addition as is the Diels-Alder reaction.[3,4] The addition of ethanol to 1-ethoxy-1,3-butadiene has been reported[5] to yield 1,1-diethoxy-2-butene, again a 1,4-addition.

The addition of an alcohol to an α,β-unsaturated ether in the presence of an acid catalyst proceeds rapidly and in nearly quantitative yield.[6] Because of this and because the addition of an alcohol to a 1-alkoxy-1,3-butadiene could yield four different products, we have investigated the addition of methanol to 1-methoxy-1,3-butadiene. The possible products are 1,1-dimethoxy-2-butene (by 1,4-addition), 1,1-dimethoxy-3-butene (by 1,2-addition), 1,3-dimethoxy-1-butene (by 3,4-addition), and 1,1,3-trimethoxybutane (by complete addition).

Two of these products were obtained with hydrochloric acid as a catalyst: 1,1-dimethoxy-2-butene (32% yield) and 1,1,3-trimethoxybutane[7] (7% yield). In contrast with these results, when sulfuric acid was used as the catalyst, no 1,1,3-trimethoxybutane was formed but 1,1-dimethoxy-2-butene was isolated in 30% yield. This product, however, also added 1,4 to the 1-methoxy-1,3-butadiene forming 1,1,5-trimethoxy-2,6-octadiene in 23% yield. Inasmuch as no other products were

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[1] Paper III, R. I. Hoaglin, D. G. Kubler, and A. E. Montagna, *J. Am. Chem. Soc.*, **80**, 5460 (1958).

[2] Furman University, Greenville, S. C.

[3] W. Flaig, *Ann.*, **568**, 1 (1950).

[4] C. G. Farmilo and R. V. V. Nicholls, *Can. J. Research* **28B**, 689 (1950).

[5] Consortium fur Electrochemische Ind. Gmbh., British Patent **757,907** (September 26, 1956).

[6] H. S. Hill, *J. Am. Chem. Soc.*, **50**, 2725 (1928).

[7] This product probably can form by the addition of methanol to 1,1-dimethoxy-2-butene. R. H. Hall and E. S. Stern [*J. Chem. Soc.*, 3388 (1954)] have shown that ethanol adds to 3,3-diethoxy-1-propene in 93% yield with hydrogen chloride catalyst.