of deuterium oxide and 1.5 mol of acetic anhydride for 2 hr. After the mixture was allowed to cool, 0.3 mol of boron triacetate, which was prepared by the method of Cook, *et al.*,[22] was added to it. The mixture was distilled to give a 104% yield of a colorless liquid, bp 114–115.8°. The nmr spectrum indicated the presence of 1.3% light acetic acid.

Hydrogenation Procedure.—To a flask which possessed a side arm containing a stopcock was added a magnetic stirring bar, 3 ml of acetic acid, and 20 mg of platinum oxide (Sargent). The flask was connected to the hydrogenation apparatus, the system was flushed with hydrogen and filled with hydrogen at atmospheric pressure, and the catalyst was prereduced by vigorous stirring. The stirring was stopped, *ca.* 1 mmol of the benzene derivative and 2 ml of acetic acid were added to the flask through the side-arm, and the stirring was resumed. Periodically, the pressure of the hydrogen was adjusted to atmospheric pressure. When the hydrogenation was completed, the solution was decanted from the catalyst, 10 ml of ethyl ether and 10 ml of water were added to the solution, and the water layer was drawn off. The ethereal layer was treated with two 10-ml portions of saturated sodium chloride solution and two 10-ml portions of saturated sodium hydrogen carbonate solution and dried ($MgSO_4$). The ether was partially removed by distillation and the residue was purified by glpc.

One deuteration of methyl benzoate was carried out in the same fashion except that 20 mg of 5% rhodium on alumina (Matheson Coleman and Bell) was used as the catalyst.

Registry No.—Acetic acid-d_1, 758-12-3.

Acknowledgment.—We thank James E. Brown for carrying out some initial experiments in this study.

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[22] H. G. Cook, J. D. Ilett, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 3125 (1950).

Notes

Dineoalkyl Ethers. A General Synthesis of the Symmetrical Ethers

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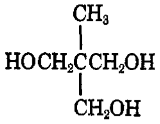
Received August 26, 1971

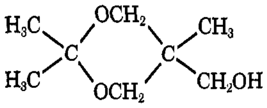
A method for the synthesis of dineoalkyl ethers has never been reported, although this type of structure should be of potential interest because of the ether functionality combined with the stability characteristics imparted by the neighboring neoalkyl groups. The di- and polypentaerythritols (obtained indirectly by the Tollens reaction of acetaldehyde with formaldehyde) are the only reported examples of this structure type excepting the parent compound itself, dineopentyl ether, which was recently prepared[1] by hydrogenolysis of neopentyl alcohol. The direct synthesis of several new members of this structure type, particularly those with tetrahydroxyl functionality as well as alicyclic β substitution, is reported.

Consideration of trimethylolethane as a starting material suggested the use of a suitable blocking group to mask two of the hydroxyl groups allowing its reaction as a monool. This was achieved by its conversion to 2,2,5-trimethyl-5-*m*-dioxanemethanol (2) in high



$\mathrm{HOCH_2\overset{CH_3}{\underset{CH_2OH}{C}}CH_2OH}$

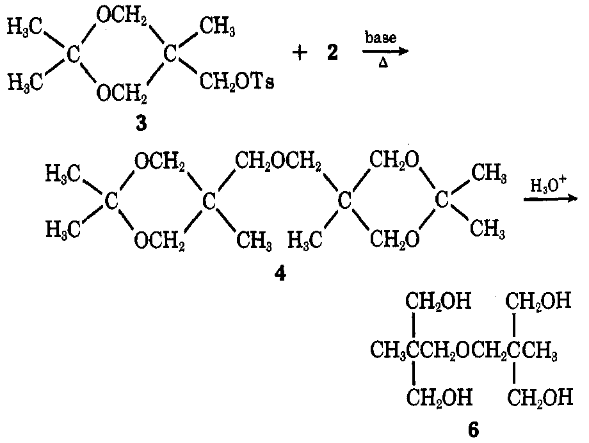
1



2

yield which should be stable to basic or neutral conditions but easily cleaved by acid to regenerate the methylol groups.

Alkaline condensation of tosylate (3) with 2 gave the desired 5,5′-(oxydimethylene)bis(2,2,5-trimethyl-*m*-dioxane) (4) in conversions ranging up to 64% depending upon solvent, base, and reaction time. Although a precipitate of tosylate salt can usually be detected early as an opalescence, the formation of this dineoalkyl ether (4) requires a minimum of 48 hr to obtain good yields of product. The mesylate **5** was also prepared and used in the alkaline condensation but offered no advantages over the tosylate. Mild acid hydrolysis of 4 gave the desired 2,2′-(oxydimethylene)bis(2-methyl-1,3-propanediol) (6) quantitatively (eq 1). Mass



$$\mathrm{CH_3\overset{CH_2OH}{\underset{CH_2OH}{C}}CH_2OCH_2\overset{CH_2OH}{\underset{CH_2OH}{C}}CH_3} \quad (1)$$

spectrographic examination of 4 showed no molecular ion species but a major peak at 287 corresponding to initial loss of a methyl group. The failure to observe a molecular ion is apparently characteristic of a 2-methyl-1,3-dioxanyl-type structure. This was confirmed by the synthesis[2] of 2,2,5,5-tetramethyl-1,3-dioxane (7). The mass spectrum of this structurally related compound showed no molecular ion but a major peak at 129 from loss of a methyl group.

Although the above analytical data on both the intermediate (4) and product (6) dineoalkyl ethers were not

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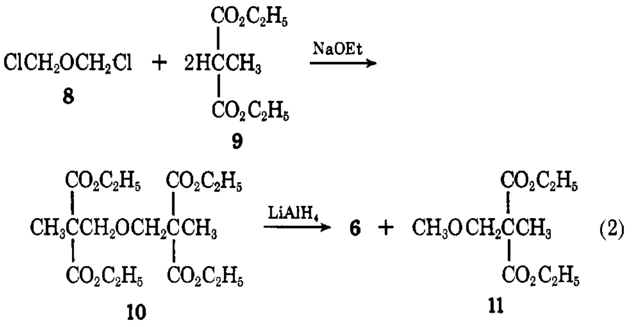
[1] H. Pines and P. Steingaszner, *J. Catal.*, **10**, 60 (1968).

[2] C. S. Rondestvedt, Jr., *J. Org. Chem.*, **26**, 2247 (1961).

ambiguous, the known facile rearrangement of neoalkyl groups required an unequivocal synthesis of **6** to establish directly its dineoalkyl ether structure. This was achieved by buildup of both neoalkyl groups around a preformed ether linkage as shown in eq 2.



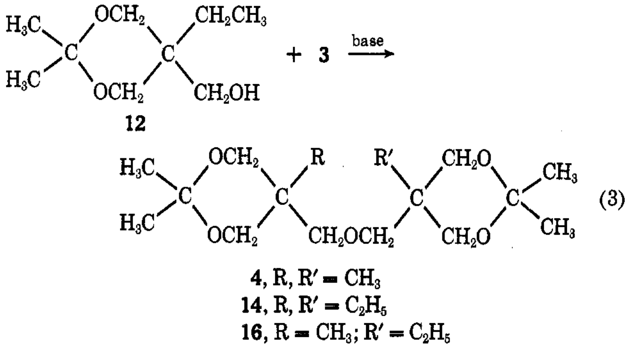
$$ClCH_2OCH_2Cl + 2HC(CO_2C_2H_5)_2CH_3 \xrightarrow{NaOEt} CH_3C(CO_2C_2H_5)_2CH_2OCH_2C(CO_2C_2H_5)_2CH_3 \xrightarrow{LiAlH_4} 6 + CH_3OCH_2C(CO_2C_2H_5)_2CH_3 \quad (2)$$

8, **9**, **10**, **11**

The by-product formation of **11** was traced to the presence of chloromethyl methyl ether in the bischloromethyl ether **8** prepared by modification of a published method.[3] Multiple fractionations of the labile ether **8** failed to remove the impurity as monitored by glc. Purification of **10** was achieved at the ester stage followed by a difficult hydride reduction to yield the dineoalkyl ether **6**. This product was identical in all respects with the dineoalkyl ether prepared by the tosylate displacement. Confirmation of this structure indicates that nucleophilic substitution of a neopentyl tosylate (or mesylate) can occur without rearrangement *even* if the attacking nucleophile is, itself, a neoalkyl structure. The absence of rearrangement products in the displacement reaction also indicates that high yields of the dineoalkyl ethers are possible in spite of the low reaction rates.

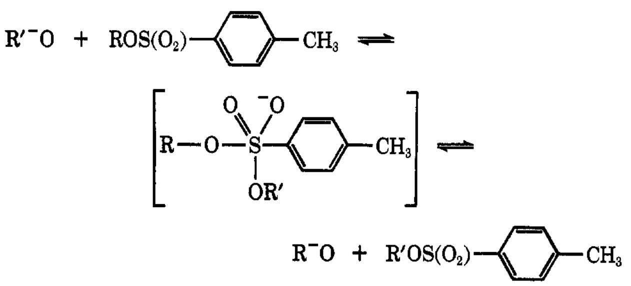
The success of the tosylate displacement reaction in the synthesis of pure dineoalkyl ethers without the formation of rearrangement products stimulated the synthesis of additional dineoalkyl ethers by the tosylate displacement reaction. Trimethylolpropane was converted to 2,2-dimethyl-5-ethyl-5-*m*-dioxanemethanol (**12**). Condensation of **12** with the tosylate **13** gave 5,5′-(oxydimethylene)bis(2,2-dimethyl-5-ethyl-*m*-dioxane) (**14**). Mild acid hydrolysis yielded the desired 2,2′-(oxydimethylene)bis(2-ethyl-1,3-propanediol) (**15**). These displacement reactions were monitored by gas chromatography and the evident lower rate of reaction of **12** with **13** must be due solely to the greater effective size of the ethyl group over the methyl group, this effect being magnified in this system of neoalkyl groups.

An unexpected result was found in the synthesis of 5-ethyl-5′-methyl-5,5′-(oxydimethylene)bis(2,2-dimethyl-*m*-dioxane) (**16**) from base condensation of the tosylate **3** with the monool **12**. In addition to the expected ether (**16**), there were also obtained significant amounts of ethers **4** and **14** (eq 3). The reaction was monitored by gas chromatography proving the formation of **4** and **14** by comparison of retention times with those of authentic samples. The elution order of **4**, **16**, and **14** was consistent with molecular weight, hence boiling point, and **16** was also in greatest amount. Further confirmation of **16** was obtained by preparative gas chromatography to obtain an analytical sample



and its hydrolysis to the crystalline 2-ethyl-2′-methyl-2,2′-(oxydimethylene)di-1,3-propanediol (**17**). The rapid scan mass spectrographic analysis of the mixture **4**, **14**, and **16** showed major peaks at 287, 301, and 315 (no parent ions) corresponding to loss of a methyl group from the respective structures.

The formation of **4** and **14** must result from a significant equilibration of the tosylate and alkoxide ions where R and R′ are neoalkyl groups. Sulfur–oxygen



bond cleavage brought about by nucleophilic attack has been reported[4-6] in aryl sulfonates and sulfur attack by an aromatic Grignard reagent on an alkyl sulfonate ester was reported[7] to yield a sulfone. This appears to be a case of alkoxide attack with elimination of another alkoxide ion. An alternate explanation for the formation of **4** and **14** involving nucleophilic displacement of alkoxide ion on the ether resulting in an equilibration mixture was ruled out by experimental evidence. Table I below describes the several intermediates and products obtained during this investigation.

Other possible routes to these dineoalkyl ethers (**6**, **15**, and **17**) were investigated with little success. The Tollens condensation of propionaldehyde with formaldehyde failed to yield any of the tetrol **6**, although analysis of the acetylated product confirmed the presence of trimethylolethane triacetate. These data would appear to preclude bis(hydroxymethyl) ether as a mechanistic pathway to explain ether formation[8] in the Tollens reaction.

Other attempts to affect etherification of these neoalkyl systems using acid–base reactions as well as dehydrating conditions on the monool **2** failed to produce more than a trace, if any, of the desired dineoalkyl ether. Hydrogenolysis of dipentaerythritol ether (a 1,3-glycol) over copper chromite catalyst yielded a

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(3) F. S. H. Head, *J. Chem. Soc.*, 2972 (1963).

(4) C. A. Bunton and Y. F. Frei, *ibid.*, 1872 (1951).

(5) C. A. Bunton and V. A. Welch, *ibid.*, 3240 (1956).

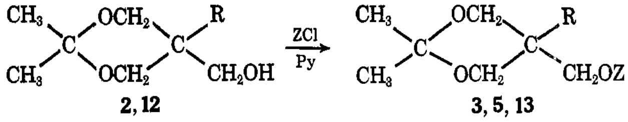
(6) J. F. Bunnett and J. Y. Bassett, Jr., Abstracts of the 131st National Meeting of the American Chemical Society, Miami, Fla., April 1957, p 28, 29–0.

(7) J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

(8) E. Berlow, R. H. Barth, and J. E. Snow, "The Pentaerythritols," Reinhold, New York, N. Y., 1958, pp 5, 6.

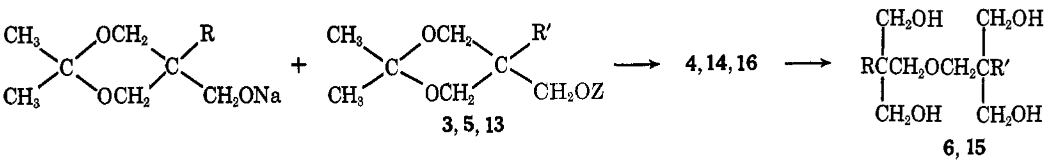
TABLE I

INTERMEDIATES



Compd	R	Z	Formula	% yield	Bp (mm), (mp), °C	$n^{25}D$	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
2	CH_3		$C_8H_{16}O_3$	94	58–63 (0.15)	1.4517	59.97	10.07		59.68	9.98	
3	CH_3	Tosyl	$C_{15}H_{22}SO_5$	95	(67–69)		57.30	7.05	10.20	57.49	7.08	10.18
5	CH_3	Mesyl	$C_9H_{18}SO_5$	86	125 (0.2)	1.4578	45.36	7.61	13.46	45.33	7.79	13.32
12	C_2H_5		$C_9H_{18}O_3$		80–90 (0.2)	1.4561	62.04	10.41		62.11	10.96	
13	C_2H_5	Tosyl	$C_{16}H_{24}O_6S$	93	(68–71)		58.51	7.37	9.76	58.42	7.18	9.72

FINAL PRODUCTS

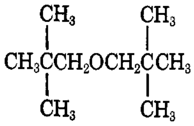


Compd	R	R′	Formula	% yield	Bp (mm), (mp), °C	$n^{25}D$	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Ir, cm⁻¹
4	CH_3	CH_3	$C_{16}H_{30}O_5$	64	97–102 (0.15), (47–50)	1.4500	63.54	10.00	63.70	9.92	. . .
6	CH_3	CH_3	$C_{10}H_{22}O_5$	96	(127–130)		54.03	9.98	53.99	9.92	3350–3250 (OH) 1120 (ether) 1018 (–CH_2OH)
14	C_2H_5	C_2H_5	$C_{18}H_{34}O_5$	55	110–116 (0.2), (34–38)	1.4544	65.42	10.37	65.26	10.31	
15	C_2H_5	C_2H_5	$C_{12}H_{26}O_5$	>90	(102–105)		57.57	10.47	57.37	10.45	3300 (OH) 1125 (ether) 1070–1020 (CH_2OH)
16	CH_3	C_2H_5	$C_{17}H_{32}O_5$	*a*	102–115 (0.15)	1.4513	64.52	10.19	64.52	10.32	

[a] No yield estimate possible because of presence of **4** and **14** in product.

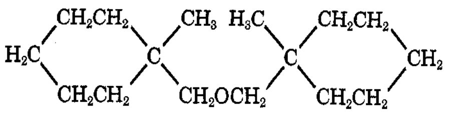
trace of **6**, determined by gas chromatography of the acetylated product, while reaction of trimethylolethane with thionyl chloride gave a stable, crystalline trisulfite **18**. The tosylate (or mesylate) displacement reaction discussed in this paper is, therefore, the only available general method for synthesis of dineoalkyl ethers. Although long reaction times are required to obtain good yields, rearrangement of the neoalkyl groups is not a problem and the bis(dioxanyl) ethers are useful intermediates since the acetonide blocking groups can be removed *in situ* for subsequent esterification or other reactions. The esters identified in Table II were prepared in this manner and showed significantly improved low temperature properties over the analogous esters of dipentaerythritol.

Dineopentyl ether (**25**)[9] and bis(1-methylcyclohexylmethyl) ether (**26**) were prepared similarly by reaction of the appropriate tosylate with alkoxide ion, usually in refluxing toluene. Formation of **25** occurred at the slowest rate relative to that of all of the ethers reported in this paper. Since the steric effect of ethyl *vs.* methyl at the carbon atom β to the oxygen changed the rate of etherification as noted above, it must be concluded that the cyclopentamethylene and cyclo-2,4-dioxapentamethylene groups offer less hindrance to nucleophilic attack on the tosylate group than do two methyl groups similarly situated.



$$CH_3C(CH_3)_2CH_2OCH_2C(CH_3)_2CH_3$$

25



26

This chemistry represents a generally useful method for the synthesis of dineoalkyl ethers and the reaction rates, although slow for the parent compounds, can be increased by selective substitution in the alcohol moiety and probably by electron-withdrawing groups on the aromatic moiety of the sulfonyl group. Neopentyl group rearrangements were not observed in this system and, although there is evidence of significant equilibration of alkoxide with tosylate, this reaction has an effect on final product composition only when the neoalkyl groups are different. The nucleophilic attack of a nonneoalkoxide ion on a neoalkyl tosylate system (or *vice versa*) would be expected to result in a major yield of a noneoalkyl ether and the dineoalkyl ether.

Experimental Section

All proton nmr spectra were measured with a Varian A-60 instrument using TMS reference. The mass spectrographic data were obtained at 68 eV with a CEC 21-130 mass spectrometer modified for rapid scanning. All melting points were uncorrected and all temperatures are centigrade unless otherwise noted. All vapor phase chromatographic analysis were performed isothermally on an F & M Model 500 instrument with a chart speed of 0.5 in./min. Elemental analysis and other analytical data reported in Tables I and II are not repeated in

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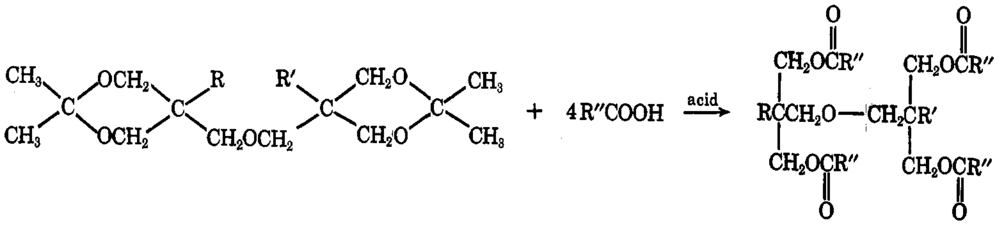
[9] The first reported synthesis of dineopentyl ether itself appeared during this work and we are indebted to Professor Pines who supplied us with a sample of the ether. The two preparations were found to have identical structures.

TABLE II

TETRAESTERS OF DINEOALKYL ETHERS



19-24

Compd	R	R′	R″	Empirical formula	Bp,[a] °F (760 mm)	Density (°F[a])	Theory, % C	Theory, % H	Found, % C	Found, % H
19	CH_3	CH_3	CH_3	$C_{18}H_{30}O_9$	663	1.1122 (77)	55.37	7.75	54.96	7.27
20	CH_3	CH_3	C_3H_7	$C_{26}H_{46}O_9$	745	1.0285 (77)	62.12	9.23	62.06	9.56
21	CH_3	CH_3	C_4H_9	$C_{30}H_{54}O_9$	716	1.0127 (68)	64.48	9.74	64.77	9.58
22	C_2H_5	C_2H_5	CH_3	$C_{20}H_{34}O_9$	701	1.0845 (100)	57.40	8.19	57.18	8.26
23	C_2H_5	C_2H_5	C_3H_7	$C_{28}H_{50}O_9$	738	1.0145 (100)	63.37	9.50	63.30	9.46
24	C_2H_5	C_2H_5	C_4H_9	$C_{32}H_{58}O_9$	802	1.0069 (68)	65.50	9.96	65.48	9.78

[a] Obtained from isoteniscope determinations of thermal stability.

this section. The Monsanto Physical Science Center cooperated in providing a part of this analytical data.

Tetraethyl(oxydimethylene)bis(methylmalonate) (10).—To a solution of sodium ethoxide, prepared under dry nitrogen from 52.4 g (2.28 g-atoms) of sodium and 900 ml of absolute ethanol, was added 394.6 g (2.27 mol) of diethyl methylmalonate and the stirred solution was refluxed for 1 hr. The bis(chloromethyl) ether (131.1 g, 1.14 mol) in 50 ml of ethanol was added dropwise to the sodiomalonate solution maintained at 40–45°, and the mixture was refluxed for 3 hr. Normal work-up and fractionation afforded 67.4 g (18.3% yield) of diethyl methoxymethylmethylmalonate (**11**), bp 85–95° (0.1 mm), $n^{25}D$ 1.4238, and 167 g (50.6% yield) of desired ester (**10**) as a colorless oil, bp 145–158° (0.1 mm), $n^{25}D$ 1.4338 (yields based on consumed malonate).

Anal. Calcd for $C_{10}H_{18}O_5$ (**11**): C, 55.03; H, 8.31. Found: C, 54.84; H, 8.30.

Anal. Calcd for $C_{18}H_{30}O_9$ (**10**): C, 55.37; H, 7.75. Found: C, 55.29; H, 7.62.

2,2′-(Oxydimethylene)bis(2-methyl-1,3-propanediol) (6).—Lithium aluminum hydride (100 g) was added to 1900 ml of cooled (0°) dry ether. A solution of 167 g (0.428 mol) of the tetraester **10** in 1 l. of dry ether was added with stirring over a 4-hr period. The mixture was refluxed for 4 hr, ethyl acetate (116 g, 1.32 mol) was added dropwise, and then a 10% excess was added. After hydrolysis of the complex at 15° with water and filtration, the ether was distilled leaving 47.2 g of the crude tetrol **6**. A sample was recrystallized from water as shiny, colorless crystals, mp 128–130°.

Anal. Calcd for $C_{10}H_{22}O_5$: C, 54.03; H, 9.98. Found: C, 53.67; H, 10.10.

2,2,5-Trimethyl-5-*m*-dioxanemethanol (2).—A mixture consisting of 30 g (0.25 mol) of 1,1,1-trimethylolethane, 36.7 ml (0.5 mol) of acetone, 0.5 g of *p*-toluenesulfonic acid, and 160 ml of benzene was stirred and refluxed until 5.25 ml of water had separated (10.5 hr) in a Dean-Stark trap. The solution was distilled to obtain 37.5 g (93.6%) of colorless liquid: bp 58–63° (0.15–0.2 mm); $n^{25}D$ 1.4517; ir (neat) 3410 cm^{-1} (OH); nmr (neat) δ 3.65 (s, CH_2OH), 3.5 (s, CH_2OH), 3.5 (m, CH_2), 1.37 (s, 2-CH_3), 1.3 (s, 2-CH_3), and 0.77 ppm (s, 5-CH_3). Rapid elimination of the hydroxyl proton resonance when shaken with deuterium oxide indicated only a weak or negligible intramolecular hydrogen bonding.

2,2,5-Trimethyl-5-*m*-dioxanemethanol Tosylate (3).—A solution of 19 g (0.1 mol) of *p*-toluenesulfonyl chloride in 25 ml of pyridine was added to a solution of 16 g (0.1 mol) of **2** in 50 ml of pyridine. A slight exothermic reaction was noted and subsequent precipitation of a crystalline solid. The mixture was heated on a steam bath for 30 min, then poured into ice water, and filtered yielding 30 g (95.4%) of the tosylate as nearly colorless crystals. A sample, recrystallized from aqueous methanol, gave pure white crystals, mp 67.5–69°.

The 2,2,5-trimethyl-5-*m*-dioxanemethanol mesylate (**5**), 2,2-dimethyl-5-ethyl-5-*m*-dioxanemethanol (**12**), and tosylate **13** of the latter compound reported in Table I were similarly prepared.

5,5′-(Oxydimethylene)bis(2,2,2-trimethyl-*m*-dioxane) (4).—To a dry solution of 44.9 g (0.280 mol) of **2** in 200 ml of toluene was added 5.9 g (0.255 g-atom) of sodium. The stirred system was slowly heated to reflux over a 1-hr period and finally refluxed for 3 hr to obtain a homogeneous solution of alkoxide. A dry solution of 80.2 g (0.255 mol) of the tosylate **3** in 110 ml of toluene was added to the above alkoxide solution at 35° and the stirred mixture was brought to reflux in 35 min. The solution was clear at reflux. An initial opalescence followed in 4 min. The reaction progress was monitored by periodic withdrawal of 1-ml samples. After washing three times with 3 ml of water, a 1-μl sample was analyzed by gas chromatography using a 6-ft 12% silicone grease on 45/50 Chromosorb P column operated at 200° and 85-ml/min helium flow. The progressive increase in product **4** was observed at 5-min elution time. After 64 hr, the cooled mixture was poured into water and the isolated organic layer was washed to neutrality. Fractionation gave 49.2 g (63.8%) of product as a colorless oil: bp 97–102° (0.15 mm); $n^{25}D$ 1.4500; nmr (neat) δ 3.78 (d, 4, ring CH_2), 3.51 (d, 4, ring CH_2), 3.43 (s, 4, ether CH_2), 1.41 (s, 12, CH_3), and 0.90 ppm (s, 6, CH_3). The product ether, which can be crystallized to a solid (mp 47–50°), has a thermal stability (T_D) of 520°F (isoteniscope measurement) and a kinematic viscosity of 28.4 cSt at 100°F and 3.39 cSt at 210°F. The use of the mesylate **5** rather than the tosylate appeared to offer no advantage in this reaction.

Hydrolysis of 4 to 2,2′-(Oxydimethylene)bis(2-methyl-1,3-propanediol) (6).—A 2-g sample of the acetonide ether **4** was dissolved in 20 ml of 50% ethanol, 10 drops of concentrated HCl was added, and the solution was brought to reflux for 5 min. The solution was evaporated leaving 1.429 g (96% yield) of colorless crystalline product **6**. The analytical sample was recrystallized from hot water as shiny crystals, mp 127–130°, and caused no melting point depression upon admixture with the tetrol obtained by the hydride reduction. Ir analysis showed a broad OH absorption at 3350–3250, ether absorption at 1120, and a primary COH absorption at 1018 cm^{-1}.

5,5′-Diethyl-5,5′-(oxydimethylene)bis(2,2-dimethyl-*m*-dioxane) (14).—This ether was prepared in the same manner as the homologous ether above. The steric effect of the ethyl group was noted in the longer reaction time required for alkoxide preparation (about twice that of the methyl compound) and in the subsequent slower condensation with the tosylate. After 70 hr, a 55% yield of the ether **14** was obtained, bp 110–116° (0.2 mm), as a colorless oil which later was crystallized. The product has a thermal stability (T_D) of 516°F, and a kinematic viscosity of 38.1 cSt at 100°F and 3.76 at 210°F.

2,2′-(Oxydimethylene)bis(2-ethyl-1,3-propanediol) (15).—This product was obtained by acid hydrolysis of the above ether (**14**) as colorless crystals from water, mp 102–105°. Ir analysis showed absorptions at 3300 (hydroxyl), 1125 (ether), and a band at 1070–1020 cm^{-1} characteristic of primary alcohol.

5-Ethyl-5′-methyl-5,5′-(oxydimethylene)bis(2,2-dimethyl)-*m*-dioxane) (16).—A stirred solution of 17 g (0.1 mol) of **12** in 75 ml of dry toluene was refluxed with 1.6 g (0.07 g-atom) of sodium until it was completely reacted. Then 22 g (0.07 mol) of dry **3** was added. After 1-hr reflux, a precipitate (sodium tosylate) was apparent. After 80-hr reflux there was no further change in the glc spectrum as monitored by a 6-ft 30% silicone grease on 45/55 Chromosorb P column at 200° and 85-ml/min helium flow. This spectrum showed the two symmetrical ethers **4** and **14** at 6.4- and 12-min retention times, respectively, and the major unsymmetrical product **16** at 8.8-min retention. The product was twice fractionated to obtain the colorless oil, bp 102–115° (0.15 mm). Acid hydrolysis of **16** gave the crystalline 2-ethyl-2′-methyl-2,2′-(oxydimethylene)di-1,3-propanediol (**17**) which was converted to the tetrabutyrate **27** by butyric anhydride. The tetrabutyrate showed a retention time of 15.5 min on the 6-ft silicone grease column at 275°, 85-ml/min flow.

Reaction of Trimethylolethane with Thionyl Chloride.—To a stirred mixture of 24 g (0.2 mol) of trimethylolethane in 150 ml benzene at 50° was added dropwise 29 ml (0.4 mol) of thionyl chloride. The homogeneous solution was refluxed 2 hr, then the solvent was removed, and the residue was poured into ice water, yielding 15 g of water-insoluble product. Recrystallization from aqueous isopropyl alcohol yielded shiny crystals of the trisulfite **18**, mp 101–103°.

Anal. Calcd for $C_{10}H_{10}O_9S_3$: C, 31.74; H, 4.79; S, 25.42. Found: C, 31.30; H, 4.75; S, 25.04.

Dineopentyl Ether 25.—A stirred mixture of 22 g (0.25 mol) of neopentyl alcohol and 5.8 g (0.25 g-atom) of sodium in 150 ml of toluene was refluxed until homogeneous; then a solution of 55.3 g (0.23 mol) of neopentyl tosylate in 70 ml of toluene was added. After a reflux period of 1 week, 84% of the tosylate had reacted as determined by glc analysis on the 6-ft silicone grease column which showed the formation of dineopentyl ether (3.7-min retention, 75°, 85-ml/min flow) and disappearance of the tosylate (4.5-min retention time, 200°, 85-ml/min flow). The pure dineopentyl ether was obtained by preparative gas chromatography as a colorless liquid: $n^{25}{}_{D}$ 1.3931; nmr (toluene) δ 0.94 (s, 9, CH_3) and 2.94 ppm (s, 2, CH_2); mass spectrum (70 eV) *m/e* (ion) 158 (molecular ion), 101 (neopentyloxymethyl), 71 (neopentyl ion).

Anal. Calcd for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 76.26; H, 13.77.

Bis(1-methylcyclohexylmethyl) Ether (26).—This dineoalkyl ether was obtained similarly as a colorless oil: bp 81° (0.25 mm); $n^{25}{}_{D}$ 1.4690; T_D 552°F; d^{0}°F 0.9381; viscosity, cSt (°F), 5114, (−40), 283 (0), 10.65 (100), 2.49 (210).

Anal. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68. Found: C, 80.50; H, 12.34.

Registry No.—**2**, 3663-46-5; **3**, 34541-77-0; **4**, 34578-24-0; **5**, 21139-47-9; **6**, 34541-79-2; **10**, 5898-79-3; **11**, 21398-92-5; **12**, 20761-68-6; **13**, 34541-83-8; **14**, 34541-84-9; **15**, 23235-61-2; **16**, 34541-86-1; **18**, 11098-52-5; **19**, 34541-87-2; **20**, 34541-88-3; **21**, 34541-89-4; **22**, 34578-25-1; **23**, 34541-90-7; **24**, 34541-91-8; **25**, 28509-24-2; **26**, 34541-92-9.

Preparation of Some Methylenecycloalkenes *via* a Novel 1,4 Hofmann Elimination Reaction[1]

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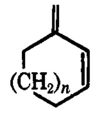
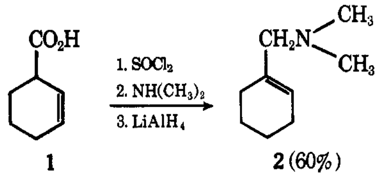
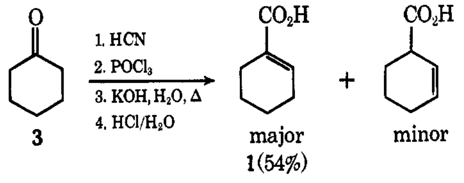
In the course of photochemical studies of conjugated dienes in this laboratory, the preparation of significant quantities of several s-trans dienes of general structure A was required. Historically, two routes that have been used are acetate pyrolysis[2] and the Wittig reaction,[3] but in our hands these reactions have given variable results (both in quantity and quality); hence it was deemed desirable to explore another method.



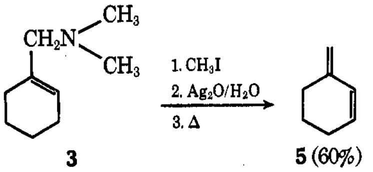
A

Since one of the better methods for the preparation of olefinic compounds is the Hofmann elimination, attention was turned to the availability of suitable amines. One possibility that immediately came to mind was a novel 1,4 Hofmann elimination sequence using a β,γ-unsaturated amine such as *N*,*N*-dimethyl-*N*-cyclohexenylmethylamine (**2**), which in turn is readily available from cyclohexene-1-carboxylic acid (**1**) *via* the sequence outlined below. Acid **1**, in turn, is readily prepared from the corresponding ketone, cyclohexanone (**3**), by cyanohydrin formation, followed by dehydration and hydrolysis. Some double-bond migration was observed, but, as both isomers should give the same product when converted to their respective amines and subjected to the Hofmann degradation sequence, the presence of minor amounts of the Δ² isomer did not present a synthetic problem.





Reaction of **2** with iodomethane in hexane solution gave the quaternary ammonium salt, which was treated with freshly precipitated, alkaline-free silver oxide to give the quaternary ammonium hydroxide, which on pyrolysis yielded methylenecyclohexene (**5**). Methylenecycloheptene (**6**), methylenecyclooctene (**7**), and 3,5-dimethylmethylenecyclohexene (**8**) were also prepared by this method. Their yields[4] (from the respec-



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[1] Abstracted in part from the Ph.D. Dissertation of M. R. S., The University of Texas at Austin, Austin, Texas, 1971.

[2] C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960); W. G. Dauben, C. D. Poulter, and C. Suter, *J. Amer. Chem. Soc.*, **92**, 7048 (1970).

[3] W. G. Dauben and J. S. Ritscher, *ibid.*, **92**, 2925 (1970).

[4] Analysis of the dienes for isomeric purity was accomplished using a Perkin-Elmer Model F-11 capillary chromatograph with a 50 ft × 0.01 in. column packed with *m*-bis(*m*-phenoxy)benzene plus Apiezon L (8:2). Purity in all cases was >95%.