termination of the reaction. Upon cooling in a salt–ice bath, dark orange crystals of product IIa precipitated, m.p. 199–201°, yield, 0.3 g. Calculated for a 2:1 adduct $C_{18}H_{18}N_4O_6$: mol. wt., 386. Found (Rast method): mol. wt., 420.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.89; H, 4.67; N, 14.51. Found: C, 55.80; H, 4.46; N, 15.02.

The filtrate was concentrated further at 0°, and the formed precipitate isolated. This product, Ia, was also orange, m.p. 119–120°, yield, 0.3 g. It was identified as the normal 1,4-adduct by its infrared spectrum.[2]

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98; N, 11.96. Found: C, 61.34; H, 6.09; N, 12.00.

Product Ia, 0.19 g. (0.8 mmole), was mixed with *p*-nitronitrosobenzene, 0.75 g. (5 mmole). An infrared spectrum in potassium bromide was taken from some of this mixture. The rest was dissolved in nitromethane at 0°, and allowed to stand for 24 hr. The solvent was then evaporated, and an infrared spectrum in potassium bromide was made of the residue. The two spectra were identical.

Product IIa, 0.39-g. (1 mmole), was suspended in 20 ml. of ice-cold chloroform, to which was added phosphorus trichloride, 2 ml. The suspension was allowed to reach room temperature and left overnight. The liquids were then removed under reduced pressure until a solid remained, which was the recrystallized from ethanol. The yield of 4,5-dimethyl-1,2-bis(*p*-nitrophenyl)-1,2,3,6-tetrahydropyradizine was 0.26 g. (74%), yellow crystals, m.p. 271–273° (lit.,[8] m.p. 272–272.5°).

Adducts of *m*-Nitronitrosobenzene.—*m*-Nitronitrosobenzene, 0.30 g. (1.9 mmoles), reacted with 2,3-dimethyl-1,3-butadiene, 0.22 g. (2.7 mmoles), in 35 ml. of dichloromethane at 0°. The solvent was evaporated, and a yellow solid was isolated. This solid was dissolved in anhydrous ether, and filtered through a column a column (12 × 10 cm.) packed with alumina. The first fraction yielded bright yellow crystals, m.p. 94–99°, yield, 0.26 g. It was identified as the normal 1,4-adduct (product Ib) by its infrared spectrum.[2]

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.54; H, 5.98; N, 11.96. Found: C, 61.34; H, 5.93; N, 11.91.

The second fraction yielded 25 mg. of bright yellow crystals, product IIb, m.p. 161.5–163°.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.98; H, 4.67; N, 14.51. Found: C, 55.01; H, 4.37; N, 14.02.

Displacement Reactions of Neopentyl-type Sulfonate Esters[1]

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Received September 24, 1962

During the course of an investigation involving synthesis of derivatives of pentaerythritol, we observed that *O*-benzylidenepentaerythritol dibenzenesulfonate reacted with sodium iodide in acetone to form *O*-benzylidene-*O*-benzenesulfonylpentaerythritol iodide in high (89%) yield. A previous investigation[3] demonstrated that *O*-isopropylidenepentaerythritol di-*p*-toluenesulfonate reacted with potassium thiolacetate to give the product of monosubstitution in good yield. The high degree of selectivity at one of the two functional groups prompted a study directed towards a better understanding of this type of reaction.

A series of sulfonate esters of *O*-benzylidene- and *O*-isopropylidenepentaerythritol was prepared (Table I), and their reactivities with sodium iodide in acetone determined by varying reaction time and temperature (Table II). Although the monosubstitution product could be isolated in high yield from *O*-benzylidenepentaerythritol dibenzenesulfonate, this intermediate could then be converted into *O*-benzylidenepentaerythritol diiodide in high (85%) yield by a second reaction for a longer period of time and at a higher temperature. As expected, *O*-benzylidenepentaerythritol di-*p*-bromobenzenesulfonate reacted to allow isolation of essentially the same high yields of mono- and di-substitution products under somewhat milder conditions. In the experiment in which the monodisplacement compound was isolated as the principal product, a small amount (5%) of the diiodide was also separated. The di-*p*-toluenesulfonate was found to yield less of the monosubstitution product under conditions comparable to that applied with the dibenzenesulfonate. *O*-Isopropylidenepentaerythritol dibenzenesulfonate and di-*p*-toluenesulfonate were found to yield products of mono- and di-substitution under milder conditions than required for the corresponding *O*-benzylidene compounds.

A variety of displacement reactions has also been studied using cyanide ion as the nucleophilic reagent. Because of complications attending this type of reaction, several acyclic substrates were included in the study (Table III). 2,2-Dimethyl-1-propanol benzenesulfonate was found to react with sodium cyanide in a *N*,*N*-dimethylformamide (DMF) solution to give 3,3-dimethylbutyronitrile in a yield of 56%, and 1,3-propanediol dibenzenesulfonate gave glutaronitrile in a yield of 81%, accompanied by varying amounts of polymeric materials depending upon the reaction conditions employed. Nelson, Maienthal, Lane, and Benderly[4] reported that no products were isolable from the reactions of di-*p*-toluenesulfonates of 1,3-propanediol and 2-methyl-1,3-propanediol with potassium cyanide in ethylene glycol. 2,2-Dimethyl-1,3-propanediol dibenzenesulfonate reacted with sodium cyanide in a dimethylformamide solution to give 3,3-dimethylglutaronitrile, isolated in a yield of 28%, and 2,2-dimethylcyclopropanecarboxylic acid, separated from the reaction mixture following base-catalyzed hydrolysis in a yield of 28%. Its precursor, 2,2-dimethylcyclopropanecarbonitrile, was undoubtedly formed in a somewhat larger amount, but undoubtedly less than the 63% previously reported[4] from the reaction of 2,2-dimethyl-1,3-propanediol di-*p*-toluenesulfonate and potassium cyanide in ethylene glycol.

Displacement reactions of *O*-benzylidenepentaerythritol derivatives with sodium cyanide gave a single crystalline compound in all instances. The structure of this compound was assigned to be *O*-benzylidene-2,2-bis(hydroxymethyl)cyclopropanecarbonitrile (I) on the basis of a variety of observations. Alkaline hydrolysis gave a crystalline compound, with analysis agreeing with *O*-benzylidene-2,2-bis(hydroxymethyl)-cyclopropanecarboxamide (II). Acid hydrolysis with hydrochloric acid gave a liquid in low yield, presumed to be 2-chloromethyl-2-hydroxymethylcyclopropanecarboxylic acid lactone (III) on the basis of elemental analysis and of the nuclear magnetic resonance spec-

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[1] Abstracted from portions of the Ph.D. theses of Donald L. Schmidt and Samuel M. Dorrence and of the M.S. thesis of Vincent D. Calbi.

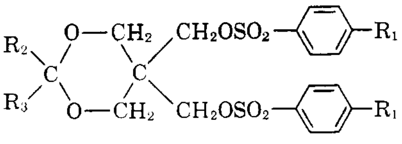
[2] An Air Force Officer on an Air Force Scholarship.

[3] P. Bladon and L. N. Owen, *J. Chem. Soc.*, 585 (1950).

[4] E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *J. Am. Chem. Soc.*, **79**, 3467 (1957).

TABLE I

SULFONATE ESTERS

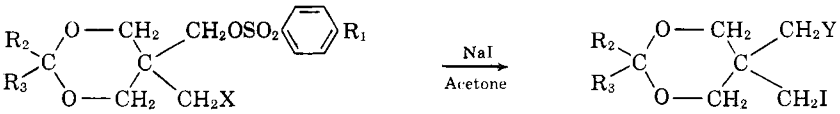


Compound			M.p.,	Yield,[a]		Calcd., %		Found, %	
R₁	R₂	R₃	°C.	%	Formula	C	H	C	H
H	C_6H_5	H	150.8–151.1	79	$C_{24}H_{24}O_8S_2$	57.13	4.79	57.38	5.13
CH_3	C_6H_5	H	176.8–177.1	66	$C_{26}H_{28}O_8S_2$	58.63	5.30	58.11	5.43
Br	C_6H_5	H	209.5–210.0[b]	84	$C_{24}H_{22}Br_2O_8S_2$	43.52	3.35	43.34	3.42
H	CH	CH_3	116.8–117.0	67	$C_{20}H_{24}O_8S_2$	52.62	5.30	52.29	5.30

[a] Yields based upon materials with melting points within 2–3° or less of the analytical samples. [b] Benzene used as recrystallization solvent.

TABLE II

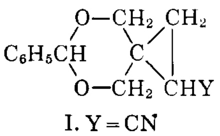
DISPLACEMENT REACTIONS OF SULFONATES WITH SODIUM IODIDE



Substrate				Reaction time, hr.	Reaction temp., °C.	Product	Yield,[a]	M.p.,		Calcd., %		Found, %	
R₁	R₂	R₃	X			Y	%	°C.	Formula	C	H	C	H
H	C_6H_5	H	$OSO_2C_6H_5$	2	100	$OSO_2C_6H_5$	89	136.5	$C_{18}H_{19}IO_5S$	45.58	4.04	45.93	4.07
H	C_6H_5	H	I	3	130	I	85	66.3	$C_{12}H_{14}I_2O_2$	32.46	3.18	32.52	3.25
Br	C_6H_5	H	$OSO_2C_6H_4Br(p)$	1.5	100	$OSO_2C_6H_4Br(p)$	84	136.5–136.7	$C_{18}H_{18}BrIO_5S$	39.08	3.28	39.07	3.28
						I	5						
Br	C_6H_5	H	$OSO_2C_6H_4Br(p)$	2.5	100	I	80						
CH_3	C_6H_5	H	$OSO_2C_6H_4CH_3(p)$	2.5	100	$OSO_2C_6H_4CH_3(p)$	65	118.5–118.7	$C_{19}H_{21}IO_5S$	46.73	4.33	46.55	4.50
CH_3	CH_3	CH_3	$OSO_2C_6H_4CH_3(p)$	2.25	85	$OSO_2C_6H_4CH_3(p)$	78	89.6–90.0	$C_{15}H_{21}IO_5S$	40.92	4.81	41.11	4.93
H	CH_3	CH_3	$OSO_2C_6H_5$	1.5	100	I	84	48.5–48.7	$C_8H_{14}I_2O_2$	24.26	3.56	24.46	3.74
CH_3	CH_3	CH_3	$OSO_2C_6H_4CH_3(p)$	2.5	100	I	80						

[a] Yields based upon materials with melting points within 2° or less of the analytical samples.

trum. Cleavage of the benzylidene acetal group, hydrolysis of the nitrile function, lactonization, and solvolysis of the remaining primary alcohol function would account for this substance. The depressed yield of compound III was expected since hydrochloric acid is known[5] to effect ring opening of compounds containing cyclopropane rings with an attached hydroxymethyl group. Hydrogenation of I gave a sirupy amine, which formed a crystalline acetate, with analysis agreeing with *N*-acetyl-*O*-benzylidene-2,2-bis(hydroxymethyl)cyclopropanecarbinylamine (IV). The amine was also converted into a crystalline quaternary ammonium iodide with correct analysis for *O*-benzylidene-*N*,*N*-dimethyl-2,2-bis(hydroxymethylcyclopropanecarbinylamine methiodide (V).

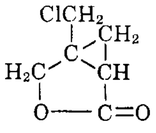


I. Y = CN

II. Y = $CONH_2$

IV. Y = $CH_2NHCOCH_3$

V. Y = $CH_2\overset{+}{N}(CH_3)_3I^-$



III

The ease of displacement of arenesulfonate or iodide by cyanide was determined by experiments effected on a series of *O*-benzylidenepentaerythritol derivatives (Table IV). Assuming that a two-step mechanism prevails as demonstrated for iodide displacement, the order of reactivity in the first step appears to be: $OSO_2C_6H_4Br(p) \sim I > OSO_2C_6H_5 > OSO_2C_6H_4CH_3(p)$. In the second step, the ease of displacement appears to be: $OSO_2C_6H_4Br(p) > OSO_2C_6H_5 > I > OSO_2C_6H_4CH_3(p)$. Other effects found in these experiments were: dimethyl sulfoxide is less effective than dimethylformamide. A sufficient amount of water is necessary to dissolve in part the sodium cyanide. Ethanol in a sealed tube is less effective than dimethylformamide as a solvent.

Experimental

Melting points are corrected. Microanalyses were made by K. W. Zimmerman, Australian Microanalytical Service, University of Melbourne.

Sulfonate Esters (Table I).—*O*-Benzylidenepentaerythritol[6] (0.075 mole) and 0.160 mole of the sulfonyl chloride in 100 ml. of anhydrous pyridine reacted at 0° for 3 hr. to yield a crystalline mass, which was transferred to a funnel with a minimum of ethanol, and recrystallized once from benzene and repeatedly from absolute ethanol to provide an analytical sample. *O*-Isopropylidenepentaerythritol dibenzenesulfonate was prepared by the procedure described[7] for the synthesis of *O*-isopropylidenepentaerythritol di-*p*-toluenesulfonate.[3]

1,3-Propanediol dibenzenesulfonate was similarly prepared but required a chloroform extraction of the reaction mixture, removal of pyridine with sulfuric acid, concentration of solvent to leave a sirup, which crystallized from a solution of ethanol, acetone, and water (5:3:2, by vol.). A single recrystallization from ethanol gave 60% yield of product, m.p. 40–40.5°.

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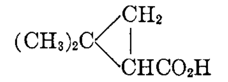
[5] R. Stoermer and F. Schenck, *Ber.*, **61**, 2312 (1928).

[6] E. Bograchov, *J. Am. Chem. Soc.*, **72**, 2268 (1950).

[7] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

TABLE III

DISPLACEMENT REACTIONS OF ACYCLIC SULFONATE ESTERS WITH SODIUM CYANIDE

Substrate	Product	Yield[a] %	B.p., °C. (mm.) Obsd.	B.p., °C. (mm.) Lit.	M.p., °C. Obsd.	M.p., °C. Lit.
$(CH_3)_3CCH_2OSO_2C_6H_5$[b]	$(CH_3)_3CCH_2CH_2CN$	56	129–130 (656)	135–136.4[c] (737)	31–33	32.5[c]
$C_6H_5SO_2O(CH_2)_3OSO_2C_6H_5$	$NC(CH_2)_3CN$[d]	81	144 (14)	144–147 (13)[e]		
$(CH_3)_2C(CH_2OSO_2C_6H_5)_2$[f]		28	98 (10)	100 (10)[g]		
	$(CH_3)_2C(CH_2CN)_2$[h]	28			100.5–101	

[a] Yields based upon analytical samples. [b] P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955). [c] A. Homeyer, F. Whitmore, and V. Wallingford, *J. Am. Chem. Soc.*, **55**, 4209 (1933). Hydrolysis of 3,3-dimethylbutyronitrile in 75% sulfuric acid containing sodium chloride gave 3,3-dimethylbutyramide, after recrystallization from absolute ethanol, m.p. 130.5–131.5°, reported in ref. *c*, 131–131.5°. [d] Hydrolysis of glutaronitrile in hydrochloric acid gave glutaric acid, m.p. and m. m.p. with an authentic sample, 95–97°. [e] C. S. Marvel and E. M. McColm, *Org. Syn.*, **5**, 103 (1925). [f] G. S. Skinner and P. R. Wunz, *J. Am. Chem. Soc.*, **73**, 3814 (1951). [g] *Anal.* Calcd. for $C_6H_{10}O_2$: equiv. wt., 114. Found: equiv. wt. (by titration), 115. M. Blanc, *Compt. rend.*, **145**, 78 (1907). 2,2-Dimethylcyclopropanecarboxamide, m.p. 175.5–177°, reported in ref. *g*, 177°, was prepared from the acid by initial formation of the acid chloride with thionyl chloride followed by treatment with ammonia. *N*-*p*-Tolyl-2,2-dimethylcyclopropane carboxamide, m.p. 117.2–117.6°, was similarly prepared using *p*-toluidine. *Anal.* Calcd. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.71; H, 8.22; N, 7.14. [h] *Anal.* Calcd. for $C_7H_{10}N_2$: C, 68.81; H, 8.25; N, 22.94. Found: C, 68.88; H, 8.10; N, 23.53. Incomplete hydrolysis of 3,3-dimethylglutaronitrile in concentrated hydrochloric acid provided crystalline 3,3-dimethylglutarimide, purified by sublimation, m.p. 147–147.5°, reported 147° by F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 422 (1911). *Anal.* Calcd. for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.82; H, 7.73; N, 9.81. From the same hydrolysis solution, 3,3-dimethylglutaric acid was isolated, m.p. 100–100.5°, reported 100–101° by K. Auwers, *Ber.*, **28**, 1130 (1895) and 101–102° by F. Blaise, *Compt. rend.*, **126**, 1153 (1898). 3,3-Dimethylglutaric anhydride, m.p. 124–125°, reported 124–125° by W. Perkin and W. Goodwin, *J. Chem. Soc.*, 69, 1457 (1896), was prepared from 3,3-dimethylglutaric acid by dehydration in acetic anhydride.

Anal. Calcd. for $C_{15}H_{16}O_6S_2$: C, 50.57; H, 4.53. Found: C, 50.89; H, 4.61.

Displacement Reactions of Sulfonates with Sodium Iodide (Table II).—In a typical procedure, 0.015 to 0.022 mole of substrate, 0.13 mole of sodium iodide, and 100 ml. of acetone were sealed in a 6-oz. carbonated beverage bottle and were heated for various lengths of time. The bottle was then cooled, the precipitated salts were separated by filtration, and the resulting solution was evaporated under reduced pressure to dryness. The residue was dissolved in a minimum of hot ethanol to recrystallize colorless products. Analytical samples were prepared by repeated recrystallizations from absolute ethanol.

Displacement Reactions of Acyclic Sulfonate Esters with Sodium Cyanide (Table III).—Sodium cyanide (30% excess) and the sulfonate ester were mixed with *N*,*N*-dimethylformamide (500 ml. for 0.2 mole NaCN; 2 l. for 1.2 moles) and heated for 5 hr. at the reflux temperature with 2,2-dimethyl-1-propanol benzenesulfonate and 1,3-propanediol dibenzenesulfonate and at 170° in a sealed carbonated beverage bottle with 2,2-dimethyl-1,3-propanediol dibenzenesulfonate. 3,3-Dimethylbutyronitrile was recovered by drowning the reaction mixture in ice and water, ether extraction, solvent removal, and distillation. Glutaronitrile was isolated by removal of solvent using a flash-evaporator and distillation. Cyclopropanecarbonitrile was not found in the reaction mixture. 3,3-Dimethylglutaronitrile was obtained by the same removal of reaction solvent, extraction with ether and its subsequent evaporation, and crystallization of the residue from ethanol–water. 2,2-Dimethylcyclopropanecarboxylic acid was isolated from another batch of the same reactants by evaporation of the reaction solvent, hydrolysis of the residue in aqueous sodium hydroxide, ether extraction of the acidified mixture, evaporation of solvent, and distillation.

Displacement Reactions of *O*-Benzylidenepentaerythritol Derivatives with Sodium Cyanide (Table IV).—In a typical procedure, 0.18 mole of sodium cyanide was dissolved in 10 ml. of water (except in experiments 5 and 6), and the resulting solution was poured into 125 ml. of boiling *N*,*N*-dimethylformamide or dimethyl sulfoxide. The *O*-benzylidenepentaerythritol derivative (0.015 to 0.023 mole) was added, and the reaction mixture refluxed for 1.5 hr. and then poured onto ice and water. The solid derived was filtered and dissolved in benzene. The solution was decolorized with carbon and ligroine added to crystallize out *O*-benzylidene-2,2-bis(hydroxymethyl)cyclopropanecarbonitrile (I). An analytical sample, m.p. 116.5–117°, was prepared by a combination of sublimation and recrystallization from benzene-ligroine and from ethanol.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51; mol. wt., 215. Found: C, 72.94; H, 6.06; N, 6.85; mol. wt. (ebullioscopic in benzene), 220, 211.

I decolorized bromine in carbon tetrachloride slowly when warmed. I and authentic cyclopropanecarbonitrile exhibited very similar behavior toward tetranitromethane. The infrared spectrum (potassium bromide disk) had a peak at 3.3 μ characteristic of stretching vibrations of C–H bonds in cyclopropane rings.[8] The 60-Mc. proton magnetic resonance spectrum in an acetone solution contained cyclopropane ring hydrogen peaks at $\tau = 8.54$ p.p.m. The relative peak areas for the phenyl, methine, six-membered ring methylene, and cyclopropane hydrogen atoms were 5, 1, 4, and 3.

***N*-Acetyl-*O*-benzylidene-2,2-bis(hydroxymethyl)cyclopropanecarbinylamine (IV)** was prepared by treating an ethanol solution of I with Raney nickel at 100° at a hydrogen pressure of 1000 p.s.i. and converting the sirupy amine into IV with acetic anhydride in pyridine. An analytical sample, m.p. 143.5°, was prepared by repeated recrystallizations from ethanol.

Anal. Calcd. for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.42; H, 7.48; N, 5.46.

***O*-Benzylidene-N,N-dimethyl-2,2-bis(hydroxymethyl)cyclopropanecarbinylamine methiodide (V)**, m.p. 217–219°, was obtained in 49% yield by treating the sirupy amine two times with methyl iodide and sodium hydroxide, and crystallizing the product from ethanol–water. Repeated recrystallizations from ethanol–water gave an analytical sample, m.p. 218–220°.

Anal. Calcd. for $C_{16}H_{24}INO_2$: C, 49.36; H, 6.21; N, 3.60. Found: C, 49.65; H, 6.22; N, 3.53.

***O*-Benzylidene-2,2-bis(hydroxymethyl)cyclopropanecarboxamide (II)**, m.p. 200–200.5°, was obtained in a yield of 74% by treating I with aqueous sodium hydroxide and recrystallizing the product from alcohol.

Anal. Calcd. for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48. Found: C, 67.30; H, 6.54.

2-Chloromethyl-2-hydroxymethylcylopropanecarboxylic acid lactone (III), b.p. 95° (0.5 mm.), 84° (0.1 mm.), $n^{25}D$ 1.4935, was obtained in a 15% yield by refluxing 54 g. of I and 100 ml. of concentrated hydrochloric acid for 30 min., extracting with benzene-ligroin, separating phases, and adding 30 ml. more of concentrated hydrochloric acid to the aqueous portion, which was refluxed for 12 hr. longer, adding 30 g. of sodium hydroxide after cooling, extracting the reaction mixture with benzene–ligroin and then with ethanol–ether, drying the latter extract and evaporating the solvent, and distilling under reduced pressure.

Anal. Calcd. for $C_6H_7ClO_2$: C, 49.16; H, 4.82. Found: C, 49.09; H, 4.90.

The 60-Mc. proton magnetic resonance spectrum of a carbon tetrachloride solution showed large peaks at $\tau = 5.76$ and

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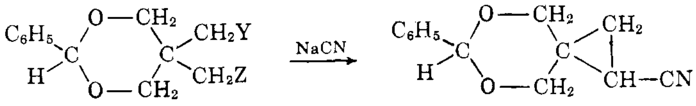
(8) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

TABLE IV

DISPLACEMENT REACTIONS OF O-BENZYLIDENEPENTAERYTHRITOL DERIVATIVES WITH SODIUM CYANIDE



Experiment no.	Substrate		Yield,[a] %	Solvent
	Y	Z		
1	$OSO_2C_6H_5$	$OSO_2C_6H_5$	45	DMF
2	$OSO_2C_6H_5$	I	77	DMF
3	I	I	45	DMF
4	$OSO_2C_6H_5$	I	36	DMSO[b]
5	$OSO_2C_6H_5$	I	31	Anhydrous DMSO,[b] solid NaCN introduced
6	$OSO_2C_6H_5$	I	30	Anhydrous DMF, solid NaCN introduced
7	$OSO_2C_6H_4Br(p)$	$OSO_2C_6H_4Br(p)$	85	DMF
8	$OSO_2C_6H_4Br(p)$	I	82	DMF
9	$OSO_2C_6H_4CH_3(p)$	$OSO_2C_6H_4CH_3(p)$	7.5[c]	DMF
10	$OSO_2C_6H_4CH_3(p)$	I	34	DMF
11	$OSO_2C_6H_5$	$OSO_2C_6H_5$	Very low	C_2H_5OH[d]

[a] Yields based upon materials with melting points within 2° or less of the analytical samples. [b] Reaction at 130–135°. [c] 38% substrate recovered. [d] Reaction carried out in a Carius bomb tube at 130° for 8 hr.

6.26 p.p.m., assignable to the methylene hydrogens of the lactone ring and the chloromethyl group, respectively. The upfield peaks were located at τ = 7.93, 8.53, and 8.86 p.p.m. for the three nonequivalent cyclopropane ring hydrogens. The approximate peak areas were 2, 2, 1, 1, and 1 for the different types of hydrogens in the order described.

Acknowledgment.—We are grateful to the Strasenburgh Laboratories for support of a portion of this investigation and thank Robert C. Hirst for the nuclear magnetic resonance spectral data and interpretation.

Synthesis of 1,5,9-Cyclododecatriene

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Cyclic dimers[1] and trimers[2] of butadiene have been obtained by several workers. We have now found that a trimer, *trans,trans,cis*-1,5,9-cyclododecatriene, is produced upon treatment of butadiene with a novel catalyst system which consists of a combination of an alkylaluminum halide and a titanium tetraalkoxide. The action of trialkylaluminum–titanium tetraalkoxide complex on butadiene has been reported by Wilke[3] to afford 1,2-polymer.

A benzene solution of diethylaluminum chloride containing titanium tetrabutoxide in a mole ratio of about 20 (Al/Ti) was treated with butadiene gas until the absorption rate decreased rapidly. Distillation of the reaction products gave a cyclododecatriene fraction in 81% yield, no appreciable quantities of dimer and tetramer being isolated. The cyclododecatriene consisted only of *trans,trans,cis*-1,5,9-cyclododecatriene and no *trans,trans,trans* isomer was isolated upon careful distillation in any case. However, the *all trans* isomer was isolated in about 5% yield from trimerization products of butadiene in the presence of a mixture of titanium tetrachloride and dialkylaluminum halide, as reported by Wilke. Consequently, it appears that our catalysts containing titanium tetraalkoxides have higher stereospecificity for trimerization of butadiene than catalysts reported by Wilke.

trans,trans,cis-1,5,9-Cyclododecatriene has been identified by measurements of molecular weight and infrared spectrum and by formation of silver nitrate complex in quantitive yield.[4] Catalytic hydrogenation and ozonization yielded cyclododecane and succinic acid, respectively, in high yeilds.

Effects of reaction variables on yields of cyclododecatriene have been examined. As summarized in Table I, the organic groups of titanium tetraalkoxides and organoaluminum compounds had minor effects on the yields of cyclododecatriene. Alkylaluminum bromides and chlorides were equally active. The halogen content of organoaluminum compounds or n in $R_{3-n}AlX_n$ must be between 0.5 and 1.5. When n was 0.5 or less, linear polymer was produced in quantities and cyclododecatriene was obtained with poor yields or in trace. Similar results were also observed when n was 1.5 or more.

Data in Table II show that the mole ratio of alkylaluminum halides to titanium tetraalkoxides must be greater than 12. When the mole ratio was less than 12, little, if any, butadiene was absorbed and polymer was produced instead of cyclododecatriene. At a mole ratio of 18 or higher, the absorption rate of butadiene was increased appreciably and yields of cyclododecatriene were greatly improved. The yields remained approximately constant at higher mole ratios. In each case certain induction period was recognized.

As shown in Table III, the reaction temperature should be kept below 65°. Higher temperatures than

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(1) (a) K. Ziegler, *Angew. Chem.*, **59**, 177 (1947); H. W. B. Reed, *J. Chem. Soc.*, 685 (1951); (b) G. Wilke, *Angew. Chem.*, **73**, 33 (1961).

(2) (a) G. Wilke, *ibid.*, **69**, 397 (1957); Studiengesellschaft Kohle m. b. H., Belg. Patent 555,180 (1957); G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959); (b) Studiengesellschaft Kohle m. b. H., Belg. Patent 566,436 (1958); G. Wilke and H. Müller, German Patent 1,043,329 (1958); (c) *cf.* also ref. 1b.

(3) G. Wilke, *Angew. Chem.*, **68**, 306 (1956).

(4) Compared with a silver nitrate complex of *trans,trans,cis*-1,5,9-cyclododecatriene obtained by method of Wilke.