Anal. Calcd. for $C_{24}H_{20}O_{12}N_4$: C, 51.8; H, 3.6; N, 10.1. Found: C, 51.4; H, 3.4; N, 10.3.

Solubilization of 4,4″-diamino-p-terphenyl. To a solution of 10 g. of 4,4″-diamino-*p*-terphenyl in 300 ml. of boiling chlorobenzene was added 15.5 g. (2 molar equivalents) of dimethyl isocyanatoglutarate. The heating was continued, and within 0.5 hr. the mixture had set to a crystalline mass. After heating for 15 min. more, the mixture was diluted with acetone, slurried, and filtered.The semisolid product was removed from the filter, slurried again in acetone, and again filtered. This was repeated with ether as the diluent. The dry product (15.5 g.) is pure 4,4″-bis(1,3-dicarbomethoxypropylureylene)-*p*-terphenyl, m.p. about 225°.

Anal. Calcd. for $C_{34}H_{38}N_4O_{10}$: C, 61.3; H, 5.7; N, 8.4. Found: C, 61.8; H, 5.9; N, 8.3.

This ester could be hydrolyzed with sodium hydroxide in dimethylformamide-methanol to give a crystalline water-soluble product. However, it was not found possible to prepare an analytically pure sodium salt or the free acid therefrom.

Solubilization of 3,7-diaminodibenzothiophenedioxide (X). To 5 g. (0.02 mole) of 3,7-diaminodibenzothiophenedioxide and 8 g. (0.04 mole) of dimethyl isocyanatoglutarate in a small flask was added 6 ml. of dimethyl sulfoxide. The flask was fitted with a drying tube containing calcium chloride and heated at 70° for 2 hr. The resulting syrup was dissolved in ethanol and treated with 4 g. (0.1 mole) of sodium hydroxide in 6 ml. of water. A taffylike product formed. After warming for 1 hr. at 60° and adding 100 ml. more ethanol, the product became solid. It was ground to a powder under alcohol, collected on a filter, washed with water, and dried; yield, 13 g. This material, which is essentially the tetrasodium salt of 3,7-bis(1,3-dicarboxypropylureylene)dibenzothiophenedioxide is highly soluble in water.

A solution of 3 g. of the sodium salt in water was acidified, warmed, and treated with ethanol until the solid which formed on acidification dissolved. On cooling, the free acid crystallized. Recrystallization from a mixture of ethylacetate and methanol gave a product melting at 175–178° dec.

Anal. Calcd. for $C_{24}H_{24}O_{12}N_4S$: C, 48.6; H, 4.1; N, 9.5; S, 5.4. Found: C, 48.3, 48.6; H, 4.4, 4.7; N, 9.1; S, 5.2.

Rochester 4, N. Y.

[Contribution from the General Electric Research Laboratory]

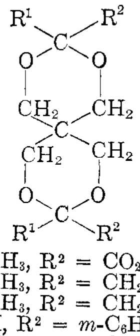
Preparation of Methyl Esters Containing the 1,3-Dioxane or 2,4,8,10-Tetroxaspiro[5.5]undecane Structure by Ketal Exchange

ROBERT M. LUKES[1]

Received September 6, 1960

Methyl diesters containing the 2,4,8,10-tetroxaspiro[5.5]undecane structure have been prepared from methyl keto esters and pentaerythritol by ketal exchange between the keto esters and the diacetone ketal of pentaerythritol. The method has been extended to the preparation of methyl hydroxy esters containing the 1,3-dioxane structure by ketal exchange between keto esters and the acetone ketal of 1,1,1-trishydroxymethylethane. Polyesters have been prepared from both types of esters, by transesterification with ethylene glycol in the case of the diesters or self-transesterification in the case of the hydroxy esters.

The coupling of aldehyde esters or keto esters through the nonester carbonyl function provides a route to the preparation of high molecular weight diesters suitable for conversion into linear polyesters by alcohol interchange with glycols. Böeseken and Felix,[2] as part of their intensive study of the structure and reactions of pentaerythritol, prepared a series of just such compounds (I–V) by condensing the appropriate ethyl esters with pentaerythritol.



I. $R^1 = CH_3$, $R^2 = CO_2C_2H_5$
II. $R^1 = CH_3$, $R^2 = CH_2CO_2C_2H_5$
III. $R^1 = CH_3$, $R^2 = CH_2CH_2CO_2C_2H_5$
IV. $R^1 = H$, $R^2 = m\text{-}C_6H_4SO_3H$
V. $R^1 = H$, $R^2 = m\text{-}C_6H_4CO_2H$

The ethyl diester III prepared according to their directions has been found to condense with ethylene glycol under alkaline catalysis to form an insoluble gel, obviously cross-linked.[3]

It was decided to prepare the methyl diester corresponding to III, since past experience had shown that this would be more likely to be a crystalline solid than would the ethyl ester, and hence would be more easily purified. However, to prepare the methyl diester from the crude ethyl diester *via* saponification and re-esterification seemed unnecessarily tedious, and to use the direct condensation of the methyl keto ester with pentaerythritol, distilling the byproduct water as an azeotrope[4] was impractical because of the likelihood of a supervening transesterification and distillation of methanol.

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[1] Present address: Locomotive and Car Equipment Dept., General Electric Co., Erie, Pa.

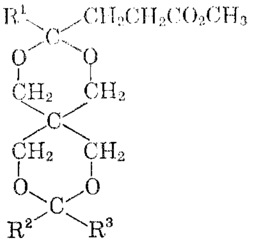
[2] J. Böeseken and B. B. C. Felix, *Ber.*, **61B**, 787 (1928).

[3] The cause of the cross linking was no mystery, since III was a liquid purified only by distillation and undoubtedly contained as a contaminant the dihydroxy ester VI, the monoketal of pentaerythritol. This compound was indeed isolated by Böeseken and Felix in their work.

[4] *Cf.* E. J. Salmi, *Ber.*, **71**, 1803 (1938); M. S. Newman and R. J. Harper, Jr., *J. Am. Chem. Soc.*, **80**, 6350 (1958); R. I. Meltzer *et al.*, *J. Org. Chem.*, **25**, 712 (1960).

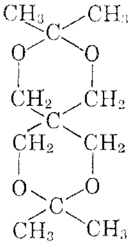
TABLE I

Esters Containing the 2,4,8,10-Tetroxaspiro[5.5]undecane Structure



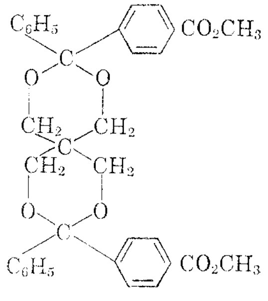
Compound	R^1	R^2	R^3	M.P.	Empirical Formula	Calcd. C	Calcd. H	Found C	Found H	Saponification Equivalent, G. Calcd.	Saponification Equivalent, G. Found
IX	CH_3	CH_3	$CH_2CH_2CO_2CH_3$	59–60	$C_{17}H_{28}O_8$	56.65	7.83	56.51	8.05	180	181
X	C_6H_5	C_6H_5	$CH_2CH_2CO_2CH_3$	127–128	$C_{27}H_{32}O_8$	66.92	6.66	67.12	6.80	242	240
XIII	C_6H_5	CH_3	CH_3	110	$C_{19}H_{26}O_6$	65.12	7.48	65.30	7.71	350	310

The preparation of the desired methyl diester by a ketal exchange technique appeared to be an attractive method. Accordingly, when an acidified methanol solution containing methyl levulinate and the acetone diketal of pentaerythritol[5] (3,3,9,9-tetramethyl-2,4,8,10 - tetraxaspiro[5.5]undecane, VIII) was distilled slowly, the distillate consisted largely of the methanol-acetone azeotrope, and the residual solution yielded the desired diester IX, a crystalline solid melting at 59–60°. By the same method, the crystalline diester X (m. p. 127–128°) was prepared from VIII and methyl β-benzoylpropionate. Both IX and X, when heated with ethylene glycol[6] in the presence of an alkaline catalyst, yielded soluble polyesters having molecular weights of the order of 100,000, as measured by light scattering in 1,2-dimethoxyethane.



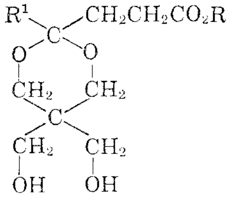
VIII

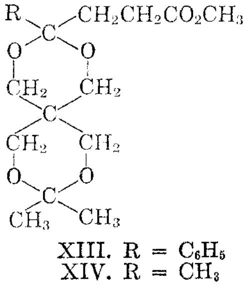
There is some evidence[7] that a 1,3-dioxane ring having two aryl substituents in the 2-position is less susceptible to acid catalyzed hydrolysis than is such a ring having one or two alkyl substituents in that position. In order to see if this held true for 1,3-dioxane rings part of a spiro structure, the preparation of the diester XI from methyl *p*-benzoylbenzoate and VIII by the same ketal exchange technique used for IX and X was attempted. After several fruitless trials in which only starting material was recovered the synthesis was abandoned. Apparently the ketone carbonyl group was too inactive to show an appreciable rate of ketal formation. This is consistent with the reluctance of benzophenone to form cyclic ketals, a phenomenon which has been observed by others.[8]



XI

The purification of crude IX and X involved chromatography over alkaline alumina, and this operation led to the isolation of two side product, the expected monoketal XII and the unexpected mixed diketal XIII respectively. In no case, over several repeats of the preparations of IX and X, were the respective alternate compounds XIV and VII isolated.





VI. $R^1 = CH_3, R^2 = C_2H_5$
VII. $R^1 = C_6H_5, R^2 = CH_3$
XII. $R^1 = CH_3, R^2 = CH_3$

XIII. $R = C_6H_5$
XIV. $R = CH_3$

The ketal exchange method was found to be applicable to the preparation of the hydroxy esters XVI–XX from 1,1,1-trishydroxymethyl-

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[5] L. Orthner, *Ber.*, **61B**, 116 (1928).

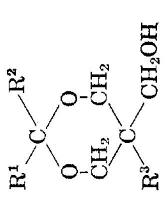
[6] *Cf.* W. H. Carothers and J. A. Ruin, *J. Am. Chem. Soc.*, **51**, 2560 (1929).

[7] O. Ceder, *Arkiv Kemi*, **6**, 523 (1954). See also M. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **119**, 305 (1926).

[8] M. Sulzbacher, E. Bergmann, and E. R. Pariser, *J. Am. Chem. Soc.*, **70**, 2827 (1948).

TABLE II

2,2,5-SUBSTITUTED 1,3-DIOXANES



Compd.	R^1	R^2	R^3	B.P.	Mm.	Empirical Formula	Calcd. C	Calcd. H	Found C	Found H	Saponification Equiv., g. Calcd.	Saponification Equiv., g. Found
XII	CH_3	$CH_2CH_2CO_2CH_3$	CH_2OH	96–97[a]		$C_{11}H_{20}O_6$	53.21	8.12	53.20	8.00	248	247
XV	CH_3	CH_3	CH_3	95	4.5	$C_8H_{16}O_3$	59.98	10.07	60.01	10.30		
XVI	CH_3	$CH_2CH_2CO_2C_2H_5$	CH_3	136–138	0.6	$C_{12}H_{22}O_5$	58.51	9.00	58.25	8.90	246	249
XVII	CH_3	$CH_2CH_2CO_2CH_3$	CH_3	163–165	1.0	$C_{11}H_{20}O_5$	56.88	8.68	56.71	8.80	232	232
XVIII	C_6H_5	$CH_2CH_2CO_2C_2H_5$	CH_3	168–170	0.1	$C_{17}H_{24}O_5$	66.21	7.85	66.30	7.90	308	295
XIX	C_6H_5	$CH_2CH_2CO_2CH_3$	CH_3	175–178	0.4	$C_{16}H_{22}O_5$	65.29	7.50	65.50	7.70	294	291
XX	$CH_2CH_2CO_2CH_3$	$CH_2CH_2CO_2CH_3$	CH_3	186–188	0.1	$C_{14}H_{24}O_7$	55.25	7.95	55.47	8.00	152	151

[a] Melting point.

ethane and the appropriate keto esters. The acetone ketal of 1,1,1-trishydroxymethylethane (XV), a viscous liquid, was prepared in the way as was the acetone diketal of pentaerythritol, and the exchanges with the keto esters were carried out as before. All the hydroxy esters prepared were very viscous liquids, and none had crystallized after standing at room temperature for a year.

When XVI was heated *in vacuo* in the presence of sodium methoxide, the product was an amorphous solid soluble in chloroform. The molecular weight (ebullioscopic) in chloroform was measured initially as about 2000, but continued boiling gave successively lower values. The other hydroxy esters (XVII-XX) in the series behaved similarly.

EXPERIMENTAL[9]

The diketal of pentaerythritol and acetone (VIII) was prepared by the method of Orthner.[5] The same general method was used to prepare the ketal (XV) of acetone and 1,1,1-trishydroxymethylethane.

2,2,5-Trimethyl-5-hydroxymethyl-1,3-dioxane (XV). A mixture of 1400 ml. of acetone, 100 g. of anhydrous cupric sulfate, and 100 g. (0.83 mole) of 1,1,1-trishydroxymethylethane was shaken vigorously for 48 hr., then filtered and evaporated to 200-ml. volume on the steam bath. The viscous residue was diluted with 500 ml. of ether, filtered, evaporated on the steam bath, and then distilled under vacuum to give 75 g. (56%) of 2,2,5-trimethyl-5-hydroxymethyl-1,3-dioxane (XV), b.p. 95° (4.5 mm.), n_D^{25} 1.4520.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 60.01; H, 10.30.

The following is an example of the procedure used to prepare the products IX and X, and to isolate the side products XII and XIII.

3,9-Diphenyl-3,9-bis(2-carbomethoxyethyl)-2,4,8,10-tetroxaspiro[5.5]undecane (X). A solution of 200 g. (1.04 moles) of methyl β-benzoylpropionate,[10] 60 g. (0.28 mole) of the diketal VIII, 300 ml. of anhydrous methanol and 0.2 ml. of 96% sulfuric acid was distilled slowly through a 3/4 × 12″ fractionating column packed with glass helices; after 6 hr. 105 ml. of distillate, b.p. 56–64° had been collected (the acetone-methanol azeotrope boils at 55.7°). The residue was poured into 1 l. of saturated sodium bicarbonate solution, and this mixture was extracted with two 1-l. portions of ethylene dichloride. The combined extracts were washed with water, dried over anhydrous sodium sulfate, filtered, and evaporated under nitrogen on the steam bath. The residue (about 250 g.) was transferred to a Claisen flask and distilled under vacuum until all the unreacted methyl β-benzoylpropionate had been collected (134 g., b.p. 102–110°). A 1.65-g. portion of the still residue was dissolved in 5 ml. of benzene, and this solution was poured into a 25-mm. chromatographic column which had been packed with 40 g. of alkaline alumina (Merck). Elution of the column with 300 ml. of a 3:2 ether–hexane mixture gave 200 mg. of 3,3-dimethyl-9-phenyl-9-(2-carbomethoxyethyl)-2,4,8,10-tetraxaspiro[5.5]undecane (XIII), m.p. 110° after crystallization from ether-hexane.

Anal. Calcd. for $C_{19}H_{26}O_6$: C, 65.12; H, 7.48. Found: C, 65.30; H, 7.71. Calcd. for saponification equivalent: 350 g. Found: 310 g.

Further elution of the chromatographic column with a 4:1 ether-hexane mixture gave 400 mg. of 3,9-diphenyl-3,9-

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[9] Melting points are corrected, boiling points are uncorrected.

[10] L. F. Somerville, and C. F. H. Allen, *Org. Syntheses*, **Coll. Vol. II**, 81 (1943).

bis(2 - carbomethoxyethyl) - 2,4,8,10 - tetroxaspiro[5.5]undecane (X), m.p. 127–128° after crystallization from ether-hexane.

Anal. Calcd. for $C_{27}H_{32}O_8$: C, 66.92; H, 6.66. Found: C, 67.12; H, 6.80. Calcd. for saponification equivalent: 242 g. Found: 240 g.

The gross residue from the distillation was dissolved in ether, and from this solution 16 g. (12%) of X was obtained by crystallization.

The preparation of XVI, XVII, XVIII, XIX, and XX is illustrated by the following example.

5-Hydroxymethyl-5-methyl-2,2-bis(2-carbomethoxyethyl)-1,3-dioxane (XX). A solution of 120 g. (0.75 gole) of the ketal XV, 200 g. (1.0 mole) of dimethyl γ-ketopimelate,[11] 300 ml. of anhydrous methanol, and 0.2 ml. of 96% sulfuric acid was distilled slowly through the fractionating column used in the preparation of X until 200 ml. of distillate, b.p. 55–65°, had been collected. The residue was cooled to room temperature, and to it was added 10 ml. of saturated aqueous sodium bicarbonate solution, 500 ml. of water, and 200 ml. of saturated aqueous sodium sulfate solution in that order. This mixture was extracted with three 300-ml. portions of ether, and the combined extracts were filtered through anhydrous sodium sulfate and then evaporated on the steam bath under nitrogen, leaving a residue of about 300-ml. volume. This residue, when distilled under vacuum, yielded 120 g. (53%) of 5-hydroxymethyl-5-methyl-2,2-bis(2-carbomethoxyethyl)-1,3-dioxane (XX), b.p. 186–188° (0.1 mm).

Anal. Calcd. for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: 55.47; H, 8.00. Calcd. for saponification equivalent: 152 g. Found: 151 g.

Polyesters. The following example illustrates the method of preparing polyesters from IX and X.

A mixture of 10 g. of the diester IX, 20 ml. of ethylene glycol, and 5.0 mg. of sodium methoxide was heated at 150° for 2 hr., all the while bubbling a fine stream of dry nitrogen through the mixture *via* a capillary tube. The mixture was then heated under vacuum according to this schedule: 1 hr. at 150° (0.1 mm.); 1 hr. at 190° (0.01 mm.); 1 hr. at 240° (0.1 mm.). The residue (10 g.), upon cooling, was a glassy solid slowly soluble in dioxane and chloroform.

The procedure for polymerizing the hydroxy esters XVI–XX was the same except that no ethylene glycol was added to the reaction mixture.

Acknowledgment. The author wishes to thank Dr. E. M. Balis and associates of this laboratory for the microanalyses reported.

SCHENECTADY, N. Y.

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(11) For a method of preparation see R. M. Lukes, G. I. Poos, and L. H. Sarett, *J. Am. Chem. Soc.*, **74,** 1401 (1952).

[CONTRIBUTION FROM RESEARCH CENTER, KOPPERS CO., INC.]

Polymers from Bisphenols. Steric Inhibition of Condensation Polymerization[1]

SAMUEL C. TEMIN

Received December 15, 1960

A series of substituted bisphenols were utilized in the attempted preparation of polyesters with adipic and sebacic acids Both *p,p'*- and *o,o'*-bisphenols, with alkylene or sulfide bridging groups, were examined. It was observed that, although all of the bisphenols readily formed diacetates with acetic anhydride, the diacetates of some of the bisphenols did not undergo the trans-acidolysis reaction which is necessary for polymerization to occur. The failure to polymerize can be related to steric hindrance and is explained in terms of transition states.

Polyesters derived from a diphenolic material and a dicarboxylic acid were first investigated by Bischoff.[2] Later, polyesters were prepared by reaction of hydroquinone diacetate with dicarboxylic acids.[3] This technique was used by Levine and Temin[4] to prepare bisphenol polyesters. Conix[5] and Eareckson[6] synthesized polyesters from acid chlorides and diphenates by interfacial polycondensation. Korshak and co-workers,[7] and others,[8] also prepared polyphenyl esters using acid chlorides. In addition, a large number of bisphenols have been used in preparing polycarbonates.[9] In this previous work it appeared that substitution in the benzene rings of a bisphenol lowered the softening point of the corresponding polyesters.

In the present work a variety of bisphenol alkanes and bisphenol sulfides were studied in an effort to prepare liquid polyesters. It was hoped that the introduction of sufficient bulky groups, particularly in the *o,o'*-bisphenols, would yield liquid polymers. This objective was not attained but it was noted that certain of the bisphenols

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(1) Presented at 138th National Meeting of the American Chemical Society, New York, September, 1960.

(2) C. A. Bischoff and A. von Hedenstrom, *Ber.*, **35,** 3455 (1902).

(3) J. G. N. Drewitt and J. Lincoln, British Pat. **621,102** (1947); *Brit. Abstr.*, **1949,** BII, 1114; E. R. Wallsgrove and F. Reeder, British Pat. **636,429** (1950); *Chem. Abstr.*, **44,** 7878d (1950).

(4) M. Levine and S. C. Temin, *J. Polymer Sci.*, **28,** 179 (1958).

(5) A. Conix, *Ind. chim. belge*, **22,** 1457 (1957); *Ind. Eng. Chem.*, **5,** 147 (1949).

(6) W. M. Eareckson, *J. Polymer Sci.*, **40,** 399 (1959).

(7) V. V. Korshak and S. V. Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, **123,** 849 (1958); *Chem. Abstr.*, **53,** 8700c (1959); *Vysokomolekulyarnye Soedineniya*, **1,** 1482 (1959).

(8) N. I. Volynkin and G. I. Braginskii, U.S.S.R. Pat. **121,556** (1959); *Chem. Abstr.*, **54,** 7357d (1960).

(9) H. Schnell, *Angew. Chem.*, **68, 633** (1956); *Ind. Eng. Chem.*, **51,** 157 (1959).