TABLE IV

COPOLYMERIZATION DATA

System	Cat.	Temp.	Time, Hr.	Cat., Mg.	Monomer, Mixture, G.	Polymer, G.	Conv., %	N, %	Molar Ratio Acrylonitrile to Styrene or Vinyl Acetate
Acrylonitrile-styrene	BSP[a]	45	66.7	11.5	8.9	0.66	7.4	6.66	2:3
Acrylonitrile-styrene	BP[b]	45	66.7	8.9	8.9	2.37	26.6	6.9	2:2.88
Acrylonitrile–vinyl acetate	BSP	45	14.8	17.9	13.8	0.28	2.0	20.8	1:5.7
Acrylonitrile–vinyl acetate	BP	45	14.8	13.0	12.1	0.24	2.0	20.6	1:5.7

[a] Benzenesulfonyl peroxide. [b] Benzoyl peroxide.

is defined as the weight of precipitated polymer obtained from a given weight of monomer expressed as per cent. Molecular weights were estimated by standard procedures[8] from the viscosities of a series of standard solutions of the polymer in benzene.

Other polymerizations. Styrene and acrylonitrile were polymerized in tubes as described above. Polyacrylonitrile, being insoluble in its monomer, precipitated as it was formed and was filtered, washed with methanol and dried *in vacuo*. The copolymerizations likewise were effected in tubes, the "monomers" consisting of equimolar mixtures of acrylonitrile-styrene and acrylonitrile-vinyl acetate. Both copolymers were removed by filtration, washed with methanol, and dried.

Reaction of benzenesulfonyl peroxide with benzene. The peroxide (58.2 mg.) was dissolved in 10 cc. of cold benzene and allowed to stand for three days. The benzene was extracted with water and evaporated to dryness. This residue was extracted with carbon tetrachloride leaving a small dark tarry residue. The carbon tetrachloride extract was concentrated to a volume of 2.0 cc. The infrared spectrum of this solution was identical with that of authentic phenyl benzenesulfonate. When compared with standard solutions of the latter at 7.25 and 11.65μ, a yield of 21.4 mg. (49%) was estimated. Two like experiments gave yields of 48% and 52%.

On a larger scale, 0.81 g. (0.0026 mol.) of the peroxide was dissolved in 150 cc. of benzene and the solution was allowed to stand at room temperature for 3 days before warming briefly on the steam bath. Water (50 cc.) was added and the mixture titrated to the phenolphthalein end point with standard base, 0.0029 mol. being consumed. The aqueous layer, shown to be free of sulfate, was separated, clarified with Norit, concentrated to 10 cc. and a saturated aqueous solution containing 0.8 g. of benzylisothiuronium chloride was added. The precipitate so obtained was recrystallized from water to give 0.61 g. of benzylisothiuronium benzenesulfonate melting at 146.5–148.5° alone and when mixed with an authentic sample. The benzene solution was evaporated to dryness and the tarry residue was extracted with 25 cc. of carbon tetrachloride. This solution was poured through a 2.5 cm. high column of alumina of about 0.5 cm. diameter and eluted with carbon tetrachloride. This afforded a water white solution which after evaporation left 0.24 g. of a white solid melting from 30–34°. After crystallization from ethanol, the material melted at 34–35°, alone and when mixed with authentic phenyl benzenesulfonate.

(8) F. Daniels, J. H. Mathews, *et al.*, *Experimental Physical Chemistry*, 4th edition, McGraw-Hill, Inc., New York, 1949, p. 243; P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953, p. 246; R. E. Burke and O. Grumitt, *High Molecular Weight Organic Compounds*, Vol. VI, Interscience Publishers, New York, 1949, p. 90; H. I. Goldberg, W. P. Hohenstein, and H. O. Mark, *J. Polymer Sci.*, **2**, 502 (1947).

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Preparation of 2,4-Dialkylhexahydropyrano-[2,3-d]-*m*-dioxins

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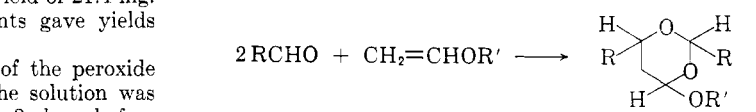
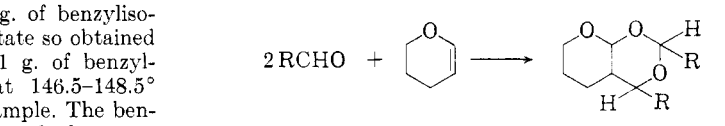
Received June 12, 1959

The preparation of 4-alkoxy-2,6-dialkyl-*m*-dioxanes by the acid-catalyzed addition of two moles of an aldehyde to one mole of a vinyl ether has been previously described.[1]



The purpose of this note is to report the extension of this reaction to include the addition of aldehydes to dihydropyran. The products are 2,4-dialkylhexahydropyrano[2,3-d]-*m*-dioxins.



The structure was assigned by analogy with the aldehyde–vinyl ether reaction products and was supported by the infrared spectra.

EXPERIMENTAL

2,4-Diisopropylhexahydropyrano[2,3-d]-m-dioxin. A mixture of isobutyraldehyde, 317 g. (4.4 mol.), and dihydropyran, 168 g. (2 mol.), was added dropwise over a 1.25-hr. period to a stirred solution of 0.5 ml. of boron trifluoride etherate in 20 ml. of ethyl ether. Moderate cooling was used to main-

(1) R. I. Hoaglin and D. H. Hirsh, U. S. Patent **2,628,257** (1953).

tain the temperature at 50–55°. Stirring was continued for 2.75 hr., and the catalyst was neutralized by addition of a solution of 10 ml. of potassium acetate in 10 ml. of water. The organic phase was separated and distilled to give 66 g. of recovered isobutyraldehyde, b.p. 62–64° at atmospheric pressure. The distillation was then continued under vacuum to give 66 g. of the isobutyraldehyde trimer, 2,4,6-triisopropyl-s-trioxane (b.p. 88° at 12 mm., m.p. 61°); 271 g. (59%) of 2,4-diisopropylhexahydropyrano[2,3-d]-*m*-dioxin, b.p. 128° (12 mm.), n_D^{20} 1.4562; and 72.5 g. of residue.

The infrared spectrum showed strong bands at 8.6 and 9.1 μ, which are the positions of C—O—C absorption in s-trioxane and tetrahydropyran, respectively. No other functional group, such as C=O or C=C, was indicated to be present.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 68.62; H, 10.73.

2,4-Dipropylhexahydropyrano[2,3-d]-m-dioxin. Under conditions similar to those described above, butyraldehyde (2 mol.) and dihydropyran (2 mol.) gave, after a small forerun, 269 g. (59%) of 2,4-dipropylhexahydropyrano[2,3-d]-*m*-dioxin, b.p. 115–121° (4–5 mm.), n_D^{20} 1.4578. The infrared spectrum was similar to that of the product from isobutyraldehyde.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 68.54; H, 10.54.

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Rate of Reduction of Some Steroid Ketones with Sodium Borohydride

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Received June 15, 1959

In connection with a previous investigation on the rate of reduction of steroid ketones in the A and B rings,[1] some other ketones in the C and D rings and in the chain inserted on C-17 were studied.

Although the experimental data (Table I) gave results as normally expected, they showed the reason for the selectivity found sometimes when polycarbonyl compounds are treated with sodium borohydride.[2]

The more interesting facts are that a C-11 ketone is reduced 1000 times slower than a 3-ketone, and that the introduction of a bromine atom in the α-position of a carbonyl increases the rate of reduction by a factor of ten. It is known[3] that sodium borohydride reduction of α-halo ketones proceeds normally to give bromohydrins and the rate increase is very probably due to the interaction between the carbonyl and halogen dipoles that is released when the keto group is reduced.

TABLE I

RATE OF REDUCTION WITH SODIUM BOROHYDRIDE[a]

	$k \times 10^4$	Ratio[b]
Cholestan-3-one	397[c]	100
2-Bromo-cholestan 3-one	5000[d]	1260
11-Keto-tigogenin	0.5[d]	0.126
Hecogenin (12 keto)	42	10.6
Estrone methyl ether	28	7.05
Estrone	30	7.55
Cyclopentanone	34[c]	8.55
Δ^5-Androsten-3β-ol-17-one	23.5	5.94
Δ^5-Pregnen-3β-ol-20-one	5.8	1.45
16-β-Methyl-Δ^5-isopregnen-3β-ol-20-one	4.5	1.13

[a] In 2-propanol at 25. Rate constants in liter mol.$^{-1}$ sec.$^{-1}$ [b] Ratio of rate constants to cholestan-3-one = 100.0. [c] From ref. (1). [d] Approximate result.

When a 3,11 diketone or a 3,20,11 triketone is reduced with one or two equivalents of sodium borohydride, the 11 keto group remains unaltered. The explanation can be seen in the kinetic values, since in the reduction of a 3,11 diketone only 0.1% of the 11-ketone would be reduced. The reason for the lack of reactivity of the C-11 position is steric in nature and it has been discussed elsewhere.[4]

The kinetic results also explain the high selectivity in the reduction of 3,17 and 3,20 diketones.[5]

The relative rates of reduction of the 3,17 and 20 keto group are 100, 5, and 1. Therefore, a minimum percentage of the 17 and 20 alcohols is obtained allowing an easy purification of the reduced product.

The 12 ketone is more reactive than the 17,11 or 20 ketones but nevertheless is reduced 12 times slower that the 3-ketone. The relative rates of reduction for steroidal keto groups can be summarized as follows: 3 keto, 100; 2-bromo 3 keto, 1000; 12 keto, 8.4; 17 keto, 5.2; 20 keto, 1.08; 11-ketone, 0.1.

Taking these results together with the data already reported[1] it is possible to establish the following order of reactivity on sodium borohydride reduction for most of the ketones in the steroid molecule: Δ^5 —3 keto > $\Delta^{8(14)}$ —3 keto > 3 keto A/B *cis* > 3 keto A/B *trans* > 6 keto > 7 keto > Δ^4 —3 keto > 12 keto > 17 keto > 20 keto > 11 keto.

The C-2 ketone is expected to be as reactive as the C-3, the C-16 as reactive as the 3-17, and the C-1 and C-4 as reactive as the C-6 ketone.

EXPERIMENTAL

The ketones used were samples carefully purified and whose melting point agreed with the ones reported in the

(1) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 1049 (1958).

(2) H. Heyman and L. F. Fieser, *J. Am. Chem. Soc.*, **73**, 5252 (1951); E. Elisberg, H. Vanderhaeghe, and T. F. Gallagher, *J. Am. Chem. Soc.*, **74**, 2814 (1952).

(3) C. W. Shoppee, R. H. Jenkins, and G. H. R. Summers, *J. Chem. Soc.*, 1657 (1958).

(4) L. F. Fieser and M. Fieser, *Natural Products Related to Phenanthrene*, Reinhold Publishing Co., New York, 1949, p. 408.

(5) A. H. Soloway, A. S. Deutsch, and T. F. Gallagher, *J. Am. Chem. Soc.*, **75**, 2356 (1953).