been described previously, but a more convenient method was developed. *p*-Toluidine (4.00 g.) was dissolved in 500 ml. of warm water and epichlorohydrin (3.30 ml.) was added over a 15-min. period while the temperature was held at 35–40°. The solution was stirred and the temperature held at 35–40° for 2 hr. When the mixture began to get cloudy, seed crystals of the product were added. The mixture was allowed to stand 20 hr., and the product (I) was recovered and washed with cold water, 5.37 g. (72%), m.p. 79–81° (lit. 81–82°[2]). Although a larger excess of epichlorohydrin gave greater yields, the product was not as pure.

N-(γ-Chloro-β-hydroxypropyl)-p-anisidine (II). This compound was prepared by the procedure used for the synthesis of I except that *p*-anisidine was condensed with epichlorohydrin (10% excess). The product was obtained as an oil. It was extracted with bromobenzene and used without purification for the synthesis of IV.

1,2,3,4-Tetrahydro-6-methyl-quinolin-3-ol (III). Compound I (3.78 g.) was dissolved in bromobenzene (450 ml.) and diethylaniline (3.00 ml.) added. The mixture was boiled under reflux for 48 hr. The product was extracted with 5% hydrochloric acid (100 ml.), and the extract washed with benzene. The acidic extract was made basic with sodium hydroxide, and a benzene extraction carried out. The benzene extract was dried over anhydrous sodium sulfate and passed over an alumina column. The column was washed with benzene, and the product eluted with benzene ether and ether. Although recrystallization of eluted product was possible, further purification was best achieved by converting III to its hydroiodide salt using a mixture of butanol (20 ml.), hydroiodic acid (5 ml.) and ether (150 ml.). The salt was recovered, and washed with ether 2.74 g. (50%).

A purified sample of the hydroiodide salt melted at 237–239° with some decomposition.

Anal. Calcd. for $C_{10}H_{14}NOI$: neut. equiv., 291. Found: neut. equiv., 292.

Neutralization of an aqueous solution of the hydroiodide salt gave III, which was recrystallized from hexane for analysis, m.p. 101.5–103°.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.77; H, 8.26; N, 8.58.

It was possible to follow the cyclization of I to III by mixing an aliquot (1 ml.) from the reaction mixture with benzene (5 ml.) and 5% hydrochloric acid (3 ml.). The aqueous layer was added to a mixture of 6*N* sodium hydroxide (4 ml.) and 1.28% sodium periodate (4 ml.). The indole that was formed was steam distilled out of the mixture, and aliquot parts of the distillate in 50% alcohol were analyzed. A sample (2 ml.) was mixed with 2.5% alcoholic dimethylaminobenzaldehyde solution (1 ml.) and 6*N* hydrochloric acid (1 ml.), and the absorption at 570 mμ was determined. Although the procedure is not a good method of analyzing for III, it gives some measure of the amount of cyclization occurring in the reaction.

1,2,3,4-Tetrahydro-6-methoxy-quinolin-3-ol (IV). This compound was prepared from a bromobenzene solution of II. The bromobenzene extract obtained from the reaction of *p*-anisidine (4.60 g.) and epichlorohydrin (3.0 ml.) was adjusted to a volume of 900 ml. of bromobenzene, and the residual water distilled with a small amount of bromobenzene. Diethylaniline (6 ml.) was added, and the mixture was boiled under reflux for 48 hr. The product was isolated by chromatography in a manner similar to the isolation of III. The product was recrystallized from a mixture of benzene and hexane, 1.30 g. (19.5%), m.p. 73.5–74.5°. An analytical sample melted at 75°.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.95; H, 7.03; N, 7.79.

5-Methylindole. Compound III was oxidized by periodate using essentially the procedure previously reported.[1] A solution of III (200 mg. in 35 ml. of ethanol) and a solution of sodium periodate (626 mg. in 35 ml. of water) were added at about the same rate over a 1.5-hr. period to 100 ml. of an 8% sodium hydroxide solution, and 5-methylindole steam-distilled from the reaction mixture as soon as it was formed. A small amount of 5-methylindole crystallized in the steam distillate which had been saturated with salt, m.p. 57.5–58° (lit. 58.5[4]), but a more efficient recovery was obtained by extracting the indole with ether, removing the ether, extracting the product with a small volume of hot water and adding the hot solution to a saturated, aqueous picric acid solution. The orange-red picrate was recovered, 121 mg. (27%), m.p. 145–148°, with some decomposition (lit. 151°[4]).

5-Methoxyindole. Compound IV was oxidized by the same method that was used for the oxidation of III. The red picrate of 5-methoxyindole was obtained in 10% yield, m.p. 142–144° with some decomposition (lit. 145°[5]).

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Some Properties of Benzenesulfonyl Peroxide

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The published chemistry of benzenesulfonyl peroxide consists of one paper[1] describing its preparation and another[2] describing its decomposition in water to form phenol, sulfuric acid, and (probably) benzenesulfonic acid. We now wish to report our unsuccessful attempts to improve the unsatisfactory yields in its preparation and the results of some exploratory work involving its use as a polymerization initiator and concerning the products of its decomposition in benzene.

Adaptations of several procedures for the preparation of benzoyl peroxide[3–6] involving interaction of benzenesulfonyl chloride and sodium peroxide or hydrogen peroxide failed to give isolable amounts of the sulfonyl peroxide. Benzenesulfonyl chloride failed to react with the urea hydrogen peroxide complex[3] and formed only the sulfonamide with the hydrogen peroxide dicyclohexylamine complex.[7]

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TABLE I

POLYMETHYL METHACRYLATE STUDIES

Sample No.	Cat.	Temp.	Time, Hr.	Cat., Mg.	Monomer, G.	Polymer, G.	Conv., %	Softening Point	Av. Mol. Wt.
I	BSP[a]	25	7	18.2	14.2	2.91	20.4	260–265	2.9×10^5
II	BSP	25	24	18.2	14.2	10.68	75.0	—	9.3×10^5
III	BSP	33	7	18.2	14.2	10.91	77.0	290–300	6.8×10^5
IV	BSP	41	7	18.2	14.2	10.51	74.0	295–300	11.4×10^5
V	BSP	48	7	18.2	14.2	9.96	67.8	290–300	11.6×10^5
VI	BSP	55	7	18.2	14.2	3.31	23.3	260–270	6.2×10^5
VII	BSP	56	7	18.2	14.2	2.54	17.9	—	—
VIII	BSP	70	7	18.2	14.2	1.74	12.3	260–270	—
IX	BP[b]	25	7	14.2	14.2	0.0	—	—	—
X	BP	33	7	14.2	14.2	0.0	—	—	—
XI	BP	41	7	14.2	14.2	0.0	—	—	—
XII	BP	48	7	14.2	14.2	0.0	—	—	—
XIII	BP	55	7	14.2	14.2	2.69	18.9	270–280	14.8×10^5
XIV	BP	70	7	14.2	14.2	9.93	70.0	290–295	9.9×10^5

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

Thus, our only contribution to the preparation of this compound lies in our procedure for crystallization.

In order to determine the ability of benzenesulfonyl peroxide to initiate polymerization, bulk polymerization of methyl methacrylate was effected at several temperatures with the sulfonyl peroxide and with benzoyl peroxide (Table I). It was found through per cent conversion data that benzenesulfonyl peroxide satisfactorily initiated polymerization at temperatures from 25° to 48° whereas benzoyl peroxide did not. Above 54°, the sulfonyl peroxide rapidly lost its effectiveness while benzoyl peroxide began to become effective. Determination of intrinsic viscosities permitted an estimation of average molecular weights.

A more superficial study of the polymerization of styrene (Table II) indicated that benzoyl peroxide was superior to benzenesulfonyl peroxide, while with acrylonitrile (Table III), the two initiators were of comparable effectiveness, the sulfonyl peroxide again being the more effective at lower temperatures. The results of some copolymerizations may be seen in Table IV.

TABLE II

POLYSTYRENE STUDIES

Catalyst	Temp.	Time, Hr.	Cat., Mg.	Monomer, G.	Polymer, G.	Conv., %
BSP[a]	45	112.2	11.8	9.1	0.14	1.5
BP[b]	45	112.2	9.1	9.1	1.29	14.2
BSP	80	7.5	11.8	9.1	0.0	0.0
BP	80	7.5	9.1	9.1	2.68	29.5

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

Since the results of the polymerizations led us to believe that benzenesulfonyl peroxide decomposed to form radicals, the products of its decomposition in benzene were investigated. As anticipated, the reaction effected at room temperature afforded

TABLE III

POLYACRYLONITRILE STUDIES

Catalyst	Temp.	Time, Hr.	Cat., Mg.	Monomer, G.	Polymer, G.	Conv., %
BSP[a]	25	0.58	15.5	12.0	0.33	2.7
BSP	35	0.58	15.5	12.0	1.83	15.3
BSP	45	0.58	15.5	12.0	1.99	16.6
BSP	55	0.58	15.5	12.2	2.10	17.5
BSP	65	0.58	15.5	12.0	1.01	8.4
BP[b]	25	0.58	12.0	12.0	0.0	—
BP	35	0.58	12.0	12.0	0.0	—
BP	45	0.58	12.0	12.0	0.0	—
BP	55	0.58	12.0	12.0	0.5	4.2
BP	65	0.58	12.0	12.0	2.79	23.2

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

phenyl benzenesulfonate in 48–52% yield together with benzenesulfonic acid:

$$(C_6H_5—SO_2—O)_2 + C_6H_5 \longrightarrow C_6H_5—SO_2—O—C_6H_5 + C_6H_5—SO_3H$$

EXPERIMENTAL

Benzenesulfonyl peroxide was prepared essentially by the procedure of Weinland[1] from 6 g. of sodium peroxide, water, and 4 g. of benzenesulfonyl peroxide in the cold. The waxy product was separated by decantation, washed with water, dissolved in 10 cc. of ether. Crystallization was effected by addition of 10 cc. of methanol, cooling in Dry Ice–ethanol, filtration, and washing with very cold methanol. The product, obtained in 8–10% yield, melted with decomposition at 53–54°. The melting point was not altered by recrystallization. The peroxide decomposes, sometimes violently, when kept overnight at room temperature but may be kept for several weeks at −20°.

Polymerization of methyl methacrylate. The monomer was distilled under deoxygenated nitrogen and 15 cc. samples were added to each of 18 tubes (6 containing 18.2 mg. benzenesulfonyl peroxide, 6 containing 14.0 mg. benzoyl peroxide, and 6 controls). The tubes were frozen until placed in the heating bath. After heating at the indicated temperature and time, the tubes were immersed in Dry Ice–methanol and opened. The contents were dissolved in benzene and the polymer was precipitated by excess methanol. Conversion

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.

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

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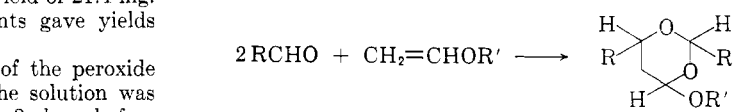
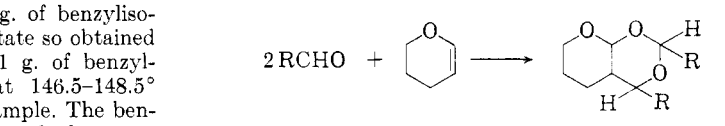
The preparation of 4-alkoxy-2,6-dialkyl-*m*-dioxanes by the acid-catalyzed addition of two moles of an aldehyde to one mole of a vinyl ether has been previously described.[1]



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).