

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Condensation of *o*- and *p*-Bromobenzyl Alcohols with Phenol and 2,6-Dibromophenol in the Presence of Aluminum Chloride

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o- and *p*-bromobenzyl alcohols have been condensed with phenol and 2,6-dibromophenol in the presence of aluminum chloride. The structure of the *p*-hydroxymonobromodiphenylmethanes formed have been proven by independent synthesis. Dimorphism has been shown to exist for the 4-hydroxy-4'-bromodiphenylmethane and one of its derivatives. Previously reported melting points of some of the *p*-hydroxybromodiphenylmethanes and derivatives are corrected.

The contributions of Huston and co-workers from this Laboratory have described the condensation by aluminum chloride of benzyl alcohol,¹ alkyl substituted benzyl alcohols² and halo ring substituted benzyl halides,³ with phenol.

As an addition to this field and as a check on certain compounds reported from this Laboratory, it was considered desirable to investigate the condensation of bromo substituted benzyl alcohols with phenol. *p*-Bromobenzyl alcohol prepared by the reaction of formaldehyde with *p*-bromophenylmagnesium bromide⁴ and *o*-bromobenzyl alcohol prepared by the electrolytic reduction of *o*-bromobenzoic acid⁵ were condensed with phenol in the presence of aluminum chloride to give 4-hydroxy-4'-bromodiphenylmethane and 4-hydroxy-2'-bromodiphenylmethane, respectively. The former exists in two dimorphic crystalline forms.

Independent proofs of the structures of the 4-hydroxy-4'-bromodiphenyl- and the 4-hydroxy-2'-bromodiphenylmethanes were obtained by reduction of the ketones 4-hydroxy-4'-bromobenzophenone and 4-hydroxy-2'-bromobenzophenone. Melting point and mixed melting point determinations showed that the stable (higher melting) form of the condensation product of phenol and *p*-bromobenzyl alcohol was identical with the product of the reduction of 4-bromo-4'-hydroxybenzophenone as was the condensation product of *o*-bromobenzyl alcohol with the product of the reduction of 2-bromo-4'-hydroxybenzophenone. The structures of these two compounds were also confirmed by the direct bromination⁶ to 4-hydroxy-3,5,4'-tribromodiphenylmethane and 4-hydroxy-3,5,2'-tribromodiphenylmethane which were proven by the method of mixed melting points to be identical with the products obtained by the condensation of *p*- and *o*-bromobenzyl alcohol with 2,6-dibromophenol. Debromination of all bromodiphenylmethanes including the two crystalline forms of 4-hydroxy-4'-bromodiphenylmethane was shown to give *p*-benzylphenol.

All condensations took place para to the phenolic hydroxyl group with the formation of benzylated phenols. No ortho-alkylation was observed.

The benzoyl- and benzenesulfonyl esters and α -naphthylurethans of the benzylated phenols were prepared. The benzoyl ester was made from both crystalline forms of the 4-hydroxy-4'-bromo-

diphenylmethane and was not dimorphic. However, dimorphism was shown to exist in the benzene sulfonyl ester.

All phenols were purified by recrystallization, conversion to a suitable ester, hydrolysis of the ester and recovery of the phenol. Each step involved recrystallization to a constant melting point.

Hydrolysis of either form of the dimorphic benzenesulfonyl ester resulted under the conditions used in the higher melting crystalline form of 4-hydroxy-4'-bromodiphenylmethane.

Two crystalline modifications of 4-hydroxy-4'-bromodiphenylmethane were also isolated from condensations between phenol and *p*-bromobenzyl chloride (from direct chlorination of *p*-bromotoluene)³ and between phenol and *p*-bromobenzyl bromide (from direct bromination of *p*-bromotoluene).

The somewhat higher melting points of the hydroxybromodiphenylmethanes and their derivatives³ are undoubtedly due to the use of purer reactants since the methods of preparation of the *o*- and *p*-bromobenzyl alcohols used in this work allows no possible halogen interchange or polyhalogenation. Unpublished work in this Laboratory indicates that direct halogenation of halotoluenes results in some halogen interchange and polysubstitution with consequent difficulty in the purification.

There is, of course, the possibility of dimorphism in the 4-hydroxy-2'-bromodiphenylmethane and the two tribromohydroxydiphenylmethanes. Mixtures of both forms of 4-hydroxy-4'-bromodiphenylmethane were frequently obtained during the many recrystallizations. These mixtures always melted at temperatures between the two forms.

The values obtained in this work should correct those previously reported.³

Experimental

Condensation, isolation of the products of condensation and examination of the products for possible benzyl ethers were by methods previously described.^{7,8}

A summary of the products and yield obtained is given in Table I. A summary of the condensations yielding 4-hydroxy-4'-bromodiphenylmethane are given in Table II.

Recrystallization from the minimum amount of hot petroleum ether, b.p. 60-90°, necessary to dissolve the hydroxydiphenylmethane in all cases yielded long, fine, soft needles, m.p. 64.5-65.0°. Slow recrystallization from twice the minimum amount of solvent yielded a fraction of coarser, shorter needles which melted at 85.0-85.5°, and concentration of the filtrate to one-half the volume gave a fraction melting at 64.5-65.0°. This procedure could be repeated until all the 4-hydroxy-4'-bromodiphenylmethane had a m.p. 85.0-85.5°.

(7) R. C. Huston and Eldridge, *THIS JOURNAL*, **53**, 2260 (1931).

(8) R. C. Huston and others, *ibid.*, **57**, 4669 (1933).

(1) R. C. Huston, *Science*, **52**, 206 (1920); R. C. Huston, *THIS JOURNAL*, **46**, 2775 (1924).

(2) F. A. Hughes, Ph.D. Thesis, M. S. C. Microfilm 1940.

(3) R. C. Huston and others, *THIS JOURNAL*, **55**, 2146 (1933).

(4) F. Ziegler and P. Tiemann, *Ber.*, **55B**, 3414 (1922).

(5) C. Mettler, *ibid.*, **39**, 2937-2938 (1906).

(6) T. Zincke and W. Walter, *Ann.*, **334**, 374 (1904).

TABLE I
CONDENSATIONS

Bromobenzyl alcohol	Phenol	Product Substituted 4-hydroxy-diphenylmethane	Yield, %	M.p., °C.		Analyses Bromine, %	
				This work	Lit. ⁹	Calcd.	Found
Para	Phenol	4 ¹ -Bromo	48-53	64.5-65.0		30.37	30.31
				85.0-85.5	82-83		30.30
Ortho	Phenol	2 ¹ -Bromo	41	83.6-84.2	71-73	30.37	30.38
Para	2,6-Dibromo	3,5,4 ¹ -Tribromo	40-44	88.0-88.2	81-82	56.95	56.73
Ortho	2,6-Dibromo	3,5,2 ¹ -Tribromo	27	89.4-89.8	78-80	56.95	56.78

TABLE II
CONDENSATIONS

Compound condensed	Method of preparation	Product 4-Hydroxy-4'-bromodiphenylmethane	M.p., °C.	Yield, %	Analy- ses, % Bromo- mine, calcd. 30.37 Found
			85.0-85.5		30.33
<i>p</i> -Bromobenzyl chloride	Alcohol + concd. HCl		64.5-65.0	48	30.39
			85.0-85.5		30.40
<i>p</i> -Bromobenzyl chloride	Chlorination of <i>p</i> -bromotoluene		64.5-65.0	47.2	30.30
			85.0-85.5		30.25
<i>p</i> -Bromobenzyl bromide	Bromination of <i>p</i> -bromotoluene		64.5-65.0	50.1	30.29
			85.0-85.5		30.28

fonyl esters were recrystallized from alcohol and the α -naphthylurethans from ligroin, b.p. 60-90°, Table III.

The benzoyl ester made from either crystalline form of 4-hydroxy-4'-bromodiphenylmethane showed identical melting points; mixtures gave no depression.

The benzenesulfonyl esters made from 4-hydroxy-4'-bromodiphenylmethane exhibited dimorphism. Mixed melting points of the two forms were between the melting points of the separate forms.

The ketone 4-hydroxy-4'-bromobenzophenone,⁹ m.p. 191° and 4-hydroxy-2'-bromobenzophenone,¹⁰ m.p. 114° were prepared by the condensation of phenetole with the appropriate bromobenzoyl chloride followed by splitting of the ether by hydrobromic acid. The ketones were reduced by the Huang-Minlon modification of the Wolff-Kishner reduction.¹¹

TABLE III
DERIVATIVES

Substituted 4-hydroxydiphenylmethanes	Melting point, °C.	Benzoyl ester		Benzenesulfonyl ester		α -Naphthylurethan	
		Lit. ⁹	Analyses Bromine, % Calcd. Found	M.p., °C.	Analyses Bromine, % Calcd. Found	M.p., °C.	Analyses Bromine, % Calcd. Found
4 ¹ -Bromo	126.5-127.0	118.5-120	21.77 22.19	68.0-68.4 79.5-80	19.82 19.68 19.71	139.0-140.0	18.62 18.49
2 ¹ -Bromo	76.0-76.5	64-65	21.77 22.46	54.0-54.5	19.82 19.61	151.8-152.4	18.62 18.51
3,5,4 ¹ -Tribromo	147.0-147.8	144-145	45.67 45.93	141.0-141.4	42.74 42.53	162.5-163.0	40.65 40.60
3,5,2 ¹ -Tribromo	107.6-108.0	45.67 45.41	133.2-133.8	42.74 42.49	159.4-160.0	40.65 40.57

Microscopic examination of a melt of either of the dimorphic forms seeded at one side of the melt by crystals of the high melting form and at the other side by crystals of the low melting form showed two typical crystal formations meeting at a common boundary. On standing the boundary moved toward the side seeded with the lower melting crystal until all the unstable form had been consumed.

Benzoyl, benzenesulfonyl esters and α -naphthylurethans were prepared by the usual procedures and recrystallized to constant melting points. The benzoyl and benzenesul-

debromination of the hydroxybromodiphenylmethanes was carried out using Raney nickel.¹²

(9) P. J. Montagne, *Chem. Weekblad.*, **14**, 526 (1917).(10) P. J. Montagne, *Rec. trav. chim.*, **42**, 509 (1923).(11) Huang-Minlon, *THIS JOURNAL*, **68**, 2487 (1946).(12) E. Schwenk, D. Papa and H. Ginsberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 376 (1943).

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Formation and Ring-Opening of Alkene Sulfides

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A mechanism for the transformation of a 1,2-epoxide to a 1,2-sulfide by alkali thiocyanates is proposed, and experimental evidence supporting this mechanism is presented. A synthesis of cyclopentene sulfide, the preparation of which fails by the above method, is described. Various conversions which point to a *trans* ring-opening of cyclohexene sulfide are presented.

A considerable bulk of evidence concerning the mechanism of 1,2-epoxide formation from 1,2-halohydrins and the ring-opening of epoxides has been accumulated in recent years.^{1a} On the other hand, the closely related 1,2-sulfides have been subjected only to a more general type of investigation; studies of the steric and mechanistic aspects of their chemistry have been limited thus far to the direction of ring-opening of propylene sulfide.^{1b}

(1) (a) For a recent review by S. Winstein and R. Henderson, see R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 1; (b) W. Davies and W. E. Savige, *J. Chem. Soc.*, 317 (1930).

It is the purpose of this work to (1) obtain some evidence relating to the mechanism of 1,2-sulfide formation from 1,2-oxides and (2) determine the stereochemical course of the ring opening of 1,2-sulfides leading to products of the type A-C-C-S-B.

Several methods of preparing 1,2-sulfides have been recorded, among which may be mentioned the treatment of 1,2-halothiocyanates or dithiocyanates with sodium sulfide²; the ring-closure of 2-chlorothiols by means of weakly alkaline buffered

(2) M. M. Delépine, *et al.*, *Bull. soc. chim. France*, **27**, 740 (1920); **29**, 136 (1921); **33**, 703 (1923).