

large metal "dry box" through which dry air is passed. Operations are conducted through two holes in the side of the box.

The sample of liquid is poured into the crucible and thoroughly mixed with the solid. Suction is applied to remove any non-adhering liquid; the suction line is then broken. Liquid butane is now prepared. A test-tube is immersed in a solid carbon dioxide-acetone mixture and *n*-butane (Ohio Chemical and Manufacturing Company) is led into this through a glass tube. This operation is also conducted in the dry box. A small amount of the liquid butane (b. p. +0.4°) is poured into the crucible to chill it; a larger addition is then made, and the liquid is mixed with the solid to free the latter from the residue of organic liquid. Suction is again applied. The sample is washed twice more, and then the crucible is weighed (after warming to room temperature).

We cannot claim as yet a very high precision for this method. Thus with methanol containing 20% water, the method gave results in error up to 1%, and the same was true of mixtures containing paraldehyde in addition. Nevertheless, we believe that the simplicity and directness of the method make it worth presentation.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY RECEIVED DECEMBER 10, 1938

Aqueous Solubility of 2,2,3-Trimethylpentanol-3

BY P. M. GINNINGS AND DORIS COLTRANE

The aqueous solubility of the least soluble octanol—normal octanol—has been determined by Butler¹ who found a mean of 0.0586 weight per cent. at 25°. Previous investigations of some lower alcohols² indicate that the most soluble octanol should be 2,2,3-trimethylpentanol-3 and it seemed worth while to measure its solubility. This compound was made by the action of *t*-butylmagnesium chloride on methyl ethyl ketone with the usual Grignard procedure, purified and the solubility measured by the same method used with the other alcohols. Results are given in the table. Although this tertiary octanol is of low solubility, it is more than ten times as soluble as the normal octanol.

(1) Butler, Thomson and MacLennan, *J. Chem. Soc.*, 680 (1933).

(2) (Pentanol) Ginnings and Baum, *THIS JOURNAL*, **59**, 1111 (1937); (hexanol) Ginnings and Webb, *ibid.*, **60**, 1388 (1938); (heptanol) Ginnings and Hauser, *ibid.*, **60**, 2581 (1938).

d_{25}^{25} of pure alc. and b. p. °C. (760 mm.)	Temp., °C.	Wt. % alc.		$d.$ of liquid phase	
				Alc. rich	Water rich
0.8420	20	0.75	98.02	0.8536	0.9975
153-154	25	.69	97.99	.8503	.9964
	30	.64	97.98	.8455	.9951

DEPARTMENT OF CHEMISTRY
GREENSBORO COLLEGE
GREENSBORO, N. C.

RECEIVED DECEMBER 22, 1938

1,4-Diiodobutane from Tetrahydrofuran

BY G. B. HEISIG

The formation of tetrahydrofuran by the action of silver oxide and water with tetramethylene iodide has been reported by Hamonet.¹ The cleavage of the tetrahydrofuran ring to form tetramethylene iodide needed in a study of the action of metals on 1,4-dihalides, however, has not been described. Since other methods of preparing the iodide described by Hamonet and by Marvel and Tanenbaum,² had been tried or eliminated because of the difficulty of obtaining starting materials or satisfactory yields, the reaction between red phosphorus, iodine and tetrahydrofuran was carried out. Tetrahydrofuran (25 g.) was added dropwise to a mixture of 5.8 g. of red phosphorus and 94.5 g. of powdered iodine (added cautiously) placed in a 100-ml. three-necked flask provided with an efficient mechanical stirrer and a reflux condenser. The mixture was refluxed for an hour on a steam-bath and then poured into water. The lower black layer was drawn off and washed with 5% sodium hydroxide until colorless. Sufficient ether was then added until the extract floated on the solution of the base. The ether solution was washed several times with water, dried over calcium chloride and quickly transferred to a 125-ml. vacuum distillation flask fitted with a 10" (25-cm.) vacuum-jacketed side column packed with 1/4" (6-mm.) Fenske glass spiral rings, condensers, etc. Any oxygen present in the fractionating apparatus or in the solution was displaced by a current of nitrogen. After removing the ether, the 1,4-diiodobutane was distilled at a pressure of 1 mm. using a slow current of nitrogen to prevent bumping. A 51% yield (5.5 g.) of a slightly yellowish product boiling at 105-110° was obtained.

Reduction of furan (59 g.) by hydrogen (100 lb. (7 atm.)) with a Raney nickel catalyst (8 g.) at 80° gave a 91% yield of tetrahydrofuran, b. p.

(1) Hamonet, *Ann. chim.*, [9] **10**, 28 (1913).

(2) Hamonet, *Compt. rend.*, **132**, 346 (1901); Marvel and Tanenbaum, *THIS JOURNAL*, **44**, 2650 (1922).

63–66°. No solvent was used. Cloke and Ayers using a nickel catalyst in a Burgess–Parr apparatus³ reported a yield of 80% using *n*-butyl alcohol as a solvent. The furan was obtained by the method described by Wagner and Simons.⁴ The water and carbon dioxide were removed by passing the effluent gases through a mixture of calcium chloride (30) and soda lime (70) instead of sodium hydroxide pellets to avoid clogging the apparatus. The yield was 96%.

The writer wishes to acknowledge a grant from the Graduate School which enabled this work to be done by Mr. P. T. Masley.

(3) Cloke and Ayers, *THIS JOURNAL*, **56**, 2144 (1934).

(4) Wagner and Simons, *J. Chem. Ed.*, **13**, 270 (1933).

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA RECEIVED DECEMBER 3, 1938

The Constitution of the So-called "Phenoldiphenoin"

BY ERNEST H. HUNTRESS AND GILBERT E. MOOS

An analyzed condensation product (m. p. 134°) of diphenic anhydride with phenol was first reported by Dutt.¹ After demonstrating that his product contained two phenolic hydroxyls and that it dissolved in alkali with a reddish-pink color, he assumed for it a structure analogous to phenolphthalein and therefore named it phenoldiphenoin. About the same time Underwood and Kochmann² prepared in this Laboratory by the same process a different but isomeric product (m. p. 250–251°) which unlike Dutt's material gave yellow (not pink) alkaline solutions. In view of its method of preparation and its analysis (C₂₆H₁₈O₄) Underwood also named his product "phenoldiphenoin" and declared: "The statements made by Dutt . . . as to the constitution and properties of phenoldiphenoin . . . appear to be in error."

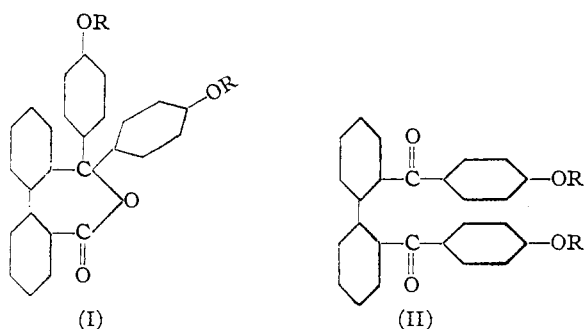
In their second paper Underwood and Kochmann³ wavered between the unsymmetrical (I) and symmetrical (II) formulations for their product (R = H) but because they were unable to obtain any reaction with hydroxylamine and because strong heating above its melting point decomposed their product with some loss of carbon dioxide, they favored the former. Underwood and Barker⁴ later showed that upon alkali fusion of their "phenoldiphenoin" evidence could be

(1) Dutt, *J. Chem. Soc.*, **123**, 226 (1923).

(2) Underwood and Kochmann, *THIS JOURNAL*, **45**, 3073 (1923).

(3) Underwood and Kochmann, *ibid.*, **46**, 2070 (1924).

(4) Underwood and Barker, *ibid.*, **52**, 4082 (1930).



obtained for the formation of *o*-phenylbenzoic acid, phenol and carbon dioxide. Moreover, their compound yielded a potassium salt containing two atoms of metal, and on treatment with methyl iodide and powdered potassium hydroxide gave a product C₂₃H₂₂O₄ (m. p. 150–151°) which they designated as "phenoldiphenoin lactone dimethyl ether." The latter was also obtained in 11% yield from the reaction of diphenic anhydride with anisole in the presence of aluminum chloride. Instead of recognizing that these facts were in complete accord with either formulation (I) or (II) but did not constitute distinguishing proof, they elected to construe the *analogy* to phenolphthalein formation as evidence and made the definite statement that "the structure of phenoldiphenoin is similar to that of phenolphthalein." From this point of view Underwood and his collaborators have never receded. Subsequent to the death of the senior author various substitution products of "phenoldiphenoin" and of "*o*-cresoldiphenoin" were reported⁵ and although their absorption spectra⁶ proved to be quite unlike those to be expected from analogs of phenolphthalein, the name "diphenoins" was retained throughout these papers.

In the meantime Bachmann⁷ reported the preparation of 2,2'-dianisoylbiphenyl as the result of Ullmann coupling of two molecules of 2-bromo-4'-methoxybenzophenone, obtained from *o*-bromobenzonitrile and *p*-methoxyphenylmagnesium bromide. The structure of his diketone is thus unimpeachable. Neither Bachmann nor Underwood, however, recognized that this 2,2'-dianisoylbiphenyl would be identical with the latter's "phenoldiphenoin lactone dimethyl ether" if phenoldiphenoin has the symmetrical structure of type (II).

Work on this problem has been in progress in

(5) Underwood and Barker, *ibid.*, **58**, 642 (1936).

(6) Underwood, Harris and Barker, *ibid.*, **58**, 643 (1936).

(7) Bachmann, *ibid.*, **54**, 1972 (1932).