

for four seconds, at 40° for nine seconds, and at -20° for thirty-five seconds.

Tetraphenylmethane derivatives containing the following substituents also show phosphorescence, although less marked: 4-hydroxy, 2,4-dihydroxy, 4-methoxy, 2,4-dimethoxy, 4-ethoxy, 4-amino, 4-methylamino, 4-ethylamino, 4-*n*-butylamino, 4-dimethylamino, 4-diethylamino, 4-di-*n*-butylamino, 4-amino-3-methyl, 4-amino-3,5-dimethyl. The color of the after-glow varies from green to blue, with visible durations of two to twelve seconds.

α -Triphenylmethylpyrrole, in which one of the phenyl groups of tetraphenylmethane has been replaced by a pyrrol group, gives a green after-glow with a duration of nine seconds. Compounds of silicon, tin, and lead, which are structurally analogous to tetraphenylmethane, also show phosphorescence. Tetraphenylsilane² and tetra-*p*-tolylsilane² show bright green phosphorescence lasting about twenty seconds. Tetra-*p*-xenylsilane,² on the other hand, does not phosphoresce under these conditions. Tetraphenyltin and tetraphenyllead both show phosphorescence, that of the latter substance being very weak at room temperature.

Kirchoff³ has reported that fluorene and benzoin on irradiation with light from a mercury vapor lamp show phosphorescence with a visible duration of several seconds. Both these substances, however, under conditions used in these experiments, give no visible after-glow. Nevertheless, several organic substances unrelated to tetraphenylmethane, as succinic acid, resorcinol, and sucrose, which do show phosphorescence, were encountered. It is known⁴ that very small traces of impurities, particularly triphenylmethane dyes, are responsible for the phosphorescence of many solid organic compounds. If this is the case with tetraphenylmethane and related substances, it would seem that this series of compounds provides a favorable "grundmaterial" for organic phosphors. The presence of traces of triphenylmethane dyes in the tetraphenylmethanes themselves seems quite possible, although such impurities would not be expected in the silicon, tin, and lead analogs.

The following tetraphenylmethane derivatives were prepared by a modification of the method used by Fischer⁵

(2) These substances were kindly furnished by Mr. C. M. Saffer, Jr., cf. Schumb, Ackermann and Saffer, *THIS JOURNAL*, **60**, 2486 (1938).

(3) Kirchoff, *Physik. Z.*, **30**, 240 (1929).

(4) Lenard, Schmidt and Tomaschek, "Handbuch der Experimentalphysik," Vol. XXIII, part 1, "Phosphoreszenz-Fluoreszenz," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928, p. 561.

(5) Fischer, *Z. physiol. Chem.*, **115**, 92 (1921).

for the preparation of 4-dimethylaminotetraphenylmethane.

4 - Ethylaminotetraphenylmethane.—Triphenylcarbinol (3.5 g.), and ethylaniline (5 g.) were added to a solution prepared from glacial acetic acid (20 cc.), hydrochloric acid (sp. gr. 1.19) (4 g.), and acetic anhydride (4 g.), and the mixture refluxed for one hour. On pouring into 100 cc. of 25% alcohol containing 10 g. of sodium hydroxide, a brown oil separated, and gradually solidified. The solid was washed thoroughly with water, dried, and purified by crystallization from ligroin (b. p. 70-80°), with the use of decolorizing carbon: yield 2 g.; m. p. 172-173°.

Anal. Calcd. for C₂₇H₂₅N: C, 89.22; H, 6.93; N, 3.85. Found: C, 89.16; H, 6.97; N, 3.76, 3.85.

4 - *n* - Butylaminotetraphenylmethane was prepared similarly from *n*-butylaniline. Purified by several recrystallizations from absolute alcohol, the yield was 2 g.; m. p. 135-136°.

Anal. Calcd. for C₂₉H₂₉N: C, 88.96; H, 7.46; N, 3.58. Found: C, 88.96; H, 7.50; N, 3.63.

4-Diethylaminotetraphenylmethane.—From diethylaniline; recrystallized from ligroin (b. p. 90-120°); yield 2.6 g.; m. p. 177.5-178.5°. *Anal.* Calcd. for C₂₉H₂₉N: C, 88.96; H, 7.46; N, 3.58. Found: C, 88.92; H, 7.51; N, 3.62, 3.63.

4 - Di - *n* - butylaminotetraphenylmethane.—From di-*n*-butylaniline; recrystallized from ligroin (b. p. 90-120°); yield 2.6 g.; m. p. 177-178°. *Anal.* Calcd. for C₃₃H₃₇N: C, 88.54; H, 8.33; N, 3.13. Found: C, 88.56; H, 8.35; N, 3.18, 3.14.

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RESEARCH LABORATORY OF ORGANIC CHEMISTRY
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The Determination of Water in Organic Liquid Mixtures

BY R. A. DAY, JR., AND ROBERT N. PEASE

We have wished to determine water in a complex mixture of alcohols, aldehydes, acids and peroxides resulting from the oxidation of hydrocarbons. A simple method which gives promise of some usefulness is the following.

The sample of liquid is added to a weighed sample of powdered anhydrous copper sulfate. After thorough mixing, the solid is filtered off, washed with liquid butane, and again weighed. The gain in weight is taken as the water content of the sample.

Use is made of a Jena sintered glass Gooch crucible of 15 cc. capacity. A sample of powdered anhydrous copper sulfate equal to two to three times that required for the formation of the trihydrate is weighed into the crucible. This is then set up in a filter flask, which stands in a

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.

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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

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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).