

## NOTES.

*The Copper Sulphide-catalysed Dimerisation of isoButylene.* By A. WASSERMANN and W. T. WELLER.

It has been shown that copper sulphide, activated by conversion of a part of its surface into copper sulphate, acts as a catalyst for the low-molecular polymerisation of *isobutylene* (Wassermann, B.P. 499,953). We have now found that in this reaction at least 40% of the starting material is converted into a mixture of the 2 : 2 : 4-trimethylpentenes, which are also obtained if *tert.*-butyl alcohol is treated with sulphuric acid (cf. Edgar, *Ind. Eng. Chem.*, 1927, 19, 146).

*isoButylene* was prepared from purified *tert.*-butyl alcohol (m. p. 25°) by a method similar to that indicated by Deanesly (U.S.P. 2,012,785); it was bubbled through water, dried with solid potassium hydroxide, and redistilled, a middle fraction boiling between -7° and -6° (761 mm.) being used. The catalyst was made by slowly adding 1.4 l. of 1M-sodium sulphide solution to 5 l. of 0.3M-cupric sulphate; the precipitate was filtered off (filter press), washed with water, spread in a thin layer on a tray, and dried for 24 hours at 80° in a stream of continuously renewed dry air at atmospheric pressure. 180 G. of catalyst were obtained, which contained 79—80% of cupric sulphide and 16—17% of cupric sulphate. 30 G. of this catalyst, 125 g. of *isobutylene*, and some nitrogen were introduced into a stainless-steel autoclave, which was placed for 100 hours in an oil-bath kept at 150° ± 0.5°, the pressure decreasing during this time from 30 to 26 atm. After being cooled to room temperature, the degassed liquid product weighed 95 g.; 80 g. of this (*viz.*, 100 cm.<sup>3</sup>) boiled below 125°, and this fraction (I) was further investigated. It was left for 12 hours in contact with solid potassium hydroxide and then redistilled through a 10-inch reflux column. The fractions thus obtained are characterised by the data in lines 1—4 of Table I. The dimer (II), referred to in line 5, was an authentic mixture of the two 2 : 2 : 4-trimethylpentenes prepared according to Edgar (*loc. cit.*; cf. also Tongberg, Pickens, Fenske, and Whitmore, *J. Amer. Chem. Soc.*, 1932, 54, 3706). The mixed m. p.'s listed in the last two lines were determined by using 50/50 mixtures. Both I and II consumed slightly more than 2 atoms of bromine per mol. of dimer.

TABLE I.

Dimer.	Fraction No.	Boiling range (760.5 mm.).	Vol. (cm. <sup>3</sup> ).	M. p.	$n_D^{20}$ .	$d_4^{20}$ .	
I	}	1	<100°	16	-97° ± 2°	1.4058	—
		2	100—101	44	-98° ± 2°	1.4109	0.7184
		3	101—102	22	-104° ± 2°	1.4111	—
		4	>102	18	—	—	—
II	—	101.1—102.2	140	-104° ± 1°	1.4109	0.7180	
I (Fraction 2) + II	—	—	10	-99° ± 1°	—	—	
I (Fraction 3) + II	—	—	10	-104° ± 1°	—	—	

TABLE II.

	Boiling range (760.0 mm.).	% of initial vol.	M. p.*	$n_D^{20}$ .	$d_4^{20}$ .
Hydrogenated dimer I .....	99—100°	86	-106° ± 1°	1.3918	0.6920
Authentic 2 : 2 : 4-trimethylpentane .....	99.4	—	-107°	1.3915	0.6918

\* The mixed m. p. of these two specimens was -106°.

In order further to identify the dimer I, fractions 2 and 3 were catalytically hydrogenated by shaking, at room pressure and temperature, with carefully purified hydrogen and 5 g. of a platinum oxide catalyst prepared according to Adams and Shriner (*J. Amer. Chem. Soc.*, 1923, 45, 2171). When 70% of the theoretically required volume of hydrogen had been consumed, the catalyst appeared to be poisoned, probably by traces of sulphur compounds in I; the theoretical amount of hydrogen was taken up when 9 g. of a fresh platinum catalyst, prepared according to Vavon (*Ann. Chim. Phys.*, 1914, 1, 144), were added. The hydrogenated product was stable towards bromine; it was dried with calcium chloride and redistilled. The fractions thus obtained are characterised by the data in Table II, which contains for comparison data relating to authentic 2 : 2 : 4-trimethylpentane (Edgar, *loc. cit.*; Smith and Matheson, *J. Res. Nat. Bur. Stand.*, 1938, 20, 641; Brooks, *ibid.*, 21, 847).—DEPARTMENT OF CHEMICAL TECHNOLOGY, IMPERIAL COLLEGE, LONDON, S.W.7. [Received, May 1st, 1946.]

*Improved Preparation of 4 : 4'-Diaminobenzil and 2 : 2'-Dihydroxybenzil.* By HERBERT L. GEE  
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THE preparation and bacteriostatic properties of 4 : 4'-diaminobenzil (I) were described by Kuhn, Möller, and Wendt (*Ber.*, 1943, **76**, 405), the compound being obtained by reduction of 4 : 4'-dinitrobenzil by hydrogenation or by ferrous sulphate and ammonia. Precise details of the mode of reduction are not given, the yield is not stated, and 4 : 4'-diaminobenzoin is obtained as a by-product.

We have found that (I) can most readily be prepared from *p*-aminobenzaldehyde, which, after acetylation, can be converted into 4 : 4'-*diacetamidobenzoin* by potassium cyanide in alcohol. The benzoin was oxidised almost quantitatively to the benzil by copper sulphate and pyridine, and hydrolysis with hydrochloric acid then yielded (I). The yield of the benzoin was rather poor (*ca.* 30%), but the ready availability of 2 : 2'-dimethoxybenzil with aluminium chloride in nitrobenzene. This procedure is not applicable to the preparation of the compound in quantity, and we have found that quantitative demethylation can readily be accomplished by heating the dimethoxy-compound with pyridine hydrochloride.

*p*-Aminobenzaldehyde and 4-acetamido-2-methoxybenzaldehyde both failed to undergo benzoin condensation with boiling alcoholic potassium cyanide.

2 : 2'-Dihydroxybenzil was prepared by Kuhn, Birkhofer, and Möller (*Ber.*, 1943, **76**, 900) by demethylation of 2 : 2'-dimethoxybenzil with aluminium chloride in nitrobenzene. This procedure is not applicable to the preparation of the compound in quantity, and we have found that quantitative demethylation can readily be accomplished by heating the dimethoxy-compound with pyridine hydrochloride.

4 : 4'-*Diacetamidobenzoin*.—Crude *p*-aminobenzaldehyde (from 40 g. of *p*-nitrotoluene) was stirred with acetic anhydride (50 c.c.). When the exothermic reaction was complete, the mixture was poured into water and the *p*-acetamidobenzaldehyde collected and recrystallised twice from aqueous alcohol. *p*-Acetamidobenzaldehyde (10 g.), alcohol (30 c.c.), and potassium cyanide (1 g.) were refluxed for 2 hours. The mixture was diluted with water, and next day the 4 : 4'-diacetamidobenzoin (2.8 g.) which had separated was collected and recrystallised from acetic acid; m. p. 244—246° (Found: C, 66.2; H, 5.8.  $C_{13}H_{13}O_4N_2$  requires C, 66.5; H, 5.5%).

4 : 4'-*Diaminobenzil*.—Copper sulphate (3 g.), pyridine (5 c.c.), and water (2 c.c.) were heated until a homogeneous solution was obtained. 4 : 4'-Diacetamidobenzoin (2 g.) was added and the mixture was kept for 2 hours at 100° with occasional stirring and then poured into water. The product (1.8 g.) was filtered off and recrystallised from acetic acid. The diacetyl derivative was boiled with concentrated hydrochloric acid (10 c.c.) for 0.5 hour. On cooling, the dihydrochloride which had separated was collected and dissolved in water, and the 4 : 4'-diaminobenzil (1.2 g.) precipitated with ammonia. After being recrystallised from alcohol it had m. p. 169°.

2 : 2'-*Dihydroxybenzil*.—2 : 2'-Dimethoxybenzil (20 g.) and pyridine hydrochloride (40 g.) were mixed and heated at 180° for 2 hours. After cooling, water was added, and the crude product collected, dissolved in 10% sodium hydroxide solution, filtered from impurities, and precipitated with dilute acid. After recrystallisation from acetic acid it had m. p. 154—155°. Yield, 16.5 g.

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