TABLE I
RATE DATA FOR THE REACTION OF 4-TRITYLPYRIDINE WITH ETHYL IODIDE 65°

Time, min.	$HClO_4$, ml.	$\frac{1}{a-x}$	k_2, l. mole^{-1} sec.$^{-1}$
		Run I	
0	. . .	14.5	
11	11.00	14.85	4.7×10^{-4}
30	10.67	15.32	
60	10.10	16.15	
90	9.58	17.04	
120.5	9.00	18.12	
		Run II	
0	. . .	14.5	
10	9.00	14.7	
30	8.51	15.36	4.4×10^{-4}
60	8.15	16.05	
90	7.79	16.79	
120	7.37	17.82	

cal effect of the triphenylmethyl group. It can be calculated from other data[5] that the reaction between unsubstituted pyridine and ethyl iodide at 65° has a velocity constant (k_2) of 4.5×10^{-4} l. mole^{-1} sec.$^{-1}$. Since the reaction of 4-tritylpyridine with ethyl iodide proceeds at almost the identical rate, it is clear that the introduction of the triphenylmethyl group into the 4-position of pyridine has no effect on the rate at which it undergoes the Menschutkin reaction. It can be concluded with confidence, therefore, that the failure of 2-triphenylmethylpyridine to react with ethyl iodide can be attributed entirely to the steric bulk the triphenylmethyl group provides in the vicinity of the nitrogen atom.

Experimental

2-Triphenylmethylpyridine.—Potassium amide [from 6.0 g. (0.15 g.-atom) potassium] was prepared in 500 ml. of liquid ammonia in a 1000-ml. flask. Iron oxide was used as the catalyst. To this amide solution was added 9.3 g. (0.1 mole) of 2-picoline, followed by the dropwise addition of 26 g. (0.23 mole) of chlorobenzene. Then, a solution of potassium amide (from 6 g. of potassium metal) in about 400 ml. of liquid ammonia was siphoned into this mixture, and the resulting solution was refluxed for 1 hr. Ammonium chloride (25 g.) was added, and the solvent allowed to evaporate overnight. Water and benzene were introduced into the reaction flask, and, after vigorous agitation, both layers were filtered. The benzene layer was separated and the solvent removed. The dark crystals which formed were filtered, washed thoroughly with cold ethanol, and recrystallized from an ethanol–benzene mixture. One gram of colorless crystals, melting at 236–237.5°, was obtained. The literature[6] m.p. is 241°.

The liquid filtrate (a dark, viscous oil) from above was extracted with 8 *N* hydrochloric acid. The acid layer was neutralized and extracted with benzene. That portion of the extract boiling above 210° at 12 mm. was collected and crystallized. An additional 0.7 g. of product was obtained (total yield 5%) in addition to a mixture (5.4 g.) of 2-benzyl- and 2-benzyhydrylpyridine.

4-Triphenylmethylpyridine.—The same procedure was employed for the 4-isomer as is described above for the 2-isomer. A yield of 1.5 g. (5%) of crystals melting (after crystallization from ethanol–benzene) at 264.5–265° was obtained.

Anal. Calcd. for $C_{24}H_{19}N$: C, 89.7; H, 5.92; N, 4.37. Found: C, 89.53; H, 6.15; N, 4.40.

Menschutkin Reaction Rates.—The rate of reaction of ethyl iodide with 2- and 4-triphenylmethylpyridine was measured at 65° using the technique developed by Brown and Cahn.[5] Since this method has been described in detail previously, it will not be repeated here.[7] The results are listed in Table I and plotted in Fig. 1.

Acknowledgment.—The authors are grateful to the Monsanto Chemical Company for financial assistance which made this work possible.

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(6) P. H. Dirstine and F. W. Bergstrom, *J. Org. Chem.*, **11**, 55 (1946).

(7) Details can also be found in the Ph.D. thesis of F. S. Clark, Purdue University, 1960.

The Reaction of 2,3,5-Trimethylphenol with Triphenylcarbinol

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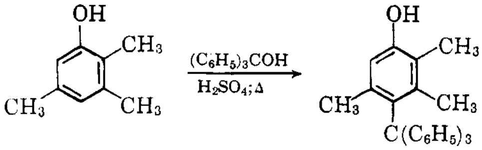
Received May 15, 1962

It has been reported[1] that 2,3,5-trimethylphenol condenses with triphenylcarbinol in the presence of sulfuric acid (Baeyer–Villiger reaction[2]) to form 2,3,5-trimethyl-4-triphenylmethylphenol. The analysis reported[1] for compound I was acceptable, but no structure proof was offered. In view of the steric requirements of the triphenylmethyl group, it seemed quite surprising that such a hindered phenol could be tritylated under these conditions.



(I)

m.p. 170°

When the tritylation reaction was repeated in our laboratory, two products were isolated. One of these was identified as triphenylmethane, and the other was a material melting about 200° with decomposition after crystallization from dimethyl sulfoxide. The latter product, upon prolonged reflux with potassium hydroxide in ethylene glycol, gave a low yield of a phenol with the formula $C_{18}H_{22}O_2$.

It could be shown that the sulfur present in the high-melting product was a result of its crystallization from dimethyl sulfoxide. The crude product contained no sulfur. When the crude material was crystallized from dimethylformamide

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(1) Ng. Ph. Buu-Hoï and R. Rips, *J. Org. Chem.*, **22**, 666 (1957).

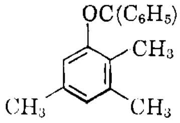
(2) D. V. N. Hardy, *J. Chem. Soc.*, 1000 (1929).

instead of dimethyl sulfoxide, the purified product contained nitrogen instead of the sulfur. The solvent could be removed from these crystalline solvates by vacuum drying at elevated temperatures. When the dark, amorphous material which remained after this treatment was pyrolyzed in vacuum, only 2,3,5-trimethylphenol was formed. This would indicate that the high-melting product was in reality a solvated low molecular weight polymer of the starting phenol.

It is clear from the foregoing results, that 2,3,5-trimethyl-4-triphenylmethylphenol (I) is *not* a product of the tritylation reaction as was originally reported.[1] Instead, it appears that the triphenylmethyl carbonium ion (generated from triphenylcarbinol and acid) oxidizes the phenol by hydride abstraction. Triphenylmethane is produced as the reduction product, and a low molecular weight polymer of the phenol as the oxidation product. The product which was isolated by treating this oxidation product with base (formula $C_{18}H_{22}O_2$) is apparently a dimer of the starting phenol ($C_9H_{12}O$).

It is not completely clear what material the earlier workers[1] had in hand which they formulated as compound I. The best guess seems to be that it was a fortuitous mixture of triphenylmethane and polymeric 2,3,5-trimethylphenol. A one-to-one molar ratio of these two materials would have an analysis approximately correct for the tritylation product they reported (I).

In order to eliminate the possibility that compound I was in reality the O-tritylated ether (II), an authentic sample of the latter was prepared for comparison. It was found to melt sharply at 81–82°, and hence was not identical to the material reported as compound I.



II

Experimental

Reaction of 2,3,5-Trimethylphenol with Triphenylcarbinol.—Five grams (0.019 mole) of purified triphenylcarbinol was added to 5.0 g. (0.037 mole) of 2,3,5-trimethylphenol dissolved in 70 ml. of warm glacial acetic acid. This was followed by the dropwise addition of 8.0 g. of concentrated sulfuric acid. The resulting deep red solution was allowed to stand several hours, during which time a mass of crystals formed. These were filtered and subjected to prolonged extraction with hot ethanol. Concentration and cooling of the ethanol extract gave 4.7 g. (98%) triphenylmethane melting at 91–92°. This material had an identical infrared spectrum with an authentic sample of triphenylmethane, and gave an undepressed mixed melting point.

The ethanol-insoluble residue was crystallized from dimethyl sulfoxide, washed with ether, and dried (4.1 g., 80% based on triphenylmethane produced). It melted at 199–201° dec. A sample which had been recrystallized three times from dimethyl sulfoxide gave the following analysis: C, 71.63, 70.88, 71.15; H, 7.37, 7.51, 7.70; S, 5.29.

The material contained no sulfur before crystallization (sodium fusion) from dimethyl sulfoxide.

When the original acid solution was poured onto ice, a brown crystalline mass precipitated, which, upon crystallization from ethanol–water gave 2.2 g. (44%) of recovered 2,3,5-trimethylphenol, m.p. and mixed m.p. 98–100°.

Treatment of High-Melting Product with Base.—Addition of 2.0 g. of the product melting at 199–201° to 5.0 g. of molten potassium hydroxide (*caution*!) followed by quenching in cold water yielded a yellow solid. Extraction of the solid with pentane and cooling gave about 0.5 g. of 2,3,5-trimethylphenol (m.p. and mixed m.p. 98–100°). The residue, after several crystallizations from ethanol, yielded 0.8 g. of a white powder melting at 165–166°.

To a solution of 20 g. of potassium hydroxide in 20 ml. of water and 120 ml. of ethylene glycol was added 10 g. of the high-melting material (199–201°) described above. After 5 days of reflux, 7.5 g. of starting material was filtered off. When the filtrate was poured into water, a flocculent precipitate formed, which, after crystallization from methanol, yielded 1.4 g. of a white powder melting at 165–166°. A mixed melting point and an infrared spectrum showed that this material was identical to that isolated above from the potassium hydroxide fusion.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15; mol. wt. 270. Found: C, 79.61; H, 8.60; mol. wt. (Rast) 265.

Identification of High-Melting Product.—Recrystallization of the high melting product (199–201°) from dimethylformamide instead of dimethyl sulfoxide, led to a white powder melting at 132–135°. This material contained nitrogen, but no sulfur. The last traces of dimethylformamide were removed by vacuum drying at 150°, leaving an amorphous tan solid melting at 210–220° dec. When this material was recrystallized from dimethyl sulfoxide, the material melting with dec. at 200–205° again made its appearance. This material contained sulfur but no nitrogen. The dimethyl sulfoxide was removed from this material by vacuum drying, and it was then pyrolyzed at 200° in vacuum. The pyrolysate was nearly pure 2,3,5-trimethylphenol (m.p. and mixed m.p. 97–99°). A *p*-toluenesulfonate of this material melted at 91° and was identical with the same derivative prepared from an authentic sample of 2,3,5-trimethylphenol in the customary fashion.

Anal. Calcd. for $C_{16}H_{18}O_3S$: C, 66.2; H, 6.21. Found: C, 66.22; H, 6.34.

2,3,5-Trimethylphenyl Triphenylmethyl Ether (II).—The sodium salt of 2,3,5-trimethylphenol was prepared by treating the phenol with an equivalent amount of sodium hydroxide in water. The water was evaporated, and the salt was dried in a vacuum desiccator. The product (2.1 g.; 0.0133 mole) was treated with trityl chloride (3.7 g.; 0.0133 mole) in a solution of dimethoxyethane for 3 days at room temperature. After filtration, water was added to the filtrate. The crystals which formed were submitted to chromatography on an alumina column. Development and elution were effected with 15% benzene–85% petroleum ether (65–67°). Recrystallization from 95% ethanol gave a product melting at 81.5–82.5°.

Anal. Calcd. for $C_{28}H_{26}O$: C, 88.9; H, 6.9. Found: C, 88.85; H, 7.03.

Acknowledgment.—The authors are grateful to the Monsanto Chemical Company and the National Science Foundation for financial support which made this work possible.