Further chlorination of the Schiff's base of α-chlorbutyraldehyde is possible to the dichloro derivative. Products derived from the chlorinated butyraldehydes were not found in this investigation but have been reported by Wright.[3]

The results indicate that di-*n*-butylamine free radicals in carbon tetrachloride undergo mainly a bimolecular disproportionation reaction. In the Hofmann–Löffler reaction the radical is protonated and is prevented from undergoing this disproportionation by the repulsion of the positive charges.

Experimental[4]

Di-*n*-butylamine (11.6 g.) was chlorinated in pentane by the method of Coleman.[5] The yield of N-chlorodi-*n*-butylamine based on active halogen titration was 85%. This yield varied in other runs from 85–95%. The pentane was removed under reduced pressure at 0° and carbon tetrachloride (100 ml.) was added to the residue. The resulting solution was irradiated with an ultraviolet lamp for 1140 hr., after which time no more active halogen could be detected. The white solid (5.93 g.) obtained proved to be di-*n*-butylamine hydrochloride from its elemental analysis. The infrared spectra were identical with that of an authentic sample.

The filtrate was made alkaline and steam distilled. The distillate upon concentration to 100 ml. and treatment with sodium hydroxide and benzenesulfonyl chloride gave a sticky solid (2.8 g.) which melted at 80.5–81.5° after three recrystallizations from 80% ethanol. This product from its elemental analysis proved to be *n*-butylbisbenzenesulfonimide.

Anal. Calcd. for $C_{16}H_{19}NS_2O_4$: C, 54.39; H, 5.38. Found: C, 54.21; H, 5.37.

Since the literature[6] reports a melting point of 89–90°, an authentic sample was synthesized by treating *n*-butylamine with benzenesulfonyl chloride in alkali and found to melt at 81–82°. A mixture melting point and infrared spectra of the two samples were identical.

Acknowledgment.—The authors wish to express their appreciation to Smith, Kline and French Laboratories for a fellowship which made this investigation possible.

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The Reaction of 2- and 4-Triphenylmethylpyridine with Ethyl Iodide

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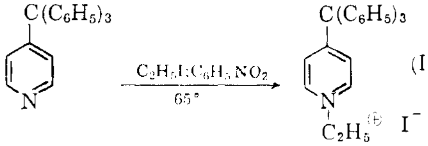
Received May 15, 1962

Several years ago we reported[1] that when the triphenylmethyl group is attached to an aromatic ring it functions as a neutral entity, *i.e.*, like hydrogen it is neither electron-supplying or -withdrawing. This conclusion was reached by a determination of its sigma constant, which was essentially zero.

Recently, in connection with another problem, we had occasion to measure the rates of reaction of 2- and 4-triphenylmethylpyridine with ethyl iodide. The results completely substantiate our earlier conclusion regarding the electrical effect of the triphenylmethyl group and provide graphic illustration of the steric bulk of this group.

The reaction of tertiary amines (like 2- and 4-triphenylmethylpyridine) with alkyl halides (Menschutkin reaction) has received considerable study.[2-4] For example, Professor Brown has used this reaction in a most effective way to demonstrate steric bulk in both the amine molecule as well as the alkyl halide.[5] Simple bimolecular kinetics are invariably observed in these reactions.



(I)

Table I lists representative rate data that were obtained for the reaction of 4-tritylpyridine with ethyl iodide (equation 1 above). The data for run I in this table are plotted in Fig. 1. *Significantly, 2-triphenylmethylpyridine did not react appreciably with ethyl iodide even after fifty hours under the same reaction conditions.*

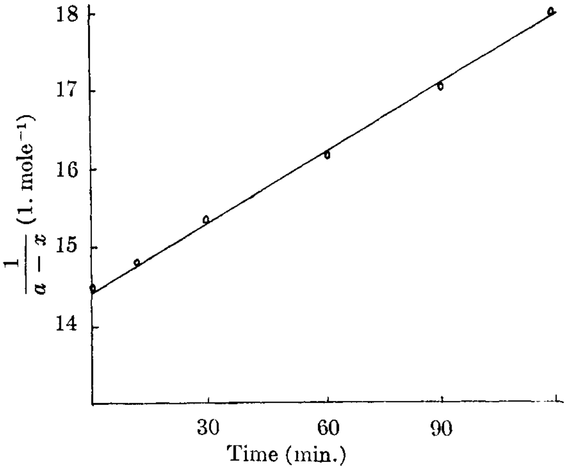


Fig. 1.—Rate data (run I) for the reaction of 4-triphenylmethylpyridine with ethyl iodide at 65°.

The data in Table I clearly substantiate our earlier conclusion[1] concerning the negligible electri-

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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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[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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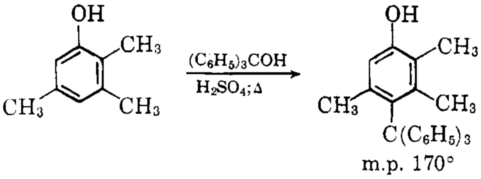
Received May 15, 1962

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)

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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