TABLE II

DISTRIBUTION OF ISOMERS IN THE MONONITRATION OF THE MONOALKYLBENZENES

Compound	Ortho	Meta	Para
Toluene[a]	58.45	4.4	37.15
Ethylbenzene[b]	45.0	6.5	48.5
Isopropylbenzene[c]	30.0	7.7	62.3
t-Butylbenzene[d]	15.8	11.5	72.7

[a] Ref. 4. [b] Previously reported (ref. 5): 55% ortho, 45% para. [c] Previously reported (ref. 6): 14% ortho, 86% para. [d] Ref. 2.

isomers formed in the mononitration of the alkylbenzenes are summarized in Table III.

TABLE III

ISOMER RATIOS FOR THE MONONITRATION OF THE MONOALKYLBENZENES

Compound	Isomer ratios *o/p*	*o/m*	*p/m*
Toluene	1.57	13.3	8.45
Ethylbenzene	0.93	6.9	7.45
Cumene	.48	3.9	8.1
t-Butylbenzene	.217	1.37	6.32

It is apparent that the ortho/para ratio decreases sharply with increasing steric requirements of the alkyl group. Since both ortho and para positions are sensitive to both polar and resonance factors, this trend alone is not significant. However, since the para/meta ratios are sensibly constant in the series we can conclude that there is no marked change in the resonance factor in this series. Therefore, the marked decrease in both the ortho/para and the ortho/meta ratios can only be attributed to a powerful steric influence of the alkyl group on substitution in the ortho position.

Recognition that *ortho* substitution must be strongly influenced by the steric requirements of both the substituent and the substituting agent should provide a valuable diagnostic tool in the study of reaction mechanisms. For example, it has frequently been suggested that Friedel–Crafts acylation of aromatics involves attack by the acylonium ion.[7]

$$C_6H_6 + RCO^+ \longrightarrow C_6H_5COR + H^+$$

However, it is generally agreed that the acylation of toluene results in the practically exclusive formation of the para isomer.[8] Since the steric requirements of the acylonium ion must be small, it follows that some other intermediate of larger steric requirements must be involved in the substitution stage.

Experimental Part

Nitration.—The ethylbenzene and isopropylbenzene were Phillips pure grade. The nitrations were carried out as described earlier[2] in lots of 2–4 moles of hydrocarbon. The yields of mononitro product were approximately 80%. The products were first distilled at 13 mm. through a Todd Precise Fractionation Assembly (12 × 900 mm. column packed with 1/8″ glass helices) and intermediate fractions were then rerectified with a miniature Podbielniak column (8 mm. × 24″ Heligrid Hastelloy packing).

***m*-Nitroisopropylbenzene.**—The meta isomer has not previously been isolated. However, since both the *o*- and *p*-nitroisopropylbenzenes are well known compounds, the third plateau could only be the meta isomer. The physical properties also correspond to those expected for the meta derivative ($\Delta n^{20}D$ for *m*- and *p*-: Et, 0.0069; *i*-Pr, 0.0066; *t*-Bu, 0.0064).

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.38; H, 6.73; N, 8.86.

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(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, pp. 295–297.

(8) R. Pajeau, *Bull. soc. chim.*, [5] **13**, 544 (1946).

The Rearrangement of 1,1-Diphenyl-3-bromopropanone with Diethylamine. A Correction

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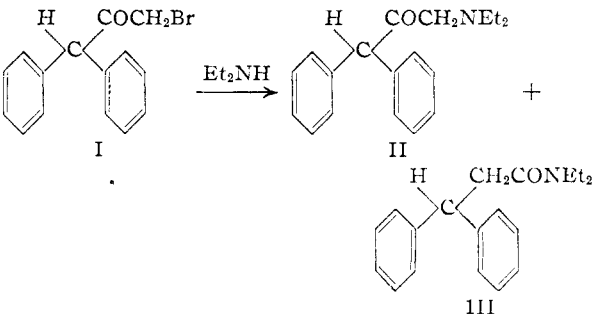
It was reported[1] recently that when 1,1-diphenyl-3-bromopropanone (I) was allowed to react with diethylamine, only the displacement product, 1,1-diphenyl-3-diethylaminopropanone (II) could be isolated. This reaction has been further investigated and we should now like to report that the rearrangement product, N,N-diethyl-3,3-diphenylpropionamide (III) is also formed although in low yield (7–15%).[2]



Experimental

Rearrangement of 1,1-Diphenyl-3-bromopropanone with Diethylamine.—A solution of 5.0 g. of the bromoketone[1] in 50 ml. of anhydrous ether was allowed to react with 5.0 ml. of diethylamine. After the exothermic reaction had subsided, the mixture was allowed to stand for 24 hours at room temperature and then filtered. The filtrate, washed free of excess diethylamine, was extracted with dilute hydrochloric acid and dried over anhydrous magnesium sulfate. Evaporation of the ether gave a yellow oil which solidified upon standing[3]; yield of crude oil was 1.24 g. Recrystallization of the material from petroleum ether (30–60°) gave pure amide, m.p. 76–77° (lit.[4] 76°), yield 0.74 g. (15%).

Processing of the above acid extract, as described previously,[1] yielded the aminoketone II as the hydrochloride, m.p. 186–187°, yield 3.4 g. (62%).

Hydrolysis of N,N-Diethyl-3,3-diphenylpropionamide (III).—A solution of 0.53 g. of amide, 5 ml. of glacial acetic acid and 5 ml. of concentrated hydrochloric acid was heated under reflux for one week. The acid so obtained amounted to 0.17 g. (40%), m.p. 154–155°, no depression upon admixture with an authentic sample of 3,3-diphenylpropionic acid.

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(1) W. G. Dauben, C. F. Hiskey and M. A. Muhs, THIS JOURNAL, **74**, 2084 (1952).

(2) Further studies on the reaction of α-haloketones with amines will be published later by Dodson and Morello.

(3) The isolation of the amide sometimes is rendered difficult due to the presence of unreacted bromo ketone in this neutral fraction and the mixture must be seeded with the amide.

(4) N. Maxim, *Ann. chim.* (*Paris*), [10] **9**, 106 (1928).