Anal. Calcd. for $C_{13}H_{10}NOBr$: C, 56.54; H, 3.65. Found: C, 56.55; H, 3.72.

3-Bromoperinaphthanol-7 (III).—To 9.5 g. of 3-bromoperinaphthanone-7 in 250 ml. of dry ether there was added 110 ml. of a 0.1 *M* ethereal solution of lithium aluminum hydride. The reaction mixture was allowed to stand for a few minutes at room temperature with stirring and then the excess reagent was decomposed by the addition of moist ether. Sufficient hydrochloric acid was added to just dissolve the precipitated hydroxides, the ether layer was separated and, after being washed with dilute alkali and water, the ethereal solution was dried over magnesium sulfate. Concentration of the ethereal solution gave 9.3 g. of a white solid. When this was recrystallized from a benzene–cyclohexane mixture, it gave 8.0 g. (84%) of white needles, m.p. 117–119° dec. A sample which was recrystallized several more times for analysis, melted at 120–122° dec. Since this compound is unstable to light and air, it is best stored in the dark under a layer of cyclohexane.

Anal. Calcd. for $C_{13}H_{11}OBr$: C, 59.33; H, 4.21. Found: C, 59.37; H, 4.05.

The phenylurethan of 3-bromoperinaphthanol-7 was prepared and obtained, after recrystallization from benzene, as soft white needles, m.p. 174–175° dec.

Anal. Calcd. for $C_{20}H_{16}NO_2Br$: C, 62.84; H, 4.22. Found: C, 62.79; H, 4.19.

Hydrogenation of 3-Bromoperinaphthanol-7.—To establish the fact that 3-bromoperinaphthanol-7 contained the perinaphthane skeleton a 1.0-g. sample of this compound in absolute ethanol was subjected to hydrogenation at room temperature and atmospheric pressure in the presence of Adams catalyst. Two moles of hydrogen was absorbed before hydrogenation was complete and, at the end of the reduction, bromide ion was shown to be present in the solution. After removal of the catalyst and solvent, the residue was taken up in pentane and purified by chromatography over alumina. Concentration of the pentane eluate gave 0.6 g. of a colorless oil which was identified as perinaphthane through formation of the corresponding picrate and *sym*-trinitrobenzene derivatives. The *sym*-trinitrobenzene derivative was obtained as yellow needles, m.p. 158–159.5°, and the picrate derivative was obtained as orange needles, m.p. 149–150°. Fieser and Hershberg give the melting points for the picrate and *sym*-trinitrobenzene derivatives of perinaphthane as 150–151° and 160–161°, respectively.[9] It is apparent that hydrogenolysis of the bromine and hydroxyl groups occurred during the catalytic reduction. The fact that perinaphthane was isolated from the reduction is adequate proof that the compound referred to as 3-bromoperinaphthanol-7 does indeed have this structure. This was important to know in view of the negative results obtained in the succeeding experiment.

Attempts to Convert 3-Bromoperinaphthanol-7 to 3-Bromoperinaphthene (IV).—The attempts to convert 3-bromoperinaphthanol-7 (III) to 3-bromoperinaphthene (IV) were carried out using anhydrous ethanolic hydrogen bromide following the same general procedure used previously for the preparation of perinaphthenes using ethanolic hydrogen chloride.[2,3] In a typical example, the yellow solution of 3-bromoperinaphthanol-7 in ethanolic hydrogen bromide was boiled under reflux for one-half hour, then cooled to Dry Ice temperature and the yellow solid, which separated, was removed by filtration in the cold. Thereupon, it immediately turned from yellow to deep-green in color and finally became a black amorphous solid melting above 360°. Various experiments were tried in which *sym*-trinitrobenzene, mercuric bromide, silver perchlorate and pyridine were added individually to solutions of 3-bromoperinaphthanol-7 in ethanolic hydrogen bromide in the hope that a stable complex would result. None of these attempts were successful. That ethanolic hydrogen bromide was a suitable reagent for the type of dehydration desired was shown by the fact that it could be used to effect the conversion of 8-methylperinaphthanol-7 to 8-methylperinaphthene[3,4] in high yield.

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(9) L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **60**, 1658 (1938).

Distribution of Isomers in the Mononitration of Ethyl- and Isopropylbenzene. Further Evidence for a Steric Effect in Isomer Distribution[1]

BY HERBERT C. BROWN AND W. HALLAM BONNER

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The isomer distribution in the mononitration of *t*-butylbenzene was recently reported from this Laboratory[2] and by Hughes and his co-workers.[3] The results showed a marked decrease in the ortho isomer as compared with the distribution realized in the nitration of toluene.[4]

Data have previously been reported for the isomer distribution in the nitration of ethylbenzene[5] and isopropylbenzene.[6] However, in neither of these studies did the investigators observe the formation of the meta isomers. From the results with toluene[4] and *t*-butylbenzene, considerable quantities of the meta nitro derivatives should be formed. It was therefore decided to investigate the nitration of these two hydrocarbons to permit a comparison of the ortho/meta and para/meta ratios in the products as the alkyl group is systematically varied from methyl to *t*-butyl. Modern fractionation equipment greatly simplifies the task of obtaining accurate values for the isomer distribution.

The hydrocarbons were nitrated with mixed acid (22.3% HNO_3, 65.6% H_2SO_4, 12.1% H_2O) and the products were fractionated in an efficient fractionating column. The individual fractions were analyzed using the refractive index values for the purified compounds. The physical properties are summarized in Table I.

TABLE I

PHYSICAL CONSTANTS FOR THE MONONITRO COMPOUNDS OF ETHYL- AND ISOPROPYLBENZENE

Ethylbenzene	B.p.,[d] °C.	$n^{20}D$	Lit. val.
2-NO_2	109	1.5352	1.5334[a]
3-NO_2	115.5	1.5390	
4-NO_2	126	1.5459	1.5455[a]
Isopropylbenzene			
2-NO_2	115	1.5248	1.5259[b]
3-NO_2[c]	125	1.5303	
4-NO_2	134	1.5369	1.5367[b]

[a] S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, THIS JOURNAL, 69, 1032 (1947). [b] W. G. Brown and H. Reagan, *ibid.*, 69, 1032 (1947). [c] Compound not previously reported. [d] All b.p.'s taken at 13 mm.

The results on the distribution of isomers are tabulated in Table II together with earlier data for toluene and *t*-butylbenzene.

As was pointed out previously,[2] the meta position in these compounds should be relatively insensitive to resonance effects and it therefore furnishes an excellent standard of reference. The ratios of

(1) Based upon a thesis submitted by W. Hallam Bonner in partial fulfillment of the requirements for the Ph.D. degree, June, 1952.

(2) K. L. Nelson and H. C. Brown, THIS JOURNAL, **73**, 5605 (1951).

(3) H. Cohn, E. D. Hughes, M. H. Jones and M. A. Peeling, *Nature*, **169**, 291 (1952).

(4) W. W. Jones and M. Russell, *J. Chem. Soc.*, 921 (1947).

(5) E. L. Cline and E. E. Reid, THIS JOURNAL, **49**, 3150 (1927).

(6) G. Vavon and A. Collier, *Bull. soc. chim.*, **49**, 3150 (1927).

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

BY R. M. DODSON, EDWIN F. MORELLO AND WM. G. DAUBEN

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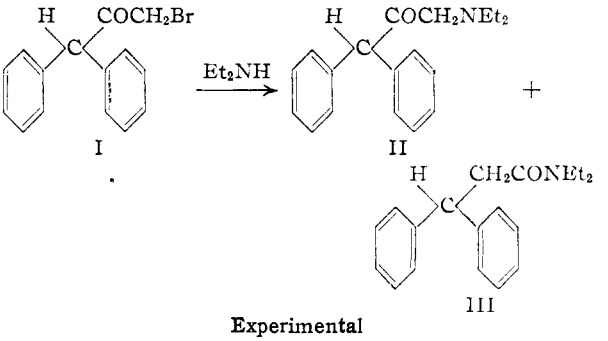
It was reported[1] recently that when 1,1-diphenyl-3-bromopropanone (I) was allowed to react with diethylamine, only the displacement product, 1,1-diphenyl-3-diethylaminopropanone (II) could be isolated. This reaction has been further investigated and we should now like to report that the rearrangement 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).