Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.7. Found: C, 79.51, 79.61; H, 6.78, 6.71.

Its **1,3,5-trinitrobenzene complex**, yellow needles from aqueous ethanol, melted at 122° (reported 121–122°,[2] 122–123°[1b]).

trans-**x,x-Dibromo-3,5-dimethoxystilbene**, white needles from ethanol, m.p. 134.5–135.0° (reported 135–136°[5]), was prepared as described by Erdtman.[6]

Potassium Permanganate Oxidation.—*trans*-3,5-Dimethoxystilbene (3 g.) was refluxed for two hours with neutral potassium permanganate in acetone. The manganese dioxide was dissolved by treating with sodium bisulfite and sulfuric acid and a colorless precipitate (1.7 g.) was collected, dissolved in dilute sodium hydroxide and reprecipitated with dilute hydrochloric acid. The acid thus obtained was recrystallized from water to yield colorless needles of 3,5-dimethoxybenzoic acid, m.p. 184–185°.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.53; neut. equiv., 182.2. Found: C, 59.27, 59.33; H, 5.56, 5.54; neut. equiv., 184, 183.

The acid filtrate was concentrated and extracted with ether; from this extract, a second acid, identified as benzoic acid, m.p. 120°, neut. equiv. 124 after crystallization from water, was obtained by alkaline extraction. The neutral fraction, 0.07 g., oil, yielded a 2,4-dinitrophenylhydrazone of m.p. 235–237° corresponding to that of benzaldehyde.

We wish to thank Dr. Julius A. Kuck and Dr. Robert C. Hirt of these laboratories for the microanalyses and ultraviolet spectra, respectively.

(6) H. Erdtman and G. Erdtman, *Ber.*, **74B**, 5 (1941).

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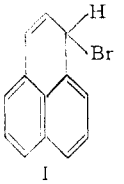
A Synthesis of 3-Bromoperinaphthanol-7

BY V. BOEKELHEIDE AND MARTIN GOLDMAN[1]

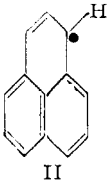
RECEIVED AUGUST 21, 1953

The two most important factors in the stabilization of long-lived radicals, such as triphenylmethyl, are generally considered to be the added resonance stabilization of the radical over that of its dimer and the steric hindrance which lowers the strength of the bond formed during dimerization. It would be highly desirable to study these factors independently of each other and it was with this purpose in mind that we recently investigated the preparation and bromination of perinaphthene.[2]

It was hoped that 9-bromoperinaphthene (I) would result and this could then be converted by standard procedures to the perinaphthenyl radical II. Because of its high degree of symmetry the perinaphthenyl radical should be highly stabilized by resonance, although there should be little or no steric hindrance to its dimerization. Thus, if the perinaphthenyl radical could be prepared, its properties would serve as an indication of the importance of resonance stabilization for long-lived radicals.

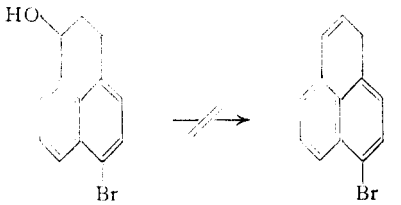


I



II

Unfortunately, attempts to obtain 9-bromoperinaphthene by the bromination of perinaphthene led only to highly colored solutions and intractable tars. We have therefore investigated other approaches which might be expected to yield 9-bromoperinaphthene (I) or its equivalent. As described in the Experimental section, we have converted α-methylnaphthalene to 3-bromoperinaphthanol-7 (III). It was hoped that this alcohol could be dehydrated in the usual fashion to give 3-bromoperinaphthene (IV). In view of recent experiments on the isomerization of perinaphthene derivatives,[3,4] it would be expected that solutions containing either IV or I would give the same tautomeric mixture of compounds and therefore a synthesis of IV would be equivalent to a synthesis of I. However, all attempts to convert 3-bromoperinaphthanol-7 to IV were unsuccessful. Highly colored amorphous solids were formed much as in the previous attempts to synthesize I. Although the lack of stability of bromoperinaphthene (I or IV) may be related to the high reactivity of the allylic halogen, attempts to stabilize the product through the formation of complex salts were also unsuccessful.



III IV

Experimental[5]

3-Bromoperinaphthanone-7.—This was prepared from α-methylnaphthalene in an over-all yield of 32%. The four steps employed in this conversion can be summarized as follows: (1) α-methylnaphthalene was brominated following the procedure of Mayer and Sieglitz[6] and gave 1-methyl-4-bromonaphthalene as a pale yellow oil (b.p. 152–154° at 12 mm., picrate, m.p. 126–127°) in 76% yield. (2) The photobromination of 1-methyl-4-bromonaphthalene was carried out according to the general procedure indicated by Wislicenus[7] and afforded 1-bromomethyl-4-bromonaphthalene as white crystals, m.p. 102–104°, in 46% yield. This bromination was also carried out using N-bromosuccinimide and benzoyl peroxide as reagents, but the latter method is less convenient than the direct photobromination and the yield of the desired product is essentially the same. (3) The conversion of 1-bromomethyl-4-bromonaphthalene to β-(4-bromo-1-naphthyl)-propionic acid by alkylation with malonic ester followed by alkaline hydrolysis was carried out following the procedure described by Fieser and Gates[8] for the preparation of β-(1-naphthyl)-propionic acid. The acid was obtained in 96% yield as white crystals, m.p. 146.5–148°.[6] (4) The cyclization of β-(4-bromo-1-naphthyl)-propionic acid was accomplished by means of anhydrous hydrogen fluoride following the procedure of Fieser and Gates for the preparation of perinaphthanone-7.[8] From 10.0 g. of β-(4-bromo-1-naphthyl)-propionic acid, there was obtained 8.8 g. (94%) of 3-bromoperinaphthanone-7 as pale yellow crystals, m.p. 96–97°, after recrystallization from cyclohexane.

Anal. Calcd. for $C_{13}H_9OBr$: C, 59.79; H, 3.47. Found: C, 59.99; H, 3.47.

The oxime of 3-bromoperinaphthanone-7 was obtained, after recrystallization from ethanol, as light yellow needles, m.p. 192–193° dec.

(1) Beaunit Mills Predoctoral Fellow, 1951–1952.
(2) V. Boekelheide and C. Larrabee, THIS JOURNAL, **72**, 1245 (1950).
(3) V. Boekelheide and C. Larrabee, *ibid.*, **72**, 1240 (1950).
(4) V. Boekelheide and M. Goldman, *J. Org. Chem.*, in press.
(5) Analyses by Miss Claire King. All melting points corrected.
(6) F. Mayer and A. Sieglitz, *Ber.*, **55**, 1835 (1922).
(7) W. Wislicenus, *ibid.*, **49**, 2822 (1916).
(8) L. F. Fieser and M. D. Gates, THIS JOURNAL, **62**, 2335 (1940).

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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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

RECEIVED JUNE 15, 1953

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).