Semicarbazone.—Recrystallized from *ca.* 80% ethanol, the semicarbazone melted at 184–185° (cor.).

Anal. Calcd. for $C_{18}H_{23}N_3OSi$: N, 12.92. Found: N, 13.09.

***m*-Bromophenyltrimethylsilane.**—*m*-Bromophenyltrimethylsilane was prepared by an adaptation of a procedure of Gilman and Melvin.[13] *n*-Butyllithium[13] (0.132 mole) was added to a stirred solution of *m*-dibromobenzene in 100 ml. of ether over a ten-minute period. Occasional application of an ice-bath was necessary in order to prevent excessive refluxing. When all the butyllithium had been added, stirring was continued at room temperature for an additional 25 minutes. To this reaction mixture was then added a solution of 14.1 g. (0.13 mole) of trimethylchlorosilane and 50 ml. of ether over a 10-minute period. Stirring was continued for two hours at room temperature and refluxing for an additional half hour. The reaction mixture was then hydrolyzed with dilute hydrochloric acid. The ethereal layer was separated, washed once with water, separated, and then dried over Drierite. After the ether had been stripped off, the residue was distilled to yield 5.1 g. (17%) of a material boiling at 96–97° (5 mm.), $n^{20}D$ 1.5290.

Anal. Calcd. for $C_9H_{13}BrSi$: Si, 12.24. Found: Si, 12.1.

***p*-Tolyl *m*-Trimethylsilylphenyl Ketone.**—Two grams (0.0088 mole) of *m*-bromophenyltrimethylsilane in 30 ml. of ether was refluxed with 0.26 g. (0.011 g. atom) of magnesium turnings for four hours. This Grignard reagent was filtered under nitrogen, and to the filtrate was added 0.59 g. (0.005 mole) of *p*-tolunitrile in 10 ml. of ether. Refluxing was continued for four more hours, the mixture was hydrolyzed and worked up as in the preparation of *p*-tolyl *p*-trimethylsilylphenyl ketone. Distillation of the residue at 0.5 mm. yielded 1.1 g. (82%) of material boiling at 130–131°. This fraction was taken up in warm ethanol and refrigerated. There was obtained a crystalline material melting at 40–42°. Recrystallization yielded a product melting at 43–44°. A mixed m.p. with the ketone prepared through the Friedel–Crafts reaction was not depressed.

LAFAYETTE, IND.

NOTES

The Isolation of *trans*-3,5-Dimethoxystilbene from Tall Oil

BY HANS ALBRECHT AND EDWARD H. SHEERS

RECEIVED SEPTEMBER 2, 1953

3,5-Dimethoxystilbene has been isolated from several natural sources[1,2] and Erdtman[1c] has shown by a study of their ultraviolet spectra that 3,5-dihydroxystilbene and its methyl ethers occur naturally only in the *trans* form.

In the course of some work on the unsaponifiable constituents of tall oil fatty acids, there was obtained by batch vacuum refractionation of unsaponifiables extracted from commercial tall oil fractionation heads,[3] a fraction boiling at 203–208° (4 mm.) which showed a strong absorption near 300 mμ. From this fraction 3,5-dimethoxystilbene was isolated as its picrate and identified by its physical properties and those of several of its derivatives and by oxidation to benzaldehyde, benzoic acid and 3,5-dimethoxybenzoic acid.

3,5-Dimethoxystilbene shows strong absorption at 300 mμ.[4] Since only one other unsaponifiable fraction (b.p. 170–171° at 4 mm.) showed an appreciable absorption in this region, and since the absorption of that fraction was such that $k_{300} = {}^1/_2(k_{280} + k_{320})$ (approximately), where k is the specific absorptivity, it was assumed that a linear background absorption should give satisfactory values for *trans*-3,5-dimethoxystilbene content. Therefore, the formula

$$\%\ trans\text{-}3,5\text{-Dimethoxystilbene} = 100\ \frac{k_{300} - 0.5(k_{280} + k_{320})}{38.5}$$

was derived from k values obtained with pure 3,5 dimethoxystilbene ($k_{280} = 78.8$; $k_{300} = 119$; $k_{320} = 82.2$) and used to determine the *trans*-3,5-dimethoxystilbene content of crude and distilled tall oil and of tall oil rosin.

The quantity of *trans*-3,5-dimethoxystilbene present in the unsaponifiables of crude and distilled tall oil is appreciable (*cf.* Table I). It is interesting to note that tall oil rosin,[5] unlike wood and gum rosins, contains no detectable amounts of *trans*-3,5-dimethoxystilbene.

TABLE I

trans-3,5-DIMETHOXYSTILBENE CONTENT OF TALL OIL AND TALL OIL DISTILLATION PRODUCTS

	% *trans*-3,5-Dimethoxystilbene		Unsaponifiables in product, %
	In unsaponifiables	In product	
Crude tall oil[5]	7.4	0.54	7.3
Distilled tall oil[5]	18.0	.32	1.8
Tall oil rosin[5]	Not detected[a]	..	5.0

[a] Estimated lower limit of detection, 0.02%.

Experimental

Ultraviolet absorption spectra were obtained using a Beckman spectrophotometer, Model DUV, and a Cary automatic recording spectrophotometer, Model 11.

Isolation of *trans*-3,5-Dimethoxystilbene.—An unsaponifiable fraction from tall oil, boiling at 203–208° (4 mm.) and weighing 0.597 g. in ethanol was treated with a saturated ethanolic picric acid solution. The yellow picrate which crystallized immediately was collected after standing overnight, 0.633 g., m.p. 109–110°, unchanged on recrystallization from ethanol. The picrate was cleaved by partition between benzene and dilute ammonia. The residue from the benzene solution solidified after standing two days, m.p. 55°. After two recrystallizations from ethanol, large colorless needles melting at 57° were obtained; boiling point 206° (3.8 mm.), $n^{25}D$ (supercooled melt) 1.5600.

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(1) (a) H. Erdtman, *Svensk Papperstidn.*, **46**, 226 (1943); (b) *Svensk Kem. Tid.*, **56**, 95 (1944); (c) *ibid.*, **56**, 134 (1944).

(2) R. F. B. Cox, THIS JOURNAL, **62**, 3512 (1940).

(3) Arizona Chemical Co., 30 Rockefeller Plaza, New York 20, N. Y.

(4) Spectrum to be published in *Applied Spectroscopy*, Vol. 8.

(5) Tall Oil Rosin, as defined under the Naval Stores Act (Regulations for the Administration and Enforcement of the Naval Stores Act, Feb. 8, 1952, paragraphs 160.2 and 160.305.)

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).

AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT

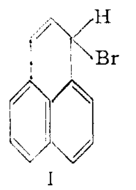
A Synthesis of 3-Bromoperinaphthanol-7

BY V. BOEKELHEIDE AND MARTIN GOLDMAN[1]

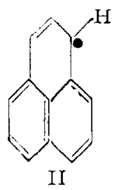
RECEIVED AUGUST 21, 1953

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.

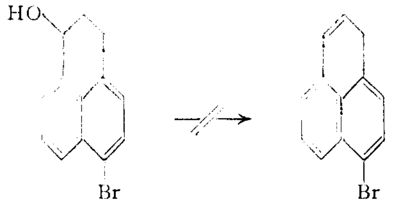


I



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[5] 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.

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(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).