volume of chloroform, and the resulting emulsions were broken up by centrifuging. Per 650 ml of production medium about 110 mg of iodinin was obtained, $\lambda_{max}^{CHCl_3}$ 530 nm (ϵ 6300) [reported[8] 530 nm (ϵ 6340)] and mp 236° dec (reported[9] 224–225° dec).

Labeled Feeding and Extraction of Active Pigments.—[6-^{14}C]-D-Shikimic acid (1 μCi, 35.6 μCi/μmol) was fed in two equal portions under sterile conditions to two 1-l. production media of *Ps. aureofaciens* each in a 2800-ml Fernbach flask, which had been grown for 12 hr at 28.5°. Growth was continued for 12 hr and phenazine-1-carboxylic acid extracted and purified as described.[1] The yield was 151 mg. The material showed an incorporation of 36% (100 × total activity isolated over total activity fed). It was diluted 3.56 times in chloroform with inactive phenazine-1-carboxylic acid.

After 44 hr of growth 1 μCi of [6-^{14}C]-D-shikimic acid was added under sterile conditions in two equal portions to each of two 650-ml production media of *Chr. iodinum*, when the characteristic purple color of iodinin was not yet apparent. The color appeared at 46 hr. Growth was continued for another 32 hr and the pigment was extracted after a total of 78 hr: yield 206 mg, 34% incorporation of fed activity. The compound was diluted 2.00 times in pyridine with inactive iodinin, obtained from previous inactive productions.

1,6-Dihydroxyphenazine from Iodinin.—Iodinin (200 mg) in 100 ml of dioxane (AR) were added to 200 mg of reduced PtO_2 in 50 ml of dioxane. Reduction at atmospheric pressure and room temperature was complete in 30 min after an uptake of 3 mol of H_2. The colorless solution, presumably of 1,6-dihydroxy-5,10-dihydrophenazine, was filtered whereupon it rapidly turned yellow. Upon passing O_2 through the solution a golden yellow color was soon attained. Evaporation yielded 171 mg (98%) of gold-brown crystals of 1,6-dihydroxyphenazine, mp 271–278° (reported[10] 274°).

Pyrazinetetracarboxylic Acid from 1,6-Dihydroxyphenazine.—A 109-mg sample was oxidized in 2 ml of 1% KOH with 7.7 ml of 17% hot $KMnO_4$ as described,[1] in 45% yield.

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Registry No.—**1a**, 2538-68-3; **1c**, 68-81-5; **2**, 138-59-0.

(8) N. Gerber and M. P. LeChevalier, *Biochemistry*, **3**, 598 (1964).
(9) H. P. Sigg, *Helv. Chim. Acta*, **50**, 716 (1967).
(10) H. Akabori and M. Nakamura, *J. Antibiotics (Tokyo) Ser. A*, **12**, 17 (1959).

Nucleophilic Displacement Reactions on 4-Bromoisophorone

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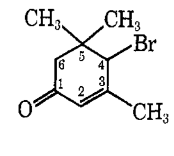
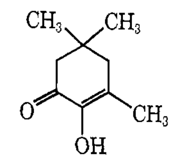
Marx and coworkers[1] have recently reported their work of nucleophilic displacements on 4-bromoisophorone (**1**) with NaOH and silver acetate. They obtained the 2-substituted products (**2** and **3**) in addition to other materials and no 4-substituted derivatives (**4a** and **4b**) as earlier reported.[2] Based upon the results of the earlier workers, we had hoped to prepare several 4-thio and 4-sulfonyl derivatives of isophorone


1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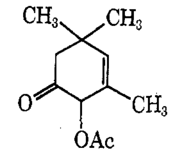
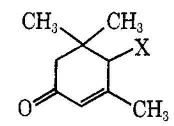
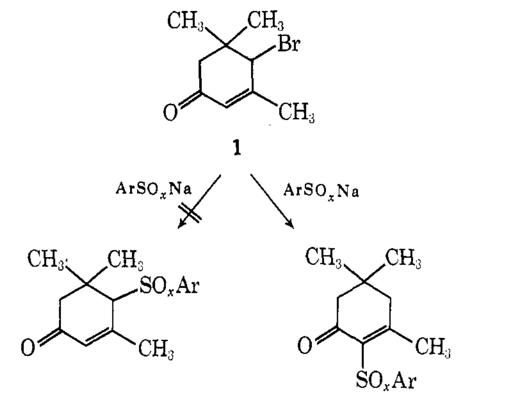

3


4a, X = OH
b, X = OAc

(**5** and **6**) *via* nucleophilic displacement upon 4-bromoisophorone as shown in Scheme I. The products obtained, however, were the 2-substituted materials **7** and **8**.

SCHEME I



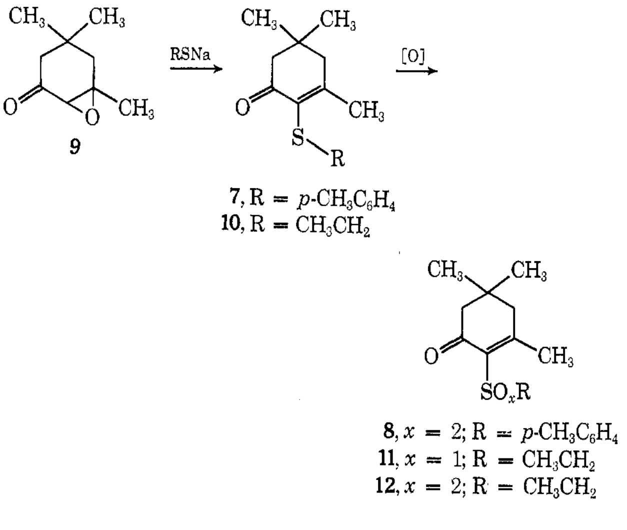
5, Ar = p-$CH_3C_6H_4$; x = 0 **7**, Ar = p-$CH_3C_6H_4$; x = 0
6, Ar = p-$CH_3C_6H_4$; x = 2 **8**, Ar = p-$CH_3C_6H_4$; x = 2

The structural assignments of these products were based on nmr and ir analyses and alternate synthesis. The nmr data given in the Experimental Section support the assignments made. The ir spectra of the 2-thio and 2-sulfonyl derivatives exhibited a carbonyl band at 1675–1680 cm^{-1} characteristic of a conjugated cyclohexenone.[3] The carbonyl band in 2-ethylsulfinylisophorone (**11**) appeared at 1650 cm^{-1}.

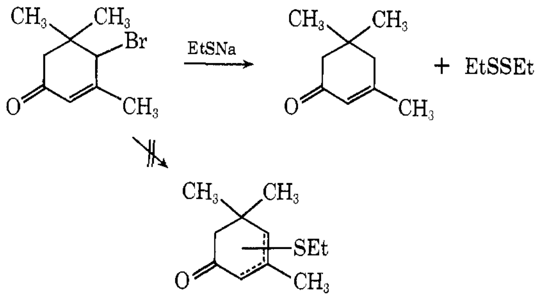
2-p-Toluenethioisophorone (**7**) was alternatively synthesized by reaction of sodium p-toluenethiolate with 2,3-isophorone oxide[4] (**9**) (Scheme II). Oxidation of **7** with m-chloroperbenzoic acid yielded **8**. Tomoeda and coworkers[5] have published the synthesis and nmr spectrum of 2-ethylthioisophorone (**10**) and therefore the preparation was repeated as shown in Scheme II for comparison of spectrum. The 2-ethylsulfinylisophorone (**11**) and 2-ethylsulfonylisophorone (**12**) were formed from **10** and the nmr spectra of these derivatives compared well with those of the corresponding p-tolyl analogs. Treatment of 4-bromoisophorone with sodium ethylthiolate gave isophorone and ethyl disulfide and no ethylthio-substituted isophorone (Scheme III), with displacement apparently occurring on the bromine and not on a carbon atom. Our work

(1) J. N. Marx, A. W. Carnrick, and J. H. Cox, *J. Org. Chem.*, **37**, 2308 (1972).
(2) A. J. B. Edgar, S. H. Harper, and M. A. Kazi, *J. Chem. Soc.*, 1083 (1957).
(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 148.
(4) G. B. Payne, *J. Org. Chem.*, **24**, 719 (1959).
(5) M. Tomoeda, M. Inuzuka, T. Furuta, M. Shinozuka, and T. Takahashi, *Tetrahedron*, **24**, 959 (1968).

Scheme II



Scheme III



supports the observations made by Marx, Carnrick, Cox[1] suggesting that nucleophilic reactions on 4-bromoisophorone take place in an S$_N$2′ fashion with formation of 2-substituted derivatives and not in an S$_N$2 reaction as earlier proposed.[2]

Experimental Section[6]

Preparation of 2-p-Toluenethioisophorone (7). Method A.—In 50 ml of EtOH was dissolved 2.3 g (0.10 mol) of sodium metal and to the solution was added 13.8 g (0.10 mol) of 90% *p*-toluenethiol. The sodium thiolate solution was then added to a solution of 21.7 g (0.10 mol) of 4-bromoisophorone dissolved in 100 ml of EtOH. After stirring for 5 hr, the precipitated NaBr was filtered and the filtrate was diluted with 100 ml of H_2O and extracted with CH_2Cl_2. The organic layer was reduced *in vacuo*, leaving 26 g of product, an oily liquid. A portion of the product was purified by distillation: bp 140–142° (0.07 mm); nmr ($CDCl_3$) δ 1.03 (s, 6, 5-$(CH_3)_2$–), 2.25 (s, 3, 3-CH_3), 2.25 (s, 3, $CH_3C_6H_4$–), 2.38 (s, 2, 6-CH_2–), 2.45 (s, 2, 4-CH_2–), 7.05 (s, 4, aromatic). This material was oxidized as given below to 2-*p*-toluenesulfonylisophorone (8).

Method B.—In 200 ml of EtOH was dissolved 10.1 g (0.44 mol) of sodium metal. To the solution was added 61 g (0.44 mol) of 90% *p*-toluenethiol and then 17 g (0.11 mol) of 2,3-isophorone oxide.[4] The solution was stirred for 12 hr and then diluted with 500 ml of H_2O. Extraction with CH_2Cl_2 and washing with H_2O and 0.1 *N* NaOH afforded 29 g of product upon removal of solvent *in vacuo*. A portion of the product was distilled, bp 142–144° (0.05 mm).

Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74; S, 12.32. Found: C, 73.48; H, 7.81; S, 12.34.

This material was shown by ir and nmr to be identical with that prepared by method A.

(6) All melting points are uncorrected. Infrared spectra data were obtained on a Perkin-Elmer Infracord spectrophotometer as Nujol mulls or neat. All nmr spectra were obtained on a Varian A-60 spectrometer in deuteriochloroform using TMS as the internal standard. Elemental analyses were obtained from the Analytical Services Laboratory of The Dow Chemical Co.

Preparation of 2-p-Toluenesulfonylisophorone (8). Method A.—To 10.8 g (0.05 mol) of 4-bromoisophorone[2] dissolved in 50 ml of DMF was added 8.9 g (0.05 mol) of sodium *p*-toluenesulfinate. The mixture was heated on a steam bath for 13 hr with precipitation of NaBr. The reaction mixture was then diluted with 200 ml of H_2O and extracted with CH_2Cl_2. The organic layer was washed with H_2O and reduced *in vacuo*, leaving 9.5 g (65% yield) of product which was recrystallized (EtOH): mp 147–149°; nmr ($CDCl_3$) δ 0.93 (s, 6, 5-$(CH_3)_2$–), 2.18 (s, 2, 6-CH_2–), 2.37 (s, 3, 3-CH_3), 2.52 (s, 2, 4-CH_2–), 2.58 (s, 3, CH_3-C_6H_4–), 7.25 and 7.83 (m, 4, *J* = 8.0 Hz, aromatic).

Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.72; H, 6.89; S, 10.97. Found: C, 65.46; H, 6.89; S, 11.18.

Method B.—To 18.8 g (0.072 mol) of 2-*p*-toluenethioisophorone prepared *via* displacement of sodium *p*-toluenethiolate as shown above dissolved in 140 ml of $CHCl_3$ was added 30.4 g (0.15 mol) of 85% *m*-chloroperbenzoic acid dissolved in 350 ml of $CHCl_3$. The reaction mixture was stirred for 4 hr and then washed with saturated $NaHCO_3$. The solvent was removed *in vacuo*, leaving 22 g (quantitative yield) of product which was recrystallized from acetone, mp 146–149°. This material was shown by ir and nmr to be identical with that synthesized by method A.

Preparation of 2-Ethylthioisophorone (10).—In 250 ml of EtOH was dissolved 16.5 g (0.72 mol) of sodium metal. To the solution was added 46.5 g (0.75 mol) of ethanethiol and then 28 g (0.18 mol) of 2,3-isophorone oxide.[4] After stirring for 12 hr, the reaction mixture was diluted with 500 ml of H_2O and extracted with CH_2Cl_2. The organic layer was reduced *in vacuo*, leaving 36 g (quantitative yield) of product which was purified by distillation: bp 128–131° (4.0 mm); lit.[5] mp 34–37.5°; nmr ($CDCl_3$) δ 1.03 (s, 6, 5-$(CH_3)_2$–), 1.15 (t, 3, CH_3CH_2S–), 2.24 (s, 2, 4-CH_2–), 2.25 (s, 3, 3-CH_3–), 2.37 (s, 2, 6-CH_2–), 2.72 (q, 2, CH_3CH_2S–).

Preparation of 2-Ethylsulfinylisophorone (11).—To 10 g (0.050 mol) of 2-ethylthioisophorone dissolved in 50 ml of glacial AcOH was added 5.72 g (0.051 mol) of 30% hydrogen peroxide. The mixture was stirred for 3 weeks at room temperature and then extracted with CH_2Cl_2. The organic layer was washed with 10% Na_2CO_3 and reduced *in vacuo*, leaving the product which was recrystallized (cyclohexane): mp 72.5–75°; nmr ($CDCl_3$) δ 1.05 (s, 6, 5-$(CH_3)_2$–), 1.28 (t, 3, CH_3CH_2SO–), 2.33 (s, 2, 6-CH_2–), 2.37 (s, 3, 3-CH_3–), 2.42 (s, 2, 4-CH_2–), 3.13 (q, 2, CH_3CH_2SO–).

Anal. Calcd for $C_{11}H_{18}O_2S$: C, 61.64; H, 8.47; S, 14.96. Found: C, 61.53; H, 8.56; S, 15.40.

Preparation of 2-Ethylsulfonylisophorone (12).—To 10 g (0.050 mol) of 2-ethylthioisophorone dissolved in 50 ml of glacial AcOH was added 11.5 g (0.10 mol) of 30% hydrogen peroxide. After stirring for 16 days, the reaction mixture was worked up by adding 200 ml of H_2O and extracting with CH_2Cl_2. The CH_2Cl_2 layer was washed with saturated Na_2CO_3 and reduced *in vacuo*, leaving 10.7 g (92% yield) of product which was recrystallized (cyclohexane): mp 71–73°; nmr ($CDCl_3$) δ 1.07 (s, 6, 5-$(CH_3)_2$–), 1.27 (t, 3, $CH_3CH_2SO_2$–), 2.38 (s, 2, 6-CH_2–), 2.48 (s, 3, 3-CH_3–), 2.55 (s, 2, 4-CH_2–), 3.38 (q, 2, $CH_3CH_2SO_2$–).

Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88, S, 13.92. Found: C, 57.36; H, 7.50; S, 14.21.

Registry No.—**1**, 16004-91-4; **7**, 40919-40-2; **8**, 40919-41-3; **9**, 10276-21-8; **10**, 17304-83-5; **11**, 40919-43-5; **12**, 40919-44-6; *p*-toluenethiol, 106-45-6; sodium *p*-toluenesulfinate, 824-79-3; sodium *p*-toluenethiolate, 10486-08-5; ethanethiol, 75-08-1.

Preparation and Photochemistry of Hexamethyl-2,5-cyclohexadienone Epoxides

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"The reaction of α,β-unsaturated ketones with peracids usually does not lead to epoxidation of the double