10°/min.). One recrystallization from ether-pentane gave the pure halide melting (with dec.) at 128–129° (in bath at 120°, 10°/min.) and exhibiting in methylene chloride (dried over Drierite) (c 0.39) $[\alpha]^{20}_{D}$ −29° (5 min.) → ±0° (97 min.) and in absolute chloroform (c 1.79) −20° (4 min.) → +42° (65 hr.).

Anal. Calcd. for $C_{19}H_{17}O_6Cl$: C, 60.56; H, 4.55; Cl, 9.41. Found: C, 60.44; H, 4.42; Cl, 9.34.

5-O-Benzoyl-1,2,3-O-benzylidyne-α-D-ribose (II) *from 2,5-di-O-benzoyl-D-ribosl chloride* (XII). Crystalline 2,5-di-*O*-benzoyl-D-ribosyl chloride (42.3 mg.) was added to a rapidly stirred suspension of 114 mg. of silver benzoate in dry benzene. Ten minutes later the insoluble salts were removed by filtration and washed with methylene chloride. The filtrate and washings were combined and concentrated to a crystalline mass. From 1:1 acetone-ether, crystallization occurred after which an equal volume of pentane was added. The crystalline product was recrystallized from methylene chloride-pentane: 20.7 mg. (55%), m.p. 180–182°, $[\alpha]^{20}_{D}$ +44° (c 1.00, chloroform). When mixed with authentic 5-*O*-benzoyl-1,2,3-*O*-benzylidyne-α-D-ribose,[1] the melting point was not depressed.

N-[3,5-Di-O-benzoyl-D-ribosyl]pyridinium chloride (XIV). Dry pyridine (0.5 ml.) was added to 500 mg. of crystalline 3,5-di-*O*-benzoyl-D-ribosyl chloride. The temperature of the mixture rose slightly and within 10 min. crystallization began. Another ml. of pyridine was added and the reaction mixture was warmed on the steam bath for 1 hr. Methylene chloride (8 ml.) was added to the cooled mixture and the crystalline product, 350 mg. (58%), removed: m.p. 164–166°. Recrystallization from ethanol gave clear prisms, m.p. 171–177° (in bath at 160°, 12°/min.), $[\alpha]^{20}_{D}$ −64.1° in water (c 1.21).

Anal. Calcd. for $C_{24}H_{22}O_6NCl$: C, 63.23; H, 4.87; N, 3.07. Found: C, 63.19; H, 4.95; N, 3.09.

Acknowledgment. Combustion analyses were performed in the Institutes' Microanalytical Laboratory under the direction of Dr. William C. Alford. We are indebted to Mr. William M. Jones for infrared absorption measurements.

BETHESDA 14, MD.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Formation of Naphthalenes from Indenes. IV.[1] The Effect of Substitution at the Ethylenic Double Bond*

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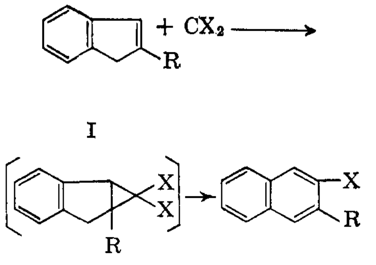
Received April 8, 1957

The yields of 2-halonaphthalenes obtained from eight substituted indenes, in which the substituent has been varied from electron withdrawing to electron donating, indicate that the addition of dihalocarbene to the indene double bond is inhibited by the groups chlorine, bromine, carbethoxy, or phenyl. When the substituent is electron-donating, such as methyl, isopropyl, or ethoxy, the yields of naphthalenes are comparable to those obtained with unsubstituted indene. These data support the view that the two electrons in the dihalocarbene are paired, and that carbenes seek centers of high electron density.

The use of 2-substituted indenes in reactions with haloform and potassium *t*-butoxide results in the formation of 2,3-disubstituted naphthalenes.

2-Chloro-, bromo-, and fluoronaphthalene, and 1-methyl-2-bromonaphthalene have recently been prepared[1,4] by a new method, which involves the reaction of indene, or 3-methylindene, with the appropriate haloform and potassium *t*-butoxide. An investigation of the reaction of eight other monosubstituted indenes with haloform and potassium *t*-butoxide has now been made in order to further define the scope of this synthesis, and to gain additional information concerning the general reaction of carbenes with olefins.

Optimum conditions for the synthesis of 2-halonaphthalenes[1,4] by this method involve the use of excess indene as solvent. In this study a standard procedure was employed using benzene as solvent. The yields of naphthalenes were not optimum (37% compared to 67% for 2-chloronaphthalene); however, the use of this procedure permitted: a direct comparison to be made of the reactivity of the various substituted indenes, the use of indenes which are solid at the reaction temperature, and the use of relatively small amounts of indenes. The indenes studied contained substituents which varied from



I

II III

a. R = CH_3, X = Cl
b. R = OC_2H_5, X = Br
c. R = Cl, X = Cl
d. R = Br, X = Cl
e. R = $CO_2C_2H_5$, X = C

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[1] Preceding paper. W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

[2] This work was supported in part by a grant (NSF-G2163) from the National Science Foundation.

[3] Visking Corporation Fellow (1954–1955).

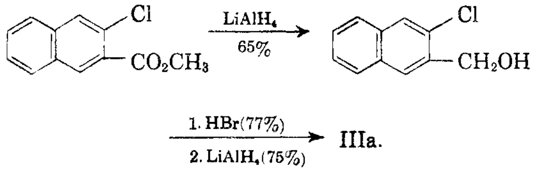
[4] W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956).

electron withdrawing to electron-donating, and from small to bulky in size.

The 2-substituted indenes Ia-Ie were prepared by modifications of existing procedures, or by new procedures; details are found in the experimental section. The yields of naphthalenes obtained from 2-methylindene (IIIa, 37%), and 2-ethoxyindene (IIIb, 34%) were comparable to the yield of 2-chloronaphthalene obtained from indene (37%); however, only trace amounts of products (<5%) were isolated from reactions in which 2-chloroindene (Ic), 2-bromoindene (Id), or 2-carbethoxyindene (Ie) were employed.

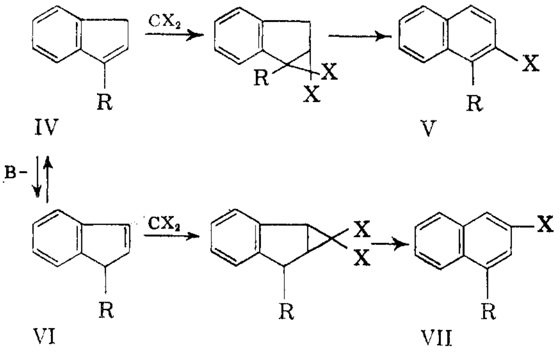
The product (m.p. 82°) obtained from 2-ethoxyindene (Ib) was assigned the structure 2-ethoxy-3-bromonaphthalene (IIIb, reported[5] m.p. 79°). This product was further characterized by its conversion to the corresponding acid (60% yield, m.p. 128–129°, reported[6] m.p. 122°) by carbonation of the intermediate Grignard reagent.

2-Methyl-3-chloronaphthalene (IIIa), obtained in 37% yield from Ia, was unknown. Its structure was confirmed by the independent synthesis shown below.



The structures of the products obtained in very low yield from Ic, Id, and Ie were not established. Two crystalline solids (m.p. 95°, mol. wt. 218–254; m.p. 81°, mol. wt. 300) were obtained by chromatography of the deep blue reaction mixture obtained from 2-carbethoxyindene. These products possessed nearly identical composition (carbon and hydrogen), and infrared spectra (two bands in carbonyl region); however, they were not IIe, IIIe, or the corresponding *t*-butyl derivatives. The naphthalene obtained (2% yield) from 2-bromoindene had the composition calculated for 2-bromo-3-chloronaphthalene (IIId); however, its melting point (130°) was not in agreement with that previously reported[7] for IIId (115°). It was not established whether the previously reported melting point of 2-bromo-3-chloronaphthalene was in error or whether the product obtained from Id was an unexpected isomer of IIId. Only a trace of naphthalenic material was obtained from 2-chloroindene (Ic).

It has been previously shown[4] that steam distillation of the product obtained from 3-methylindene (IVa ⇄ VIa) and dibromocarbene gives only one (Va) of the two possible naphthalenes (Va or VIIa). The initial reaction involved only the most stable isomer IVa, and there was no indication of steric preference for the reaction of the carbene with the least hindered isomer VIa.



a. R = CH_3, X = Br
b. R = $(CH_3)_2CH$, X = Cl
c. R = Cl, X = Cl
d. R = C_6H_5, X = Br

It has now been shown that the reaction of 3-isopropylindene (IVb) with chloroform and potassium *t*-butoxide, with subsequent decomposition of the resulting cyclopropyl intermediate by steam distillation, gives predominantly, if not exclusively, a single naphthalene. Evidence that the product was not a mixture of isomeric naphthalenes was obtained by its conversion, in high yield (< 75%), into a pure solid picrate. The structure of this product was assumed to be 1-isopropyl-2-chloronaphthalene (Vb) by analogy to the results previously obtained with 3-methylindene,[4] and by its infrared spectrum.[8]

The reactions in which 3-chloroindene (IVc) and 3-phenylindene (IVd) were employed resulted in low yields of naphthalenic materials (5% each). These products were assigned the structures 1-phenyl-2-bromonaphthalene (Vd, oil, previously unknown), and 1,2-dichloronaphthalene (Vc, m.p. 35°, reported[9] m.p. 35°). A red hydrocarbon (m.p. 216–217°, $C_{16}H_{10}$) was also obtained in low yield from the reaction with 3-phenylindene; the structure of this product is being examined.

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[5] R. Huisgen and G. Sorge, *Ann.*, **566**, 179 (1950).

[6] H. Gilman, C. E. Arntzen, and F. Webb, *J. Org. Chem.*, **10**, 374 (1945).

[7] H. H. Hodgson and D. E. Hathway, *J. Chem. Soc.*, 842 (1945).

[8] The infrared spectrum of this product was compared with three 1,2-disubstituted naphthalenes (1-methyl-2-bromonaphthalene, 1-methyl-2-aminonaphthalene, and 1-methyl-2-hydroxynaphthalene) which were available in these laboratories, and with the spectra of 1,2-dimethylnaphthalene and 1,3-dimethylnaphthalene (Infrared Spectral Data: American Petroleum Institute, National Bureau of Standards, Spectra Serial Nos. 766, 767). The spectra of all of the 1,2-disubstituted naphthalenes, and of the naphthalene in question, were similar in that three strong bands were present at 739–741, 757–775, and 796–815 cm^{-1}. Only two strong bands were present in this region of the spectrum of 1,3-dimethylnaphthalene. The out-of-plane deformation of aromatic hydrogen atoms gives rise to the bands described. Structure Vb is consistent with the observed spectrum; however, these data cannot be considered as conclusive evidence for the structural assignment in view of the limited number of spectra available.

[9] P. T. Cleve, *Ber.*, **20**, 1989 (1887).

Since significant amounts of naphthalenic products were not obtained from any of the three haloindenes studied, the possibility remained that the haloindene reacted with the potassium *t*-butoxide before the haloform had been added. That this was not the case was shown by a high recovery (80%) of 2-bromoindene from a mixture of Id and potassium *t*-butoxide, which had been allowed to react for two and one-half hours. Since dihalocarbenes are known to form under the conditions of the reaction,[4,10–12] it was concluded that a halogen substituent on the ethylenic bond of indene deactivates this bond to attack by the carbene.

The experiments described above show that the addition of dihalocarbenes to the indene double bond is inhibited by substituents which are electron-withdrawing, such as chlorine, bromine, carbethoxy, or phenyl. Such deactivation is not observed when the ethylenic substituent in an electron donating group such as methyl, isopropyl, and ethoxy. These results are in accord with the view that the two electrons of the carbene are paired, and that carbenes seek centers of high electron density.[10,12]

EXPERIMENTAL

Reaction of 2-methylindene, chloroform and potassium t-butoxide. General procedure. A solution of 2-methylindene[13] 15.6 g., 0.12 mole) in dry thiophene-free benzene (15 ml.) was added to dry pulverized potassium *t*-butoxide (maintained under dry oxygen-free nitrogen) prepared from potassium (2.00 g., 0.051 mole) and *t*-butyl alcohol. The orange slurry was stirred vigorously, and cooled in an ice bath, while 4.8 g. (0.040 mole) of freshly distilled chloroform was added over a period of about 15 min. A static nitrogen atmosphere was maintained during the addition, and the mixture was then allowed to stand at room temperature overnight. The entire mixture was steam-distilled from water containing 0.08 mole of sodium carbonate. An undetermined amount of nonvolatile red tar remained in the flask. The distillate was extracted with petroleum ether (b.p. 60–68°), and the condenser was washed with the same solvent. The organic washes and extracts were dried, filtered, and the solvent was removed by distillation. Fractional distillation of the residue afforded 9.6 g. (0.0727 mole) of unreacted 2-methylindene. The light green residue, m.p. 113–120°, was recrystallized once from ethanol, and was obtained as refractive pale green platelets (2.61 g., 37%, m.p. 122.5–123°). This material was further purified (m.p. 123.5–124°) by recrystallization from ethanol using charcoal.

Anal. Calcd. for $C_{11}H_9Cl$: C, 74.79; H, 5.14. Found: C, 74.72; H, 5.34.

The product was identical (m.p., mixture m.p. and infrared spectrum) with authentic 2-methyl-3-chloronaphthalene.

2-Chloro-3-hydroxymethylnaphthalene. A solution of methyl 2-chloro-3-naphthoate[14] (16.3 g., 0.074 mole) in dry ether (40 ml.) was added to lithium aluminum hydride (3.1 g., 0.082 mole) in dry ether (150 ml.) at such a rate as to maintain gentle reflux. The resulting mixture was stirred for 0.5 hr. and then saturated aqueous ammonium chloride (10 ml.) was added. The white solid residue, obtained from the dried ether solution, was recrystallized from a mixture of petroleum ether (600 ml., b.p. 60–68°) and benzene (30 ml.) to give 9.2 g. (65% yield) of 2-chloro-3-(hydroxymethyl)naphthalene (m.p. 110.5–112°, reported[15] 111°).

2-Chloro-3-methylnaphthalene. A solution of 4.0 g. (0.016 mole) of 2-chloro-3-bromomethylnaphthalene (prepared in 77% yield from 2-chloro-3-hydroxymethylnaphthalene by the method reported by Shoesmith and Mackie[15]) in the minimum amount of dry ether was added dropwise to a stirred solution of lithium aluminum hydride (0.50 g., 0.013 moles) in dry ether (60 ml.), and the resulting mixture was heated at the reflux temperature for 3 hr. The mixture was processed as described above, and the product was recrystallized from ethanol. There was obtained 2.1 g. (75% yield) of 2-chloro-3-methylnaphthalene (m.p. 123–123.5°).

2-Ethoxy indene. Dry hydrogen chloride (0.7 g., 0.02 mole) in absolute ethanol (2.5 ml.) was added to a solution of 87.4 g. (0.66 mole) of indanone-2 (prepared[16] from indenebromohydrin[17]), ethyl orthoformate (133 g., 0.90 mole), and absolute ethanol (350 ml.). The resulting solution was allowed to stand at room temperature for 24 hr., and was then made alkaline by the addition of sodium methoxide (4.2 g.). The mixture was processed by distillation, and 76.4 g. (56% yield) of 2,2-diethoxyindane (b.p. 99–101°/3.4 mm., n_D^{25} 1.5303–1.5426, licorice odor), contaminated with 2-ethoxyindene, was obtained.

A mixture of the ketal (45.4 g., 0.220 mole) and *p*-toluenesulfonic acid (0.011 g.) was heated for 1 hr. at 25–60° (25–30 mm.), and the ethanol which was formed was removed by distillation. Distillation of the residue afforded 30.1 g. (86% yield) of 2-ethoxyindene (b.p. 86°/1.6 mm., m.p. (from ethanol-water) 42–45°).

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.10; H, 7.24.

2-Ethoxyindene was stored under oxygen-free nitrogen in a tight container. The product rapidly turns yellow when exposed to air, and was easily hydrolyzed to indanone-2 (m.p. and mixture m.p. of oxime, 155°).

Reaction of 2-ethoxyindene, bromoform, and potassium t-butoxide. The reaction mixture obtained from potassium *t*-butoxide (from 3.2 g., 0.082 g. atoms, of potassium), 2-ethoxyindene (26.3 g., 0.164 mole), benzene (25 ml.) and bromoform (14.3 g., 0.0565 mole) was processed by the procedure previously described for 2-methylindene. The organic product, obtained from the steam distillate, was distilled to give indanone-2 [12.1 g., 0.0915 moles, b.p. 77°/1.6 mm., m.p. 56–58° (reported m.p. 58°[18]), oxime m.p. 155° (reported 152°[19])], and black tarry residue (7.9 g.). The residue was dissolved in benzene (4 ml.) and chromatographed on acid-washed alumina (200 g.), using petroleum ether (b.p. 60–68°, 1900 ml.) as eluant. The white product (5.4 g., m.p. 76–80°) was recrystallized from methanol to give 4.78 g. (34% yield) of 2-ethoxy-3-bromonaphthalene melting at 79–82.5° (reported m.p. 79°[5]). The melting point of the product was raised to 81.5–82° (A) by

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(10) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954); W. von E. Doering and P. La Flamme, *J. Am. Chem. Soc.*, **78**, 5447 (1956).

(11) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950), and other papers by Hine and his coworkers.

(12) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956); P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(13) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).

(14) E. Strohbach, *Ber.*, **34**, 4158 (1901).

(15) J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 1584 (1930).

(16) P. Pfeiffer and T. Hesse, *J. prakt. Chim.*, **158**, 315 (1941).

(17) C. M. Suter and H. B. Milne, *J. Am. Chem. Soc.*, **62**, 3473 (1940).

(18) J. Read and E. Hurst, *J. Chem. Soc.*, **121**, 2554 (1922).

(19) H. D. Porter and C. M. Suter, *J. Am. Chem. Soc.*, **57**, 2022 (1935).

recrystallization from methanol, and 82.2–82.7° (B) by recrystallization from petroleum ether.

Anal. Calcd. for $C_{12}H_{11}BrO$: C, 57.39; H, 4.42. Found: (A): C, 57.80; H, 4.42. (B): C, 57.93; H, 4.66.

2-Ethoxy-3-naphthoic acid. A sample of 2-ethoxy-3-bromonaphthalene (1.5 g.) was converted, by a standard procedure involving the Grignard reagent, into the corresponding acid. The crude product (0.785 g., 60%, m.p. 119–124°) was recrystallized from ethanol and a white acid (m.p. 128.5–129.5°), presumed to be 2-ethoxy-3-naphthoic acid, was obtained. The reported melting point of this acid is 122°.[6]

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.35; H, 5.83.

3-Isopropylindene. A solution of indanone-1 (50.0 g., 0.378 mole) in ether (100 ml.) was added (under a nitrogen atmosphere) over a 30-min. period to the Grignard reagent prepared from isopropyl bromide (63 g., 0.515 mole), magnesium (12.1 g., 0.50 g. atoms) and ether (200 ml.). The mixture was allowed to stand for 48 hr., and was then decomposed with saturated ammonium chloride solution (88 ml.). The residual oil (60.7 g., 91% yield as 1-isopropyl-1-indanol), obtained from the ether, was added to benzene (250 ml.) containing phosphorus pentoxide (47 g.), and the resulting mixture was heated at the reflux temperature for 12 min. The cooled organic phase was washed with dilute sodium hydroxide, dried (magnesium sulfate), and fractionally distilled. 3-Isopropylindene,[20] contaminated with a small amount of indanone-1 (infrared absorption at 1700 cm^{-1}), was collected at 57.5°/0.55 mm. (25 g., 43% yield, n^{25}_{D} 1.5472–1.5482).

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.04; H, 8.99.

Reaction of 3-isopropylindene, chloroform, and potassium t-butoxide. The reaction of 3-isopropylindene (17.3 g., 0.110 mole), potassium *t*-butoxide (from 1.95 g., 0.05 g. atoms, of potassium), chloroform (4.63 g., 0.0388 mole) in benzene (17.3 g.) was carried out as previously described for 2-methylindene. The reddish oil, obtained from the steam distillate, had a strong odor of hydrochloric acid which suggested that the dichlorocyclopropyl intermediate was present; consequently this oil (17.4 g.) was treated with hot ethanol (75 ml.) containing potassium hydroxide (2.05 g., 0.036 mole) for a period of 75 min. Water (75 ml.) was added to the residue after the ethanol had been removed by distillation, and the organic products were extracted with petroleum ether (b.p. 60–68°). The ether solution was dried (magnesium sulfate) and distilled and two fractions were obtained: (*1*) 3-isopropylindene (11.41 g., 0.072 mole), and (*2*) 1-isopropyl-2-chloronaphthalene (3.59 g., b.p. 90°/0.37 mm., n^{25}_{D} 1.6005–1.6052). The naphthalenic product was redistilled to give 3.04 g. of product (38% yield, b.p. 96–97°/0.6 mm., n^{25}_{D} 1.6047–1.6059. The product was redistilled (n^{25}_{D} 1.6055–1.6061) for analysis.

Anal. Calcd. for $C_{13}H_{13}Cl$: C, 76.28; H, 6.40. Found: C, 76.18; H, 6.71.

The picrate (75% yield, orange needles, m.p. 91–92°) was recrystallized from ethanol.

Anal. Calcd. for $C_{19}H_{16}ClN_3O_7$: C, 52.60; H, 3.73; N, 9.69. Found: C, 52.76; H, 4.03; N, 9.86.

The high yield of picrate obtained establishes that one of the two isomeric naphthalenes is formed predominantly. The structure was assigned as 1-isopropyl-2-chloronaphthalene, instead of 1-isopropyl-3-chloronaphthalene, by analogy to the results previously reported employing 3-methylindene,[4] and from infrared spectral data.[8]

The reaction of 2- and 3-haloindenes with potassium t-butoxide and chloroform. The reaction mixture of potassium *t*-butoxide (0.024 mole), *2-chloroindene*[21] (11.4 g., 0.076 mole), chloroform (5.70 g., 0.048 mole) and benzene (10 ml.) was processed by the method described above for 2-methylindene. Unreacted 2-chloroindene (8.76 g., 0.058 mole) was obtained by distillation. The residue from this distillation was chromatographed; however, the small amount of product (yellow semisolid, 200 mg.) was not processed.

Similar results were obtained with *3-chloroindene*[22] (13.5 g., 0.09 mole). The product (0.55 g.) was recrystallized from ethanol to give 0.271 g. (4.7% yield) of 1,2-dichloronaphthalene (m.p. 31–32°). The product melted at 34–35° after recrystallization from petroleum ether (30–60°). The reported melting point of 1,2-dichloronaphthalene is 35°.[9]

Anal. Calcd. for $C_{10}H_6Cl_2$: C, 60.94; H, 3.08. Found: C, 60.91, 60.85; H, 3.85, 3.91.

When *2-bromoindene*[19] (18.0 g., 0.092 mole) was employed, there was obtained: (*1*) unreacted bromoindene (12.0 g., 0.061 mole), and (*2*) a trace of white solid (0.009 g., m.p. 125–129°, by chromatography). In another reaction the steam-distillation step was omitted. The organic products were extracted with petroleum ether (60–68°). Petroleum ether and unchanged 2-bromoindene were removed by distillation at reduced pressure; the residue was chromatographed. There was obtained 0.54 g. of bluish white solid. This product was recrystallized from petroleum ether which afforded 0.184 g. (1.6% yield) of naphthalenic material melting at 126–129°. The melting point was raised to 130° by subsequent recrystallization from petroleum ether.

Anal. Calcd. for $C_{10}H_6BrCl$: C, 49.74; H, 2.50. Found: C, 49.40; H, 2.66.

This product was not identified; however, the expected 2-bromo-3-chloronaphthalene is reported to melt at 115°.[7]

Preparation of 3-phenylindene. A solution of indanone-1 (50.0 g., 0.378 mole) in absolute ether (100 ml.) was added over a period of 50 min. with stirring to the Grignard reagent prepared from magnesium (11.4 g., 0.470 mole) and bromobenzene (75.7 g., 0.48 mole) in absolute ether (390 ml.). The mixture was stirred for 3.5 hr. and was hydrolyzed by the slow addition of saturated ammonium chloride solution (70 ml.). The ether layer was decanted, filtered, dried (magnesium sulphate), and distilled to remove solvent. The yield of crude 1-phenyl-1-indanol was 78.9 g. (99%).

A mixture of crude 1-phenyl-1-indanol (66.9 g., 0.318 mole), phosphorus pentoxide (45.2 g., 0.318 mole), and benzene (300 ml.) was heated at the reflux temperature for 20 min. The benzene solution was cooled, decanted, washed with dilute base, dried (magnesium sulfate), and distilled to remove solvent. Fractional distillation of the orange residue afforded 46.1 g. (76% yield) of 3-phenylindene, b.p. 113–116° (0.40 mm.), n^{25}_{D} 1.6335–1.6341. The physical constants which are reported in the literature are: b.p. 200–201° (29 mm.),[23] 148–150° (3 mm.),[24] 113–117° (0.05 mm.); n^{18}_{D} 1.6357,[25] n^{24}_{D} 1.6313.[24]

Reaction of 3-phenylindene, bromoform, and potassium t-butoxide. The reaction product obtained from potassium *t*-butoxide (0.105 g. atom), 3-phenylindene (45.6 g., 0.237 mole), bromoform (19.85 g., 0.0785 mole), in benzene (45 g.), was steam distilled until 4 liters of distillate were collected. Water was decanted from the product not steam-distilled, and the residual oil was extracted with petroleum ether. The ether extract was dried (magnesium sulfate), and petroleum ether and unchanged 3-phenylindene (b.p. 104–107°/0.10 mm., n^{25}_{D} 1.6318–1.6338) were removed. The black tarry residue (11.4 g.) was dissolved in benzene and chromatographed on alumina (200 g.), using petroleum ether (b.p. 60–68°) as eluant. Three combined fractions were obtained: (*1*) 3.21 g., blue oil, 185 ml. eluant, (*2*) 1.10 g.,

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(20) J. Thiele and K. Merck, *Ann.*, **415**, 257 (1918).

(21) C. M. Suter and G. A. Lutz, *J. Am. Chem. Soc.*, **60**, 360 (1938).

(22) Prepared in 60% yield by the method of J. von Braun and H. Ostermayer, *Ber.*, **70**, 1006 (1937).

(23) J. von Braun, *Ber.*, **50**, 1659 (1917).

(24) C. M. Suter and G. A. Lutz, *J. Am. Chem. Soc.*, **60**, 1365 (1938).

(25) P. A. Plattner, R. Sandrin, and J. Wyss, *Helv. Chim. Acta*, **29**, 1604 (1946).

green-brown oil, 300 ml. eluent, (*3*) 1.36 g., red semi-solid, 650 ml. eluant. Fraction *1* was composed principally of product (1.1 g., 5% as 1-phenyl-2-bromonaphthalene, n_D^{25} 1.6763–1.6768) boiling at 143°/0.45 mm.

Anal. Calcd. for $C_{10}H_{11}Br$: C, 67.86; H, 3.92. Found: C, 68.06; H, 4.22.

Fraction *3* was recrystallized from chloroform-methanol to give 0.154 g. of red needles melting at 197–207°. The melting point of this product, or of one component of the product, was raised to 216–217.3° by subsequent recrystallization.

Anal. Calcd. for $C_{31}H_{22}$: C, 94.38; H, 5.62; mol. wt., 394.5. For $C_{16}H_{10}$: C, 95.01; H, 4.98; mol. wt., 202. Found: C, 94.15, 94.45; H, 5.61, 5.62; mol. wt. (benzene), 199.

2-Carbethoxyindene. Ethyl α-formylhydrocinnamate (41.6 g., 0.202 mole, b.p. 96–98°/0.9 mm., n_D^{25} 1.5142–1.5156, prepared in 22% yield by the method of von Auwers[26]) was added to a warm (70°) solution prepared from phosphorus pentoxide (426 g.) and phosphoric acid (85%, 426 g.). The resulting mixture was stirred vigorously and maintained at 70° for 30 min. The resulting red mixture was poured onto an excess of ice, and the viscous oil was stirred vigorously until the red color disappeared. The hydrolysis mixture was extracted four times with ether and the ether extracts were washed with dilute sodium hydroxide. The basic aqueous wash was extracted once with ether. The combined ether extract was dried, filtered, and distilled to remove solvent. The red oily residue (33.7 g.) was dissolved in the minimum amount of petroleum ether (b.p. 60–68°), absorbed on a column of alumina, and eluted with petroleum ether (b.p. 60–68°). Evaporation of the first eluant fraction (475 ml.) afforded 17.3 g. of product which crystallized from petroleum ether (b.p. 30–60°) as small white needles (16.8 g., 44% yield, m.p. 46.5–49°). Two additional recrystallizations of this product afforded 13.6 g. of 2-carbethoxyindene, m.p. 48.8–50° (reported melting point is 50°).[27]

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.92; H, 6.73.

Reaction of 2-carbethoxyindene, chloroform and potassium t-butoxide. Benzene was removed (at room temperature) from the brilliant blue mixture obtained from 2-carbethoxyindene (13.60 g., 0.0723 mole), potassium *t*-butoxide (0.031 mole), chloroform (2.87 g., 0.024 mole), and benzene (16 ml.). A portion (16.9 g.) of the bluish black residue (21.1 g.) was dissolved in benzene (7 ml.) and chromatographed on alumina (200 g.), using petroleum ether (60–68°) as developer and eluant. A viscous clear blue oil (6.22 g.) was obtained from the first 600 ml. of eluant. This oil was chromatographed again and the crystalline and oily products were processed by recrystallization from petroleum ether; three white crystalline products were isolated in low yield: (A) unchanged 2-carbethoxyindene (m.p. 48–50°), (B) solid B (less soluble in petroleum ether than C), m.p. 95–96°, (C) solid C, m.p. 80–81°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.61; H, 6.43; mol. wt., 188. Found: Solid B; C, 76.72; H, 6.43; mol. wt., (benzene) 254, 218. Solid C; C, 77.18; H, 6.30; mol. wt. (benzene) 300.

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On the Mechanism of Oxidation of *o*-Quinone by Hydrogen Peroxide[1,2]

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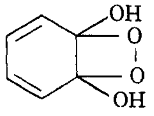
For the hydroperoxide, formed by the action of anhydrous ethereal hydrogen peroxide on *o*-quinone in chloroform solution, structure VIII is suggested which makes it a derivative of *o*-quinone dimer (IV). The latter has been crystallized and its structure proven by rearrangement to the catechol V, which was characterized by its phenazine derivative VI. The products arising from acid- and base-catalyzed rearrangements and by hydrogenation of the hydroperoxide VIII were studied chromatographically (Fig. 1 and 2), electrophoretically (Fig. 3) and chemically (Chart I). A major product, obtained in the base-catalyzed rearrangement of VIII and in the oxidative cleavage of *o*-quinone dimer (IV) by hydrogen peroxide, is also present in the mother liquors of VIII; it is 2,3,6-tricarboxy-4-cyclohexeneacrylic acid X which was converted by partial hydrogenation and oxidation to an epimer (presumably XVa or b) of cyclohexane-1,2,3,4-tetracarboxylic acid. By reduction of the hydroperoxide VIII with Lindlar catalyst a phenolic (or diosphenolic, *cf.* IX) compound $C_{12}H_{12}O_6$ was obtained which could be converted *via* its hexahydro derivative XII to 2,3,6-tricarboxycyclohexanepropionic acid (XI), the hydrogenation product of X.

The mechanism of the enzymatic oxidation of catechol to *cis,cis*-muconic acid (III) by pyrocatechase,[4] has been discussed in terms of an intermediate peroxide II or its cyclic tautomer XVII.[5] The enzymatic intermediate, be it II or XVII, was directly derived from catechol and oxygen, thus rul-



XVII

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(1) This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(2) Oxidation Mechanisms. XX. Preceding papers in this series, *cf.* ref. 5 and *J. Am. Chem. Soc.*, **79**, 3191 (1957).

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(4) O. Hayaishi, M. Katagiri, and S. Rothberg, *J. Am. Chem. Soc.*, **77**, 5450 (1955).

(5) O. Hayaishi, A. A. Patchett, and B. Witkop, *Ann.*, **608**, 158 (1957). Corrections should be made for some typographical error in the experimental part, p. 166, as follows: line 18: molecular weight of peroxide $(142.1)_2$; lines 20 and 36: Tetracarbonsäure $C_{12}H_{12}O_8$; line 31: Tetracarbonsäure $C_{12}H_{16}O_8$.