acid gave additional precipitate. The precipitates were recrystallized from ethyl acetate–petroleum ether, yielding pale yellow needles (1.22 g., 53%): m.p. 217–217.5°; $\lambda_{max}^{95\% \, EtOH}$, mμ (log ε), 229 (4.20), 347 (4.12); ν_{NH} 3300 (m), ν_{OH} 2670 (w), $\nu_{C=O}$ 1742 (s), ν_{NO_2} 1524 (s), 1361 (s), 1344 (s), or 1314 (s) cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_9H_5N_3O_6$ (251.15): C, 43.04; H, 2.01; N, 16.73. Found: C, 43.12; H, 2.08; N, 16.99.

3,7-Dinitroindole (31).—A mixture of 3,7-dinitroindole-2-carboxylic acid (0.80 g., 0.00318 mole) and copper(II) oxide (0.15 g.) in quinoline (25 ml.) was refluxed for 1 hr. and then cooled and poured into ice-cold aqueous 20% hydrochloric acid. The precipitate and the solution were extracted with ethyl acetate, and the extracts were dried, treated with charcoal, and concentrated. Addition of petroleum ether caused separation of pale yellow needles (0.17 g., 26%): m.p. 260–261.5°; $\lambda_{max}^{95\% \, EtOH}$, mμ (log ε), 225 (4.20), 347 (4.16); ν_{NH} 3230 (m), ν_{NO_2} 1522 (s), 1383 (vs), 1333 (vs) cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_8H_5N_3O_4$ (207.14): C, 46.38; H, 2.43; N, 20.29. Found: C, 46.64; H, 2.48; N, 20.28.

Reactions of 3,α-Epoxyoxindoles and Their Rearrangement to 2,3-Disubstituted Indoles

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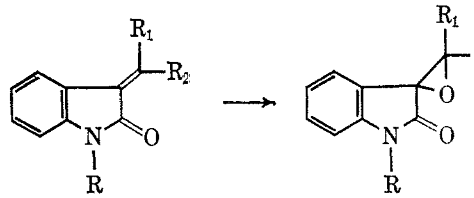
The reaction of alkylindeneoxindoles and alkaline hydrogen peroxide yields 3,α-epoxyoxindoles. Conversion of these compounds in the presence of alkali to 2,3-disubstituted indoles appears to be a general reaction. Evidence is presented in support of the assigned structures.

In the course of our studies of oxindole chemistry, it became desirable to prepare epoxides of the general structure II. It appeared that this could be accomplished by epoxidation of I with hydrogen peroxide.

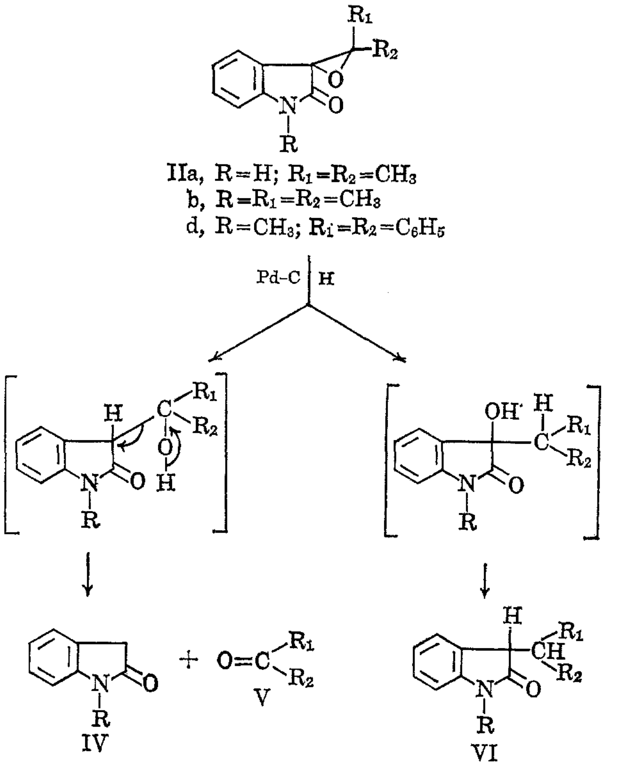


I II

When an alcoholic solution of 3-isopropylideneoxindole (Ia, Table I) was treated with 30% hydrogen peroxide under alkaline conditions, a new compound was obtained in high yield. Evidence in this paper shows that the new compound is the 3,α-epoxyoxindole IIa (Table II). Under the same reaction conditions, all the compounds in Table I (Ia–h) were subsequently converted into the corresponding epoxides IIa–h (Table II).

Support for the structural assignment of compounds II was obtained by catalytic hydrogenation of IIa, IIb, and IId (see Chart I).

CHART I



IIa, R=H; R_1=R_2=CH_3
b, R=R_1=R_2=CH_3
d, R=CH_3; R_1=R_2=C_6H_5

Compounds IV, V, and VI have been isolated from the reaction mixtures and identified. The epoxides II apparently yielded the expected two isomeric alcohols, both of which are unstable under the reaction conditions. As shown in the equation, the β-hydroxy carbonyl compound undergoes a dealdolization, similar to the dealdolization of diacetone alcohol studied by Westheimer and Cohen,[1] to give the oxindoles IV and the ketones V. The α-hydroxy carbonyl compound (a dioxindole), however, undergoes hydrogenolysis to yield the 3-substituted oxindoles VI. No attempt was made to isolate acetone (V, R_1 = R_2 = CH_3) in these reactions, but its presence was presumed because of the formation of oxindole IV. To verify this presumption, benzophenone (V, R_1 = R_2 = C_6H_5) was isolated and identified from the hydrogenation of IId as well as the corresponding oxindoles IV and VI. No attempt was made to isolate VI from the reduction of IIb.

A recent publication[2] describes the synthesis and structure proof of IId. The procedure described was repeated in our laboratories and the product was shown to be identical with IId prepared by the method described in this paper.

Compounds II behave in an interesting manner in the presence of base. When IIa, IIb, and IId were refluxed in dilute methanolic sodium hydroxide for several days, no reaction was observed. On the other hand, pyrrolidine at its boiling point converted IIa to acetone and an unstable material. Except for a small amount of unidentified material, no reaction was

[1] F. Westheimer and Cohen, *J. Am. Chem. Soc.*, **60**, 90 (1938).

[2] A. Schönberg and K. Junghans, *Ber.*, **96**, 3328 (1963).

TABLE I

ALKYLIDENEOXINDOLES (I)

Compd.	R	R_1	R_2	M.p., °C.	Yield, %	Ref.	Recrystn. solvent	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N	λ_{max}^{EtOH}, mμ, ($\epsilon \times 10^{-3}$)	λ_{infl}^{EtOH}, mμ ($\epsilon \times 10^{-3}$)	ν_{max}^{Nujol}, cm.$^{-1}$
Ia[a]	H	CH_3	CH_3	189–191	57	b	Ethanol	$C_{11}H_{11}NO$	76.26	6.40	8.08	76.24	6.46	7.80	250 (27.7) 253 (27.5) 259 (33.1) 290 (6.6) 346 (1.8)	216 (9.4) 300 (5.1)	3120, 1690, 1625, 1612, 1589, 1490
Ib[a]	CH_3	CH_3	CH_3	72–74	94		Ethanol	$C_{12}H_{13}NO$	76.97	6.99	7.48	77.05	7.39	7.10	252 (29.4) 256 (29.4) 261.5 (34.1) 280 (4.9) 291 (5.9) 346 (1.2)	220 (9.4) 300 (4.9)	1687, 1627, 1604, 1590, 784, 743, 689
Ic[a]	H	CH_3	$CH(CH_3)_2$	Semisolid			Not purified										3145, 1685, 1610, 1585, 1486, 1225, 745, 735 (smear)
Id[a]	CH_3	Phenyl	Phenyl	165.5–167.5	16		Methanol	$C_{22}H_{17}NO$	84.85	5.50	4.49	84.89	5.58	4.55	254 (18.0) 388 (10.5)		1698, 1605, 1518, 1490, 796, 734, 726, 703
Ie[a]	CH_3	Phenyl	4-Pyridyl	167–169	16		Ethanol	$C_{21}H_{16}N_2O$	80.74	5.16	8.97	80.26	5.03	8.85	258 (20.3) 323 (8.1) 410 (1.5)		1700, 1624 (w), 1605, 1540, 1490, 1100, 823 780, 760, 750, 697
If	H	Phenyl	CH_3	189–190	64	c	Ethanol	$C_{16}H_{13}NO$									
Ig[a]	H	$-(CH_2)_5-$		216–218	77		Ethanol	$C_{13}H_{13}NO$	78.36	6.57	7.03	78.40	6.75	7.34	217 (9.0) 251 (26.2) 255 (27.2) 261 (33.2) 293 (7.7) 348 (1.8)	303 (6.3)	3160, 3130, 3070, 3020, 1695, 1635, 1615, 1590, 1225, 1200, 745, 735
Ih[a]	H	$-(CH_2)_6-$		196–198	56		Ethanol	$C_{13}H_{13}NO_2$	78.84	7.09	6.57	79.09	7.21	6.66	218 (9.6) 255 (26.8) 262 (51.1) 293 (7.8) 349 (2.0)		3160, 3080, 1685, 1610, 1580, 1217, 789, 745

[a] Prepared by the general procedure for I. [b] See ref. 6. [c] A. Windows, H. Jensin and A. Schrams, *Ber.*, **57**, 1876 (1924).

TABLE II

3,α-EPOXYOXINDOLES (II)[a]

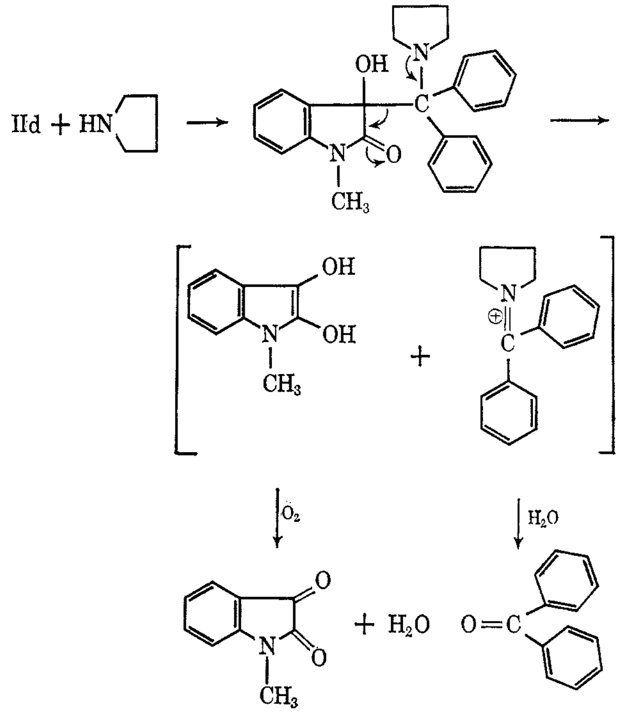
Compd.	R	R_1	R_2	M.p., °C.	Yield, %	Recrystn. solvent	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N	λ_{max}^{EtOH}, mμ ($\epsilon \times 10^{-3}$)	λ_{infl}^{EtOH}, mμ ($\epsilon \times 10^{-3}$)	ν_{max}^{Nujol}, cm.$^{-1}$
IIa	H	CH_3	CH_3	166–168	87	20% aqueous ethanol	$C_{11}H_{11}NO_2$	68.87	5.85	7.50	69.06	5.82	7.29	218 (2.8) 302 (1.5)	248 (5.2) 260 (4.2) 268 (2.7)	3220, 1727, 1625, 1600, 1493, 760, 717, 690
IIb	CH_3	CH_3	CH_3	86–88	76	20% aqueous ethanol	$C_{12}H_{13}NO_2$	70.91	6.44	6.89	70.49	6.52	6.67	219 (29.2) 302 (1.3)	242 (4.9) 252 (4.7) 262 (4.2) 273.5 (2.8)	1718, 1615, 1575, 1493, 767, 695

IIc[b]	H	CH_3	$CH(CH_3)_2$	Oil	b	None	$C_{13}H_{15}NO_2$	71.86	6.95	6.44	71.81	7.27	6.75	218 (28.0) 302 (1.5)	248 (5.4) 270 (2.4)	3240, 1720, 1623, 1600
IId	CH_3	Phenyl	Phenyl	174–177	96	Methanol	$C_{22}H_{17}NO_2$	80.70	5.23	4.27	81.09	5.50	4.68	230 (23.9) 313 (1.9) 344 (1.1)	256 (9.8) 274 (3.8)	3000, 1726, 1615, 1585, 1495, 748, 737, 695, 685
IIe[b]	CH_3	Phenyl	4-Pyridyl	140–180	92	Ethyl acetate–Skellysolve B	$C_{21}H_{16}N_2O_2$	76.81	4.91	8.53	76.33	5.08	8.47	229 (27.8) 314 (11.8)	260 (8.5) 268 (6.1)	3020, 1725, 1615, 1600, 1558, 1500, 827, 800, 773, 760, 745, 702
IIf	H	Phenyl	CH_3	203–204.5	60	Methanol	$C_{16}H_{13}NO_2$	76.47	5.21	5.57	76.34	5.41	5.66	305 (1.6)	259 (4.8) 265 (3.9) 273 (2.3)	3130, 3060, 3010, 1721, 1622, 1603, 1500, 782, 757, 740, 730, 690
IIg	H	$-(CH_2)_5-$		216–218	77	Ethanol	$C_{13}H_{13}NO$	78.36	6.57	7.03	78.40	6.75	7.34	219 (28.4) 302 (1.4)	251 (4.5) 260 (3.9) 270 (2.5)	3190, 1725, 1710, 1685, 1625, 1605, 1230, 1195, 1160, 1100, 756
IIh	H	$-(CH_2)_5-$		168–169.5	100	50% aqueous ethanol	$C_{14}H_{15}NO_2$	73.34	6.59	6.11	72.99	6.64	6.30	218 (28.0) 302 (1.5)	246 (5.3) 270 (2.4)	3180, 3040, 1725, 1690, 1625, 1600, 1487, 1215, 1125, 780, 740, 705

[a] Prepared by general procedure for II. [b] Isolation different from the general procedure. See Experimental Section.

observed with IIb even at higher temperatures and a longer reaction time. IId, however, reacted readily with boiling pyrrolidine to produce benzophenone (Vd) and 1-methylisatin (VIId). These products can be explained by the mechanism shown in Chart II. An aldol-like cleavage of the β-aminocarbonyl intermediate similar to the cleavage of diacetone alcohol by amines as discussed by Hammett[3] would lead to the compounds isolated.

CHART II



VIId Vd

The reaction appears to be very fast, as only Va and VIId were detected in the reaction medium by thin layer chromatography. Under the same conditions, 1-methyldioxindole, when warmed with pyrrolidine, immediately produced a spot corresponding to 1-methylisatin (VIId) plus an additional spot with a higher R_f value.

The reaction of II with concentrated aqueous alkali proceeds by a different path to produce 2,3-disubstituted indoles VIII. The reaction appears to be quite general. Although the indoles can be obtained directly from the basic reaction mixture, the yields of VIIIg and VIIIh are improved by warming the crude products with acid. These compounds are possibly formed in a manner analogous to that previously described by Robinson[4] for the acid rearrangement of 3,3-disubstituted indolenines to 2,3-disubstituted indoles. A possible mechanism for the alkaline rearrangement is shown in Chart III.

Experimental Section[5]

Alkylideneoxyindoles (I). General Procedure.—These compounds were prepared essentially by the method of Wahl and

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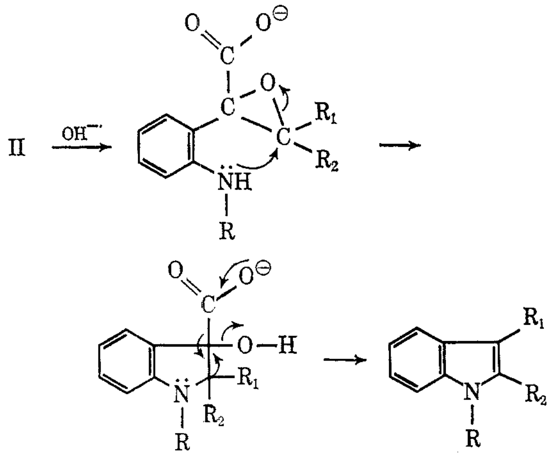
[3] L. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 345.

[4] R. Robinson and H. Serginome, *J. Chem. Soc.*, 298 (1932).

[5] Melting points were taken in a capillary tube and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 or 421 spectrophotometer. Ultraviolet spectra were determined using a Cary Model 14 or 15 spectrophotometer.

CHART III



VIIIa, R = H; R_1 = R_2 = CH_3
b, R = CH_3; R_1 = R_2 = phenyl
g, R = H; R_1, R_2 = $-(CH_2)_4-$
h, R = H; R_1, R_2 = $-(CH_2)_5-$

Livorschi.[6] When high-boiling ketones were used, other bases such as quinoline were successfully employed without an autoclave.

3,α-Epoxyoxindoles (II). General Procedure.—To a solution of I and methanol (warming was necessary in some instances) was added 1.5 equiv. of 30% hydrogen peroxide and 1.0 equiv. of 1 *N* sodium hydroxide. After 4 days at room temperature, the solution was filtered, treated with acetic acid, and concentrated to dryness under reduced pressure. The residue was recrystallized from an appropriate solvent.

1-Methyl-3-isopropylideneoxindole (Ib).—A mixture of 21.0 g. (0.14 mole) of 1-methyloxindole, 125 ml. of acetone, and 3.0 ml. of piperidine was heated in a stirred autoclave at 190° for 17 hr. The solution was concentrated to dryness. The residue was recrystallized from ethanol to yield 24.5 g. (94%) of product, m.p. 72–74°.

3′,3′-Dimethylspiro[indoline-3,2′-oxiran]-2-one (IIa).—A solution of 6.8 g. (0.04 mole) of 3-isopropylideneoxindole, 600 ml. of methanol, 6.6 ml. (0.06 mole) of 30% hydrogen peroxide, and 40 ml. of 1 *N* sodium hydroxide was allowed to stand at room temperature for 4 days and filtered, and 2 ml. of acetic acid was added. The filtrate was concentrated to dryness under reduced pressure. The residue was recrystallized from 20% alcohol to yield 6.5 g. (87%) of product, m.p. 166–168°.

3′-Isopropyl-1-methylspiro[indoline-3,2′-oxiran]-2-one (IIc).—A mixture of 26.6 g. (0.2 mole) of oxindole, 50 ml. of methyl isopropyl ketone, and 3.0 ml. of piperidine was heated in a stirred autoclave at 190° for 17 hr. The red liquid was concentrated to dryness and the residue was extracted with 4000 ml. of boiling Skellysolve B and filtered. The filtrate was concentrated to 50 ml., cooled, and decanted. The remaining oil was refluxed with Nuchar 190-N in methanol and filtered. The filtrate was concentrated to yield 6.5 g. of a reddish purple semisolid (Ic).

A solution of 5.0 g. of the semisolid, 600 ml. of methanol, 6.6 ml. of 30% hydrogen peroxide, and 40 ml. of 1 *N* sodium hydroxide was allowed to stand at room temperature for 4 days. The mixture was filtered and the filtrate was neutralized with acetic acid and concentrated to dryness to yield 3.1 g. of an oil.

A solution of 3.0 g. of the oil was chromatographed over 300 g. of Florisil in Skellysolve B. The column was eluted with four 600-ml. portions of 3% acetone–Skellysolve B, four 600-ml. portions of 6% acetone–Skellysolve B, four 600-ml. portions of 9% acetone–Skellysolve B, and four 600-ml. portions of 12% acetone–Skellysolve B. Fractions 6–10 gave 1.77 g. of an oil. The oil was rechromatographed over 30 g. of neutral alumina using 5% acetone–Skellysolve B to yield 1.2 g. of a viscous oil.

1-Methyl-3′-phenyl-3′-(4-pyridyl)-spiro[indoline-3,2′-oxiran]-2-one (IIe).—A solution of 5.0 g. (0.017 mole) of 1-methyl-3-(phenyl-4′-pyridylmethylene)oxindole, 300 ml. of methanol, 4.0 ml. (0.034 mole) of 30% hydrogen peroxide, 10 ml. of water, and 1.4 g. (0.034 mole) of sodium hydroxide was allowed to stand at room temperature for 60 hr. and filtered. The filtrate was concentrated to a small volume, enough water was added to cause complete precipitation, and the mixture was filtered. The solid was refluxed in ethyl acetate and decanted. The solution was diluted with Skellysolve B and refrigerated at −5° for 16 hr. The mixture was filtered to yield 100 mg. of a yellow solid. The filtrate was further diluted with Skellysolve B, refrigerated at −5° for 16 hr., and filtered. The solid was again recrystallized from the same mixture to yield 5.1 g. (92%) of product, m.p. 140–180°. Repeated recrystallization did not alter the melting point.

Reduction of Ia.—A mixture of 10.0 g. (0.057 mole) of Ia, 20 ml. of acetic acid, and 1.0 g. of 10% palladium on carbon was shaken for 5 min. at 50 lb. of hydrogen pressure. The mixture was filtered. The filtrate was concentrated to dryness to yield 10.0 g. (100%) of 3-isopropyloxindole, m.p. 105–106°. This melting point was in agreement with the literature value.[7]

Reaction of IIa.—A mixture of 1.9 g. (0.01 mole) of IIa, 150 ml. of methanol, and 1.0 g. of 10% palladium on carbon was shaken in a hydrogen atmosphere for 1 hr. and filtered. The filtrate was concentrated to dryness. The residue was recrystallized from dilute ethanol to yield 0.5 g. of oxindole. The filtrate was concentrated to dryness and the residue was chromatographed over 75 g. of silica (0.02–0.5 mesh) using an acetone–Skellysolve B mixture to yield 0.6 g. of oxindole and 0.2 g. of 3-isopropyloxindole, m.p. 105–106°. This compound was identical with the reduction product of Ia.

Reduction of IIb.—A mixture of 4.0 g. (0.02 mole) of IIb, 200 ml. of methanol, and 1.0 g. of palladium on carbon was hydrogenated on a Parr apparatus for 1 hr. and filtered. The filtrate was concentrated to dryness and the residue was recrystallized from Skellysolve B to yield 1.9 g. (65%) of 1-methyloxindole, m.p. 86–87°.

Reduction of Id.—A mixture of 2.0 g. (0.0064 mole) of 2-diphenylmethylene-1-methyloxindole, 250 ml. of methanol, and 0.2 g. of platinum oxide was shaken under hydrogen until the solid dissolved, and 0.5 g. of 10% palladium on carbon was added. The mixture was shaken an additional 1 hr. and filtered. The filtrate was concentrated to dryness and the residue was recrystallized from Skellysolve B. The product was collected in two fractions of 1.3 g., m.p. 105–107°, and 0.6 g., m.p. 118–122°. The compounds were shown by infrared spectroscopy to be isomorphs. Isomorph I was identical with the product obtained by the reduction of the corresponding oxide.

A repeat experiment yielded 1.6 g. (84%) of isomorph II, m.p. 125–126.5°.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.60; H, 5.79; N, 4.72.

Reduction of IId.—A mixture of 3.0 g. (0.0095 mole) of IId, 200 ml. of methanol, and 1.0 g. of 10% palladium on carbon was shaken 1 hr. in a hydrogen atmosphere at 50-lb. initial pressure. The mixture was filtered and the filtrate was concentrated to dryness. The residue was chromatographed over 200 g. of silica (0.05–0.2 mesh) using a 15% acetone–85% Skellysolve B mixture. The fractions were collected in 250-ml. aliquots. Fraction I yielded 0.4 g. of benzophenone. Fraction II, after rechromatography, yielded 1.2 g. of 3-diphenylmethyl-1-methyloxindole: m.p. 105.5–107° (isomorph I); $\nu_{\max}^{\text{Nujol}}$ 1700, 1605, 1085, 750 cm.$^{-1}$; $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (ϵ 7981), 267 mμ (ϵ 5790) (slight shoulder).

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 83.75; H, 6.39; N, 4.47.

Fractions III–VII yielded 0.8 g. of 1-methyloxindole, m.p. 85.5–87°.

IId and Pyrrolidine.—A solution of 4.4 g. (0.012 mole) of IId and 25 ml. of pyrrolidine was heated at reflux for 20 hr. and concentrated to dryness. The residue was chromatographed over 400 g. of silica (0.05–0.2 mesh) using a mixture of 1% acetic acid, 15% acetone, and 84% Skellysolve B. The material was collected in 350-ml. fractions. Fraction I yielded 1.0 g. of benzophenone. Fraction II yielded 1.0 g. of 1-methylisatin, m.p. 128–129°. The benzophenone was identified by spectral data and by its hydrazone. The 1-methylisatin was identified by comparison with an authentic sample prepared by methylation of isatin.

IIa and Pyrrolidine.—A solution of 5.0 g. (0.026 mole) of IIa and 25 ml. of pyrrolidine was refluxed for 4 hr. and the solvent was blown by a stream of nitrogen into an acid solution of 2,4-dinitrophenylhydrazine to yield 2.0 g. (62%) of acetone

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(6) A. Wahl and V. Livorschi, *Bull. soc. chim. France*, **5**, 653 (1938).

(7) H. Schwarz, *Monatsh.*, **24**, 569 (1903).

2,4-dinitrophenylhydrazone, m.p. 120–122°. The residue was slurried with about 2% hydrochloric acid. The dark crude material was slurried in a solution of potassium bicarbonate and filtered. The solid was chromatographed over 175 g. of silica (0.05–0.2 mesh) using a mixture of 20% methanol, 20% acetone, and 60% Skellysolve B. The product (0.9 g.) decomposed upon attempted purification.

IIb and Pyrrolidine.—A solution of 3.5 g. (0.017 mole) of IIb and 25 ml. of pyrrolidine was heated at 120° in a glass bomb for 14 hr. The solvent was blown into an acid solution of 2,4-dinitrophenylhydrazine. No precipitate was observed. The residue was twice chromatographed over 200 g. of silica (0.05–0.2 mesh) using a mixture of 10% methanol, 10% acetone, and 80% Skellysolve B. The product was refluxed with Nuchar 190-N in methanol and filtered. The filtrate was concentrated to dryness and the residue was extracted with Skellysolve B to yield 0.5 g. of unstable solid. The filtrate was concentrated to a small volume and refrigerated to yield 1.2 g. of unchanged starting material.

2,3-Dimethylindole (VIIIa). A.—A mixture of 1.5 g. (0.0079 mole) of IIa, 2.0 g. of sodium hydroxide, and 10 ml. of water was refluxed for 16 hr., and 75 ml. of boiling acetic acid was added. The mixture was filtered and the solution was taken to dryness. The residue was treated with 50 ml. of water and filtered. The solid (0.72 g.) was refluxed twice with Nuchar 190-N in ethanol and filtered. The filtrate was diluted with water, refrigerated 3 hr., and filtered to yield 300 mg. of a solid, m.p. 95–110°. The solid was extracted with hot Skellysolve B, concentrated to a small volume, and refrigerated to yield 200 mg. (18%) of solid, m.p. 94–96°. When this was mixed with an authentic sample of 2,3-dimethylindole[8] (m.p. 104–105°) the melting point was 99–102°. The infrared and ultraviolet spectra were identical with the spectra of the authentic 2,3-dimethylindole.

B.—A mixture of 1.0 g. (0.005 mole) of IIIa, 6.0 g. of sodium hydroxide, and 8.0 ml. of water was refluxed in a stainless steel flask for 20 hr. The sublimed solid (0.4 g., 55%) was collected from the receiver: m.p. 103–104.5°. There was no depression on mixture with an authentic sample of 2,3-dimethylindole.

1-Methyl-2,3-diphenylindole (VIIId).—A mixture of 0.5 g. (0.0015 mole) of IId and 10 ml. of 50% sodium hydroxide was refluxed for 18 hr. The mixture was then refluxed 2.5 hr. with 70 ml. of acetic acid. The mixture was cooled in an ice bath and filtered. After recrystallization from acetic acid, the solid weighed 300 mg. (71%), m.p. 137–138°. There was no depression on mixture with an authentic sample of 1-methyl-2,3-diphenylindole.[9] The infrared and ultraviolet spectra were identical with the spectra of an authentic sample of 1-methyl-2,3-diphenylindole.

1,2,3,4-Tetrahydrocarbazole (VIIg).—A solution of 5.0 g. (0.023 mole) of IIg and 50 ml. of 50% sodium hydroxide was heated at 125° for 17 hr., 10 ml. of water was added, and the solution was heated at 145° for 4 hr. The cooled mixture was poured into 400 ml. of water and stirred, and 100 ml. of concentrated hydrochloric acid was added. The mixture was maintained at 90° approximately 1 hr., cooled, and filtered. The solid was dissolved in ethanol, refluxed with Nuchar 190-N, and filtered. The filtrate was diluted with water, cooled in an ice bath, and filtered. After three recrystallizations, the product weighed 0.9 g. (22%), m.p. 114–115°. There was no melting point depression on mixture with an authentic sample.[10]

2,3-Cycloheptenindole (VIIIh).—A solution of 1.9 g. (0.083 mole) of IIh, 6.0 g. of sodium hydroxide, and 25 ml. of water was heated at 135° for 17 hr., cooled, and poured into 75 ml. of water. The mixture was stirred until a fine suspension resulted and filtered. The filtrate was treated with 20 ml. (0.2 mole) of concentrated hydrochloric acid. The mixture was held at 90° for 30 min., cooled, and filtered. The solid was dissolved in ethanol, refluxed with Nuchar 190-N, and filtered. The filtrate was diluted to 80% with water and refrigerated to yield 0.8 g. of product (53%), m.p. 141–143°.

This compound showed no melting point depression when mixed with an authentic sample.[11]

Acknowledgment.—The author is indebted to Drs. J. J. Ursprung and J. Szmuszkovicz for their helpful discussions and criticisms during the course of this work. The author is also indebted to Dr. W. A. Struck for elemental analyses and Drs. R. W. Rinehart and M. Grostic and Mr. J. Stafford for infrared and ultraviolet data.

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Chemistry of *gem*-Dihalocyclopropanes. III.[1] A New Synthesis of Indenes

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A number of *gem*-dihalocyclopropane derivatives reacted with aromatic compounds in the presence of aluminum chloride or ferric chloride. The products were in most cases indene derivatives. The mechanism of the reaction is discussed.

Halogen-substituted cyclopropane derivatives were an obscure class of compounds until the discovery by Doering and Hoffmann[2] that addition of dihalocarbene to olefins produced *gem*-dihalocyclopropanes in good to excellent yields. Since then the chemistry of these compounds has been actively studied.[3] In the present paper we want to report on reactions of *gem*-dihalocyclopropanes with aromatic compounds under Friedel–Crafts conditions, which resulted in formation of indene derivatives.

The reaction of 1,1-dibromotetramethylcyclopropane (I) with an equimolar amount of aluminum chloride in benzene was the first studied. A liquid was obtained in 80% yield, and it was shown to be homogeneous by gas chromatography. On the basis of elemental analysis and spectroscopic evidence the structure 1,1,2,3-tetramethylindene (II) was assigned. This compound had previously been prepared by Colonge and Pichat,[4] and its properties were identical with those of our sample. The compound was oxidized with chromic acid to 2-(2-carboxyphenyl)-2-methylbutanone-3,[5] and hydrogenation over Raney nickel gave 1,1,2,3-tetramethylindan. The 1,1-dichloro analog of I also yielded the indene II as the only product, and with both halides ferric chloride worked almost equally well as a catalyst; with tin tetrachloride, how-

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