TABLE I

PROPERTIES OF THE 6-SUBSTITUTED 3-OXA-6-AZABICYCLO[3.1.0]HEXANE DERIVATIVES

6-Substituent	Formula	Yield, %	M.p., °C.	Calcd, %			Found, %		
				C	H	N	C	H	N
Benzoyl	$C_{11}H_{11}NO_2$	83	73–75	69.82	5.86	7.40	69.98	5.77	7.58
p-Chlorobenzoyl	$C_{11}H_{10}NO_2Cl$	92	106	59.07	4.51	6.26	59.12	4.63	6.09
p-Nitrobenzoyl	$C_{11}H_{10}N_2O_4$	95	158–159	56.41	4.31	11.96	56.53	4.29	11.76
Benzenesulfonyl	$C_{10}H_{11}NO_3S$	87	78–80	53.31	4.92	6.22	53.60	5.03	6.49
p-Bromobenzenesulfonyl	$C_{10}H_{10}NO_3SBr$	96	140–141	39.48	3.31	4.60	39.70	3.60	4.62
p-Iodobenzenesulfonyl	$C_{10}H_{10}NO_3SI$	81	137–139	34.20	2.87	3.99	33.98	2.88	4.26
Trichloromethylmercapto	$C_5H_6NOSCl_3$	32	71–74	25.60	2.58	5.97	26.01	2.69	5.92
p-Chlorophenylmercapto	$C_{10}H_{10}NOSCl$	96	77–79	52.74	4.43	6.15	53.02	4.30	6.00
p-Bromophenylmercapto	$C_{10}H_{13}NOSBr$	92	81–83	44.13	3.70	5.15	44.45	3.69	4.80
Phenylcarbamyl	$C_{11}H_{12}N_2O_2$	47	128–130	64.69	5.93	13.72	64.95	6.02	13.94
Phenylthiocarbamyl	$C_{11}H_{12}N_2OS$	88	115–119	59.97	5.49	12.72	60.19	5.69	21.69

of benzene was stirred at room temperature under a nitrogen atmosphere. After 2 days, the product was collected by filtration and recrystallized from benzene–alcohol, yield 1.0 g. (78%), m.p. 199–202°. *Anal.* Calcd. for $C_6H_{13}I_2NO$: C, 19.53; H, 3.55; N, 3.79. Found: C, 19.77; H, 3.76; N, 3.68.

N,N,N-Trimethyl-*dl-trans*-3-iodotetrahydro-4-furylammonium Iodide (IVb).—Formation of a white precipitate commenced within 10 min. when a solution of 3.0 ml. of methyl iodide and 1.0 ml. of compound IIIb in 25 ml. of benzene was stirred at room temperature under a nitrogen atmosphere. After 2 days the product was collected by filtration, yield 4.4 g., m.p. 207° with violent decomposition. The melting point was not altered upon recrystallization from ethanol. *Anal.* Calcd. for $C_7H_{15}I_2NO$: C, 21.95; H, 3.95; N, 3.61. Found: C, 21.92; H, 4.29; N, 3.37.

Other Derivatives of 3-Oxa-6-azabicyclo[3.1.0]hexane.—The aroyl, arenesulfonyl, and organomercapto derivatives were prepared by treatment of the parent aziridine IIa with the corresponding acid chloride in benzene solution in the presence of triethylamine. The carbamyl derivatives were prepared by treatment of the aziridine with phenyl isocyanate and isothiocyanate in benzene solution. All of the derivatives were solids, which were recrystallized from ethanol or benzene–petroleum ether. Yields, melting points, and elemental analyses are summarized in Table I.

Pyrolysis of 6-Benzoyl-3-oxa-6-azabicyclo[3.1.0]hexane (IX).—A solution of 0.531 g. of compound IX in 5 ml. of benzene was heated in an autoclave at 235–250° for 16 hr. Evaporation of the benzene gave a black tar, which was extracted with hot heptane to give a 33% yield of **2-phenyl-*cis*-tetrahydrofuro[3,4-*d*]oxazoline (XI)** white needles, m.p. 112–114°. After recrystallization from benzene–heptane, an analytical sample melted at 114–115°. When the pyrolysis was conducted for 16 hr. at 185–195°, the yield of oxazoline was 6%, and 41% of unreacted starting material was recovered. *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.05; H, 6.08; N, 7.30.

Reaction of 6-Benzoyl-3-oxa-6-azabicyclo[3.1.0]hexane (IX) with Sodium Iodide.—A solution of 0.378 g. of compound IX and 2.0 g. of sodium iodide in 50 ml. of acetonitrile was stirred under nitrogen at room temperature for 16 hr. The solvent was evaporated and the solid residue was extracted with three 20-ml. portions of benzene. Distillation of the benzene extracts gave 0.30 g. (79% yield) of oxazoline XI, m.p. 111–113°. After recrystallization from benzene–heptane, the sample melted at 115–116°, and was found by mixture melting point and infrared absorption spectrum to be identical with the product obtained by pyrolysis. The same oxazoline was also obtained in 59% yield when the reaction was run in acetone and the distillation step was omitted. Oxazoline XI gave a negative potassium permanganate test for unsaturation, and absence of an NH bond was demonstrated in the infrared absorption spectrum.

Reaction of 6-(*p*-Nitrobenzoyl)-3-oxa-6-azabicyclo[3.1.0]hexane (IXa) with Sodium Iodide.—A solution of 0.300 g. of compound IXa and 2.0 g. of sodium iodide in 50 ml. of acetone was stirred at room temperature for 4 days, then refluxed for 1 hr. Hexane (200 ml.) was added and the reaction mixture was filtered to remove sodium iodide. Evaporation of the filtrate left 0.256 g. (85% yield) of **2-(*p*-nitrophenyl)-*cis*-tetrahydrofuro[3,4-*d*]oxazoline (XIa)**, yellow-white solid, m.p. 204–206°. Recrystallization from alcohol gave an analytical sample, m.p. 209–210°. *Anal.* Calcd. for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.31; N, 11.96. Found: C, 56.31; H, 4.36; N, 11.40.

The Reaction of 2,3-Dichloronaphthoquinone with Nucleophiles. III. Reaction with 1,3-Indandione

J. A. VANALLAN, R. E. ADEL, AND G. A. REYNOLDS

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

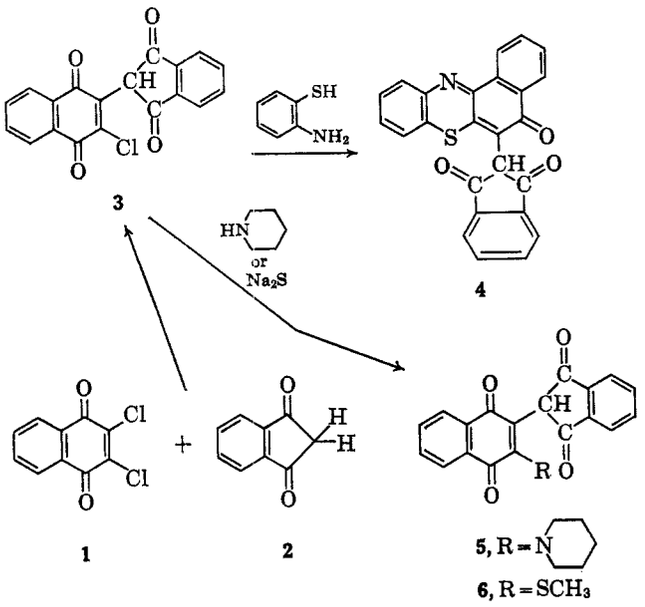
Received June 16, 1965

The rearrangement of 2-chloro-3-(1,3-dioxoindan-2-yl)-1,4-naphthoquinone into bindone has been investigated. A mechanism for this rearrangement is proposed.

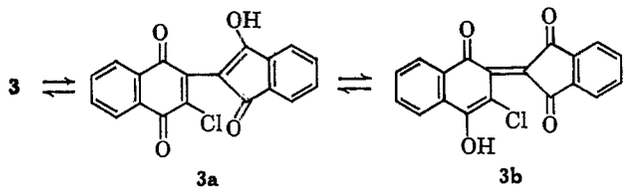
In the previous paper of this series,[1] the reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) with ethyl acetoacetate was investigated and structures were assigned to the reaction products. As part of the general problem of the study of the reaction of **1** with various nucleophilic reagents, we have extended the investigation to the reaction of 1,3-indandione (**2**) with **1**. This reaction proceeded at 25–30° in alcohol, N,N-diisopropylethylamine being used as the base to give **3** in 92% yield. The structure assigned to **3** was demonstrated by allowing *o*-aminobenzenethiol to react with **3** to give the phenothiazine derivative **4** which had an ultraviolet absorption spectrum similar to spectra of related compounds.[2] Treatment of **3** with piperidine and with sodium sulfide, followed by methyl sulfate, resulted in the replacement of the chlorine atom of compound **3** to give compounds **5** and **6**, respectively.

(1) G. A. Reynolds, J. A. VanAllan, and R. E. Adel, *J. Org. Chem.*, **30**, 3819 (1965).

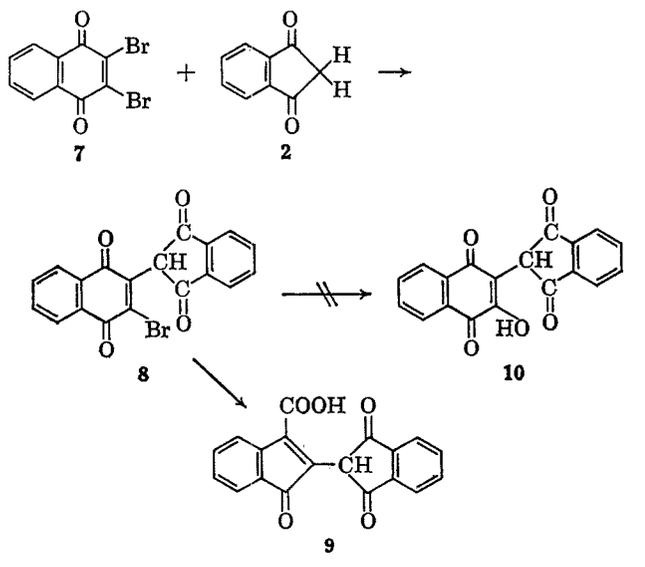
(2) J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *ibid.*, **27**, 1659 (1962).

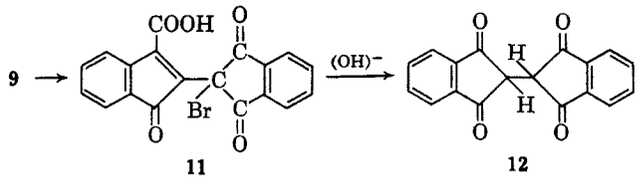


The n.m.r. spectrum of **3** in dimethyl sulfoxide showed two broad proton absorptions at δ 5.00 and 5.40. Addition of deuterium oxide to the dimethyl sulfoxide solution caused the two peaks to disappear rapidly. No evidence of intramolecular hydrogen bonding was present in the n.m.r. spectrum. A model of this compound suggests that its geometry is not favorable to intramolecular hydrogen bonding because of interference of the indanone moiety with the adjacent chlorine atom. These data indicated that the solution of **3** was composed of at least two of the following tautomers.

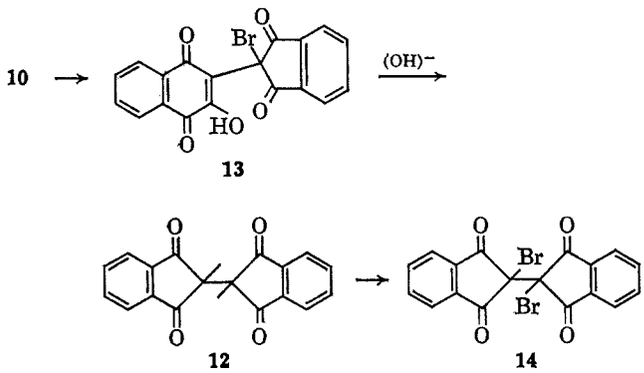


Stadler reported[3] that 2,3-dibromo-1,4-naphthoquinone (**7**) reacted with **2** to give **8**, which, on treatment with potassium hydroxide, gave **9** rather than the expected **10**. Bromination of **9** was reported[3] to give **11**, which, on treatment with alkali, yielded the bindone (**12**). Mechanisms for these rearrangements were given.[3]





We have found that alcoholic potassium hydroxide converted **3** to a compound which had the properties described by Stadler and to which he assigned the structure **9**. This material has now been assigned the structure **10** for the following reasons. Polarographic examination of **10** showed reduction waves at $E_{1/2}$ = −1.038 and −0.142 v. *vs.* s.c.e., which compared favorably with the model compounds 1,3-indandione ($E_{1/2}$ = −1.05 v. *vs.* s.c.e.) and 2-hydroxy-1,4-naphthoquinone ($E_{1/2}$ = −0.206 v. *vs.* s.c.e.). The ultraviolet spectra of **3, 5, 6,** and **10** were all similar, which indicated that **10** had undergone no skeletal rearrangement (see Table I). Bromine in acetic acid with **10** again gave the material described by Stadler to which he assigned structure **11**, but to which we assign structure **13**, since its ultraviolet spectrum corresponded to that of the 2,3-disubstituted 1,4-naphthoquinone (see Table I). Supporting evidence for the structures of **10** and **13** was obtained by comparison of the infrared spectra of 2-hydroxynaphthoquinone (A), **2**, and 2-bromo-2-phenyl-1,3-indandione (B) with those of **10** and **13**. The spectrum of A showed typical absorption at 5.98 μ; **2** and B had characteristic indandione absorption at 5.78 and 5.82 μ. The infrared spectra of **3, 10,** and **13** had both these characteristic absorptions, indicating the presence of a quinone and an indandione moiety.



Sodium acetate or potassium hydroxide in alcohol converted **13** to bindone (**12**), which was identical with an authentic sample of **12** prepared from bis-(ethylene phthalide).[4] In addition, **12** was converted to the known **14**.[5]

We suggest that the following mechanism accounts for the formation of **12** from **13**. Dehydrohalogenation of **13** gave the intermediate C, which, under the basic conditions of the reaction mixture, underwent the benzilic acid rearrangement to give D, and this, in turn, was decarboxylated to yield **12**. Treatment of **13** (to which Stadler assigns structure **11**) with

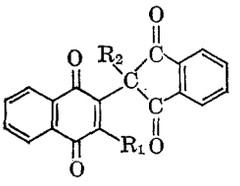
(3) W. Stadler, *Ber.*, **35**, 3957 (1902).

(4) S. Gabriel and A. Michael, *ibid.*, **10**, 1560 (1877).

(5) S. Gabriel and E. Leupold, *ibid.*, **31**, 1169 (1898).

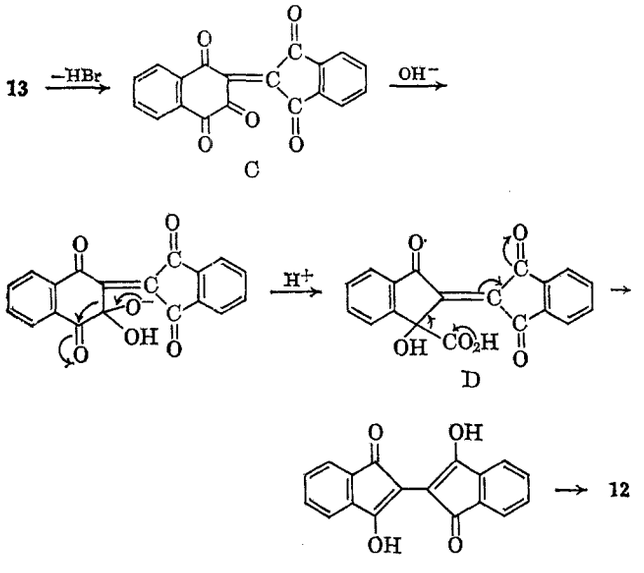
TABLE I

ULTRAVIOLET SPECTRA OF 2,3-DISUBSTITUTED 1,4-NAPHTHOQUINONES

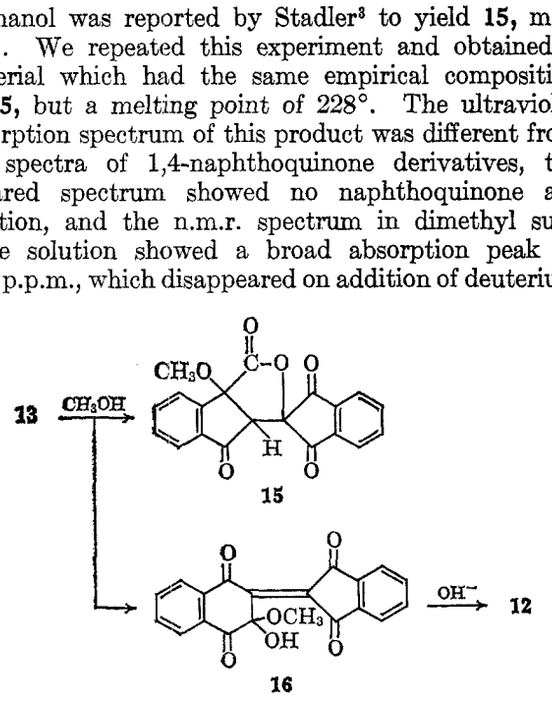


Compd.[a]	R_1	R_2	λ_a, mμ ($\epsilon \times 10^{-3}$)	λ_b, mμ ($\epsilon \times 10^{-3}$)	λ_c, mμ ($\epsilon \times 10^{-3}$)	λ_d, mμ ($\epsilon \times 10^{-3}$)	λ_e, mμ ($\epsilon \times 10^{-3}$)
3	Cl	H	224 (63.5)	248 (29.8) 253 (31.4)	272 (14.0)	302 (6.0) 340 (3.9)	
10	OH	H		248 (25.6) 253 (27.6)	276 (16.8)	333 (3.4)	
13	OH	Br	232 (30.0)	248 (32.3) 254 (32.5)	275 (16.3)	335 (4.0)	
6	CH_3S–	H		250 (23.8)		303 (6.7)	427 (22.9)
5		H	222 (5.0)	241 (30.0)	285 (14.0)		510 (4.8)

[a] Solvent in all cases is acetonitrile.



methanol was reported by Stadler[3] to yield **15**, m.p. 198°. We repeated this experiment and obtained a material which had the same empirical composition as **15**, but a melting point of 228°. The ultraviolet absorption spectrum of this product was different from the spectra of 1,4-naphthoquinone derivatives, the infrared spectrum showed no naphthoquinone absorption, and the n.m.r. spectrum in dimethyl sulfoxide solution showed a broad absorption peak at 5.05 p.p.m., which disappeared on addition of deuterium



oxide. The isomeric structure **16** seems more reasonable for this product than structure **15**, since the reaction was carried out under such mild conditions, but an unequivocal choice cannot be made on the basis of the physical data just mentioned. Stadler reported that treatment of **15** with alkali gave **9**. We found that methanolic potassium hydroxide converted this material to bindone (**12**), presumably by the mechanism described for the conversion of **13** to **12**.

Experimental Section

2-Chloro-3-(1,3-dioxoindan-2-yl)-1,4-naphthoquinone (3).—A mixture of 4.54 g. (0.02 mole) of 2,3-dichloro-1,4-naphthoquinone (**1**), 3 g. (0.02 mole) of 1,3-indandione (**2**), and 6 g. (8 ml., 0.04 mole) of N,N-diisopropylethylamine in 50 ml. of alcohol was stirred at room temperature for 2 hr. The resulting deep red solution was diluted with 20 ml. of water and filtered. The filtrate was acidified with hydrochloric acid; the precipitate was collected, dried, and crystallized from 1,2,3-trichloropropane to give 6.2 g. of **3** (92%), m.p. 258°.

Anal. Calcd. for $C_{19}H_9ClO_4$: C, 67.9; H, 2.7; Cl, 10.6. Found: C, 67.8; H, 2.5; Cl, 10.6.

6-(1,3-Dioxoindan-2-yl)benzo[*a*]phenothiazin-5-one (4).—A suspension of 6.7 g. (0.02 mole) of **3** and 2.5 g. of *o*-aminobenzenethiol in 60 ml. of pyridine was heated under reflux for 1 hr. After cooling, 60 ml. of methanol was added. The precipitate was collected and crystallized from dimethylformamide to give 6.1 g. of **4** (75%): m.p. 348–350°; ultraviolet spectrum in acetonitrile, λ_{max}, mμ (ϵ), 248 (42,200), 255 (42,800), 317 (17,800), 374 (10,100), 388 (9950), 479 (11,200).

Anal. Calcd. for $C_{25}H_{13}NO_3S$: C, 73.6; H, 3.2; N, 3.4; S, 7.9. Found: C 73.6; H, 3.5; N, 3.4; S, 8.0.

2-(1,3-Dioxoindan-2-yl)-3-methylmercapto-1,4-naphthoquinone (6).—To a suspension of 6 g. of **3** in 40 ml. of methanol was added a solution of 6 g. of sodium sulfide in 20 ml. of water. The quinone dissolved and the solution turned purple. The mixture was stirred for 15 min.; 6 ml. of dimethyl sulfate was added. After the reaction mixture had been stirred for 3.5 hr., it was refluxed for 0.5 hr. A small amount of precipitate was filtered off, and the filtrate was poured into water and acidified with hydrochloric acid. The solid was collected and crystallized from 2-ethoxyethanol to yield 4.6 g. of product, m.p. 278°.

Anal. Calcd. for $C_{20}H_{12}O_4S$: C, 69.0; H, 3.5; S, 9.2. Found: C, 68.8; H, 3.6; S, 9.0.

3-(1,3-Dioxoindan-2-yl)-2-hydroxy-1,4-naphthoquinone (10).—A solution of 20 g. of **3** in 100 ml. of 10% methanolic potassium hydroxide was heated to 50° for 5 min. The mixture was diluted with an equal volume of water and the resulting solution was acidified with acetic acid. The bright yellow precipitate was

collected and crystallized from acetic acid to give 16 g. of **10**, m.p. 240°.

Anal. Calcd. for $C_{19}H_{10}O_6$: C, 71.6; H, 3.1. Found: C, 71.4; H, 3.3.

Bindone (12).—A suspension of 2.0 g. of **13** and 2 g. of sodium acetate in 20 ml. of methanol was stirred until the reactants were in solution (about 10 min.), 20 ml. of water was added, and the resulting deep red solution was filtered. The filtrate was refluxed for 1 hr., and the dark precipitate was collected and crystallized from 1,2,4-trichlorobenzene to give 0.9 g. of **12** as dark red crystals, m.p. 310°.

3-(2-Bromo-1,3-dioxoindan-2-yl)-2-hydroxy-1,4-naphthoquinone (13).—A suspension of 10 g. of **10** in 75 ml. of acetic acid containing 2 ml. of bromine was heated to 80°. The mixture solidified after about 5 min. Heating was continued at 90–100° for 1 hr., and the product was collected by filtration and crystallized from a large volume of acetic acid to give 11 g. of **13**,[3] m.p. 240°.

2,2'-Dibromobindone (14).—A suspension of 2 g. of **13** in 15 ml. of 10% methanolic potassium hydroxide was heated under reflux for 0.5 hr., 15 ml. of water was added, and heating was continued for a further 10 min. Acidification of the reaction mixture gave crude bindone, which was brominated in acetic acid solution at 60° to give **14**,[5] m.p. 278°.

3-(1,3-Dioxoindan-2-ylidene)-2-hydroxy-3-methoxy-2,3-dihydro-1,4-naphthoquinone (16).—A suspension of 6 g. of **13** in 600 ml. of methanol was refluxed on the steam bath for 5 hr. and filtered hot to remove a small amount of starting material. The filtrate was cooled to give 3.8 g. of **16**: m.p. 228° (from a mixture of chloroform and methanol); ultraviolet spectrum in acetonitrile, λ_{max}, mμ (ϵ), 231 (76,800), ~250 (26,700), ~290 (2500).

Anal. Calcd. for $C_{20}H_{12}O_6$: C, 69.0; H, 3.5. Found: C, 68.7; H, 3.2.

Acknowledgment.—We gratefully acknowledge the assistance of T. H. Regan and R. L. Young, of these laboratories, for the determination and interpretation of the n.m.r. spectra which were determined by using a Varian A-60 spectrometer at the ambient probe temperature, 35°. The polarographic data were supplied by D. G. Bush, also of these laboratories, to whom we are also indebted.

Nitration of Indoles. IV. The Nitration of 2-Phenylindole[1]

WAYLAND E. NOLAND, KENT R. RUSH,[2a] AND LOWELL R. SMITH[2b]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received July 16, 1965

Nitration of 2-phenylindole (**1**) follows the orientation rules previously established for 2-methylindole, except that trinitration has not been observed. Thus, nitration of **1** in concentrated sulfuric acid gives 5-nitro-2-phenylindole (**8**), while nitration of **1** in concentrated nitric acid gives 3,6-dinitro-2-phenylindole (**4**) and further nitration of **8** in concentrated nitric acid gives 3,5-dinitro-2-phenylindole (**9**). Catalytic hydrogenation of **8** gives 5-amino-2-phenylindole (**12**). The nitration product of 2-phenylisatogen (**13**) and nitric acid has been shown to be 5-nitro-2-phenylisatogen (**14**), an observation of interest because of the structural resemblance of **13** to the conjugate acid (**15**) of **1**.

In 1900 Angeli and Angelico[3] reported the preparation of a dinitro-2-phenylindole (**4**) by nitrosation of 2-phenylindole (**1**) to 2-phenyl-3H-indol-3-one oxime (**2**), followed by *in situ* nitration (accompanied by oxidation) with nitric acid in acetic acid. Alternatively (see Chart I), **4** could be obtained from 3-nitro-2-phenylindole (**3**), isolated from a prior oxidation of **2**, by warming **3** with nitric acid in acetic acid. These reactions establish that one of the nitro groups in **4** is in the 3-position of the indole nucleus. In 1938 Womack, Campbell, and Dodds[4] showed that **4** could best be obtained by direct nitration of **1** with concentrated nitric acid. Attempted further nitration of **4** to a trinitro derivative of **1** was unsuccessful, giving either unchanged **4** or, under the more vigorous conditions of boiling concentrated nitric acid, oxidation to acidic compounds, from which a small amount of N-benzoyl-5-nitroanthranilic acid (**10**) was reported[4] to have been isolated. Furthermore, oxidative degradation of **4** with potassium permanganate in acetic acid gave a product (m.p. 257–258°) which was said[4] to be "identical" with a sample (m.p. 257–260°) of N-benzoyl-5-nitroanthranilic acid (**10**) prepared from authentic 5-nitroanthranilic acid.[5] Consequently, Womack, Campbell, and Dodds[4] assigned to their dinitro derivative the structure (incorrect, see below) 3,5-dinitro-2-phenylindole, and drew the further inference (now disproved[1]) that the dinitro derivative of 2-methylindole,[6] formed under similar conditions, was 3,5-dinitro-2-methylindole.

Since the orientation claimed (3,5)[4] for nitration of **1** was at variance with that which we have observed (3,6)[1] for nitration of 2-methylindole under similar conditions (concentrated nitric acid), and since the melting point observed[4] for the oxidation product of **4** is also similar to that reported (m.p. 251° dec.,[7] 252°[8]) for N-benzoyl-4-nitroanthranilic acid (**5**), the expected oxidation product of 3,6-dinitro-2-phenylindole, we repeated the oxidative degradation of **4**. Our sample of the oxidation product (m.p. 248.5–251°) of **4** was identical, as shown by infrared and mixture melting point comparison, with a sample of N-benzoyl-4-nitroanthranilic acid (**5**) prepared[7] by oxidation of 5'-nitro-*o*-benzotoluidide (**7**), but depressed (233–247°) the melting point of N-benzoyl-5-nitroanthranilic acid (**10**). Furthermore, our sample of **5** from oxidation of **4** was decarboxylated to the known 3'-nitrobenzanilide (**6**), prepared[9] by benzoylation of *m*-nitroaniline. Thus, the

(1) Paper III: W. E. Noland, L. R. Smith, and K. R. Rush, *J. Org. Chem.*, **30**, 3457 (1965).

(2) Taken in part from (a) K. R. Rush, Ph.D. Thesis, University of Minnesota, Sept. 1963; *Dissertation Abstr.*, **25**, 2241 (1964); National Science Foundation Graduate Fellow, 1961–1963; and (b) L. R. Smith, 1960, research not included in his Ph.D. Thesis; Dow Chemical Co. Fellow, 1959–1960.

(3) (a) A. Angeli and F. Angelico, *Gazz. chim. ital.*, **30**, II, 268 (1900); (b) A. Angeli, *Samml. Chem. Chem.-Tech. Vortr.*, **17**, 311 (1912).

(4) E. B. Womack, N. Campbell, and G. B. Dodds, *J. Chem. Soc.*, 1402 (1938).

(5) M. T. Bogert and G. Scatchard, *J. Am. Chem. Soc.*, **41**, 2066 (1919).

(6) R. von Walther and J. Clemen, *J. prakt. Chem.*, [2] **61**, 249 (1900).

(7) P. Ruggli, A. Zimmerman, and O. Schmid, *Helv. Chim. Acta*, **16**, 1249 (1933).

(8) P. Ruggli and W. Leonhardt, *ibid.*, **7**, 898 (1924).

(9) (a) C. A. Bell, *Chem. Ber.*, **7**, 497 (1874); (b) F. Sachs and M. Goldman, *ibid.*, **35**, 3342 (1902).