7.88–8.35 (m, 4, aromatic); mass spectrum *m/e* 294 (molecular ion), 248, 193, 179, 150, and 102.

Anal. Calcd for $C_{14}H_{18}N_2O_5$: C, 57.11; H, 6.16; N, 9.52. Found: C, 57.44; H, 6.02; N, 9.80.

Ethyl 4-(*p*-Tolylsulfonyl)-3-triphenylphosphoranylbutanoate (11).—A mixture of 197 mg of *p*-tolylsulfonylaziridine,[9] 348 mg of **1**, and 25 ml of dry toluene was refluxed for 15 min. On cooling, a white solid, mp 240–260°, precipitated and was filtered. Evaporation of the filtrate gave 166 mg of crude **11**. Four recrystallizations from 95% ethanol gave **11**, mp 184–186°.

Anal. Calcd for $C_{31}H_{32}NO_4PS$: C, 68.23; H, 5.91; N, 2.56. Found: C, 68.27; H, 6.21; N, 2.61.

Conversion of 11 into 12.—To 272 mg of **11** in 20 ml of 10% aqueous methanol was added a solution of 28 mg of KOH in 15 ml of 50% aqueous methanol. The mixture was refluxed for 1 hr, cooled, and added to 175 ml of H_2O. The volume of solvent was reduced to 25 ml by evaporation and the triphenylphosphine oxide that had precipitated was filtered. The pH of the filtrate was adjusted to *ca.* 2 by 10% H_2SO_4 and then the filtrate was evaporated to give 115 mg of **12**. Recrystallization three times from aqueous ethanol gave **12**, mp 132–134°. An authentic sample of **12** prepared according to a published method[18] melted at 133–134°; the ir spectra of the two samples were identical.

Compound 11 was prepared by refluxing a mixture of 348 mg of **3**, 192 mg of 1-aziridinecarboxanilide,[19] and 25 ml of dry toluene for 4 hr. The solvent was evaporated and 306 mg of crude **11** was obtained and recrystallized from CCl_4–hexane, mp 182–184°. An authentic sample was prepared by a published method.[6] This sample of **11** melted at 188–189° and had an ir spectrum identical with that of **11** prepared from the 1-aziridinecarboxanilide.

Ethyl 3-Phenyl-4-(N-*p*-nitrobenzylidene)amino-2-butenoate (15).—A mixture of 268 mg of 2-*p*-nitrophenyl-3-benzoylaziridine, 351 mg of **1**, and 30 ml of $CHCl_3$ was refluxed for 24 hr. The solvent was evaporated and the glassy residue was slurried with a small amount of 95% ethanol. The yellow crystals of **15** were filtered and recrystallized from 95% ethanol to give 150 mg of **15**, mp 113–115°.

Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.43; H, 5.36; N, 8.28. Found: C, 67.14; H, 5.46; N, 8.20.

Hydrolysis of 7 to 4-(*p*-nitrobenzamido)pentanoic acid was effected by adding 227 mg of **7** to 20 ml of CH_3OH-H_2O (1:1) and heating until **7** dissolved. A solution containing 28 mg of KOH in 20 ml of CH_3OH–H_2O (1:1) was added and the mixture was refluxed for 2 hr. Evaporation of the CH_3OH caused precipitation of Ph_3PO, which was filtered. The filtrate was acidified to pH 1–3 with 10% H_2SO_4. Evaporation of the filtrate gave 75 mg of 4-(*p*-nitrobenzamido)pentanoic acid. Recrystallization from aqueous ethanol gave material melting at 145–146°. Reaction of 4-aminopentanoic acid[20] with *p*-nitrobenzoyl chloride also formed 4-(*p*-nitrobenzamido)pentanoic acid in poor yield. The two samples gave identical ir spectra; mass spectrum molecular ion *m/e* 266, fragments *m/e* 249, 220, 193 [*p*-$O_2NC_6H_4CONHCHCH_3]^+$, 150, and 120.

Registry No.—**1**, 1099-45-2; **2**, 22487-52-1; **3**, 22433-20-1; **4**, 22433-21-2; **5**, 22433-22-3; **6**, 22433-23-4; **7**, 22433-24-5; **8**, 5717-37-3; **9**, 22433-26-7; **10**, 22433-27-8; **11**, 22433-28-9; **12**, 1213-42-9; **15**, 22487-54-3.

Acknowledgment.—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and Mr. Richard Adams for the experiments dealing with *trans*-2-*p*-nitrophenyl-3-benzoylaziridine. The authors are also indebted to Professor Charles Sweeley for the mass spectrum of compound **10**.

(18) D. Todd and S. Teich, *J. Amer. Chem. Soc.*, **75**, 1895 (1953).
(19) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).
(20) J. Cologne and J. M. Pouchol, *Bull. Soc. Chim. Fr.*, 598 (1962).

Cyclization Reactions of Ninhydrin with Aromatic Amines and Ureas[1]

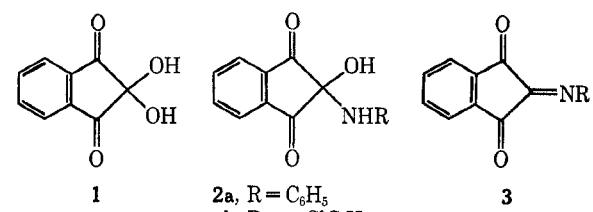
ROBERT SHAPIRO AND NITHIANANDA CHATTERJIE

Department of Chemistry, New York University, New York, New York 10003

Received March 25, 1969

Ninhydrin (1,2,3-indantrione monohydrate, **1**) condenses with aromatic amines that contain an additional activating group in the *meta* position. The reaction proceeds with cyclization to give structures of type **5** (X = OH, OCH_3, or NH_2; R = H). These products are stable, show the appropriate number of aromatic protons in their nmr spectra, give strong parent peaks in their mass spectra, and yield well-characterized acetyl derivatives. These properties distinguish them from the products formed from **1** and less activated aromatic amines, in which reaction takes place only at the central carbonyl group of **1**. The reaction of **1** with urea and 1,3-dimethylurea also proceeds with cyclization, to give structures of type **6** (R = H or CH_3; R′ = H). 1,1-Dimethylurea does not react with ninhydrin.

In recent studies in this laboratory,[2,3] it was reported that ninhydrin reacted with the amino heterocycles guanine and cytosine to afford products which contained an additional heterocyclic ring. These results stood in contrast to earlier reports in the literature about the reactions of ninhydrin with simpler aromatic amines and ureas. Thus the reaction products of **1** with aniline,[4] *p*-chloroaniline,[4] *o*- and *m*-hydroxyaniline,[4] *p*-aminobenzoic acid,[5] 2-aminopyridine,[4] urea,[6,7] 1,1-dimethylurea,[6] and guanidine[7,8] were assigned structures of type **2**, while the corresponding dehydrated products (**3**) were obtained from *p*-hydroxyaniline and

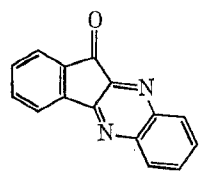


1 **2a**, R = C_6H_5; **b**, R = *p*-ClC_6H_4; **c**, R = *m*-HOC_6H_4; **d**, R = $CONH_2$ **3**

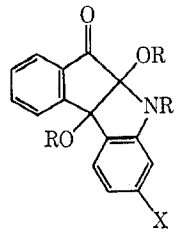
p-phenylenediamine.[5] Only in the reaction of *o*-phenylenediamine with ninhydrin was a cyclized structure (**4**) ascribed to the product.[9]

(1) This investigation was supported by a grant (GM-11437) from the U. S. Public Health Service.
(2) R. Shapiro and J. Hachmann, *Biochemistry*, **5**, 2799 (1966).
(3) R. Shapiro and S. C. Agarwal, *J. Amer. Chem. Soc.*, **90**, 474 (1968).
(4) M. Friedman, *Can. J. Chem.*, **45**, 2271 (1967).
(5) R. Moubasher, *J. Chem. Soc.*, 1038 (1949).
(6) M. Polonovsky, P. Gonnard, and G. Glotz, *Bull. Soc. Chim. Fr.*, **6**, 1557 (1939).
(7) D. A. Mac Fayden, *J. Biol. Chem.*, **186**, 1 (1950).
(8) S. Ruhemann, *J. Chem. Soc.*, **97**, 2025 (1910).
(9) S. Ruhemann, *ibid.*, **97**, 1438 (1910).

We have now reinvestigated these reactions and wish to report that aromatic amines with an electron-releasing group (hydroxy, methoxy, or amino) in the *meta* position react with ninhydrin to give the corresponding indeno[2,1-*b*]indole derivative (**5**). If the



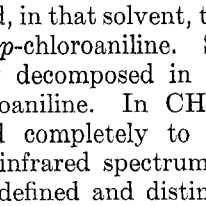
4



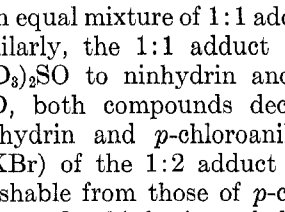
5a, X = OH; R = H
b, X = O_2CCH_3; R = $OCCH_3$
c, X = OCH_3; R = H
d, X = OCH_3; R = $OCCH_3$

activating group is not present, then cyclization does not occur, but rather simple addition to the central carbonyl group of ninhydrin takes place. Urea and 1,3-dimethylurea react with **1** to give cyclized products of structure **6**. No reaction occurs with 1,1-dimethylurea and ninhydrin.

The products of reaction of ninhydrin and aniline and *p*-chloroaniline were unstable. Unlike the cyclized products discussed below, they reverted to their components upon thin layer chromatography, gave acetanilide and *p*-chloroacetanilide upon attempted acetylation, and exhibited no molecular ion in the mass spectrum. Our analysis of the ninhydrin–aniline product agreed with that of Friedman,[4] and we agree with assignment of structure **2a** to this compound. The analysis and nmr spectrum of the product of reaction of ninhydrin and *p*-chloroaniline indicated that it contained one indandione residue and two amine molecules. Upon recrystallization of this from chloroform–hexane, a 1:1 adduct analogous to that of Friedman[4] was obtained. Inspection of the nmr spectrum of the 1:2 adduct in $(CD_3)_2SO$ revealed that it had decomposed, in that solvent, to an equal mixture of 1:1 adduct and *p*-chloroaniline. Similarly, the 1:1 adduct partially decomposed in $(CD_3)_2SO$ to ninhydrin and *p*-chloroaniline. In CH_3OD, both compounds decomposed completely to ninhydrin and *p*-chloroaniline. The infrared spectrum (KBr) of the 1:2 adduct was well defined and distinguishable from those of *p*-chloroaniline and the 1:1 adduct. On this basis, we believe it to represent a distinct compound as a solid (if not in solution) and have assigned structure **7** to it.



6a, R = R′ = H
b, R = R′ = $COCH_3$
c, R = CH_3; R′ = H
d, R = CH_3; R′ = $COCH_3$



7

The product obtained from *m*-hydroxyaniline and ninhydrin has quite different properties from those of **2a** and **7**. It recrystallized well, gave a well-defined spot upon thin layer chromatography, and showed an intense molecular-ion peak in its mass spectrum. Its nmr spectrum in $(CD_3)_2SO$ revealed the presence of four indanone protons, three benzenoid protons (with the proton *meta* to nitrogen split by a single adjacent proton), and four exchangeable protons. Friedman[4] has assigned structure **2c** to the reaction product of *m*-hydroxyaniline and ninhydrin. This assignment was apparently made by analogy to the aniline reaction, as it was stated that the nmr spectra of the product in dimethyl sulfoxide-d_6 and CF_3CO_2H were too complex for unequivocal analysis. However, we feel that the properties of this compound are quite readily interpretable in term of structure **5a**. Further confirmation of this structure was provided by the conversion of **5a** into a stable tetracetyl derivative, **5b**. This product exhibited absorptions for four different CH_3CO groups in the nmr, as expected.

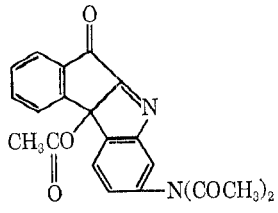
m-Anisidine gave with ninhydrin a product similar in its properties to **5a**. Its nmr spectrum was consistent with that expected from a cyclized product of structure **5c**. Acetylation of this substance afforded a triacetyl derivative, **5d**. An adduct prepared from *m*-phenylenediamine and ninhydrin crystallized well only from an acetone–water mixture. It crystallized with a molecule of acetone, but its properties and nmr spectrum were otherwise analogous to those of **5a** and **5c**. Structure **5e** was assigned to this adduct. Upon acetylation, it yielded a dehydrated, triacetyl derivative to which structure **8** has been assigned.

The ready formation of an adduct of urea and ninhydrin has been reported by several groups of workers.[6,7,10] Structure **2d** (or a tautomer involving the enol from of the urea moiety) was assigned to it.[6,7] This was supported largely by the observation that 1,1-dimethylurea gave an analogous adduct with **1**, but that 1,3-dimethylurea did not. In reexamining these results, however, we obtained the exact opposite result. Urea and 1,3-dimethylurea readily gave adducts with ninhydrin. No new product could be isolated when 1,1-dimethylurea and ninhydrin were brought together under a variety of conditions. Only unchanged ninhydrin was observed by tlc, and unchanged 1,1-dimethylurea was recovered from the reaction mixture. The urea–ninhydrin product ran as a well-defined spot on tlc, exhibited a peak for the molecular ion in the mass spectrum, and had absorptions for four different NH and OH protons in its nmr spectrum. It formed a well-characterized tetracetyl derivative, whose nmr spectrum confirmed the presence of four nonequivalent acetyl groups. On this basis, structures **6a** and **6b** were assigned to the urea–ninhydrin product and its tetraacetyl derivative, respectively. The properties of the product of 1,3-dimethylurea and ninhydrin were fully analogous, and in accord with the structure **6c**. A diacetyl derivative, **6d**, was prepared from this compound.

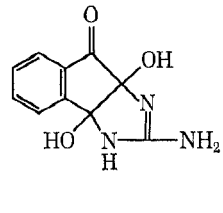
A reaction product of guanidine and ninhydrin was also reported by earlier workers.[7,8] We found this compound to be insoluble in most neutral solvents and to streak badly on tlc. Its nmr spectrum (CF_3CO_2H) showed one NH absorption which integrated as two protons, and another NH (one proton) absorption over-

(10) D. D. Van Slyke and P. B. Hamilton, *J. Biol. Chem.*, **150**, 471 (1943).

lapping the aromatic hydrogen peak. These results suggested structure **9**, or a tautomer, for this compound.



8



9

However, the mass spectrum showed a number of peaks of *m/e* values higher than the expected molecular ion, and it seems likely that the substance is dimeric or polymeric. Only intractable mixtures were formed upon attempted acetylation.

Experimental Section

The general procedures used were similar to those already described,[3] with the following exceptions. Mass spectra were determined with a Varian M-66 mass spectrometer at 70 eV. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., or on an automatic CHN analyzer (F & M Scientific Corp., Model 185). Thin layer chromatography was performed on plates prepared with Merck silica gel, except where otherwise noted.

2-Hydroxy-2-N-phenylamino-1,3-indandione (2a).—The procedure of Friedman was followed, using 1.85 g (10.4 mmol) of ninhydrin and 0.97 g (10.4 mmol) of aniline. A yield of 1.20 g (45%) of **2a** was obtained, as a yellow powder: mp 106–108° dec; the ir and uv were similar to those reported;[4] nmr (CD_3SOCD_3), τ 1.95 (s, 4, indandione H) and 2.80–3.65 (m, 7, aniline H, NH, and OH); after addition of D_2O, the peak at 2.80–3.65 integrated as five protons.

Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53. Found: C, 71.18; H, 4.05; N, 5.11.

2,2-Di-(*p*-chlorophenylamino)-1,3-indandione (7).—To a solution of 1.27 g (10 mmol) of *p*-chloroaniline in 200 ml of H_2O at 45° was added 0.89 g (5 mmol) of ninhydrin in 100 ml of H_2O. The reaction mixture was stirred for 1 hr at 25° and allowed to stand for 16 hr at 5°. The resulting yellow, crystalline precipitate was filtered and dried under vacuum for 2 days to yield 1.55 g (79%) of **7**. An analytical sample was prepared by recrystallization from ethanol–water: mp 119–121° dec; ir (KBr) 2.95, 5.71, 6.22 (shoulder), 6.28, and 6.70 μ; nmr (CD_3SOCD_3) τ 2.00 (s, 4, indandione H), 2.86 (s, 5, *p*-ClC_6H_4NH of **2b** and NH or OH of **2b**), 2.90, 3.04, 3.36, and 3.52 (q, 4, *p*-$ClC_6H_4NH_2$), 3.21 (s, 1, NH or OH of **2b**), and 4.83 (s, broad, 2, *p*-$ClC_6H_4NH_2$); nmr (CH_3OD) τ 2.00 (s, 4, ninhydrin aromatic H) and 2.86, 3.00, 3.25, and 3.40 (q, 4, *p*-$ClC_6H_4NH_2$).

Anal. Calcd for $C_{21}H_{14}N_2O_2 \cdot H_2O$: C, 60.74; H, 3.89; N, 6.75; Cl, 17.09. Found: C, 61.11; H, 3.96; N, 6.81; Cl, 17.48.

Attempts to remove the water of hydration resulted in decomposition of the compound.

Reaction of Ninhydrin with *m*-Hydroxyaniline. Formation of 5a.—A solution of 3.27 g (30 mmol) of *m*-hydroxyaniline and 5.34 g (30 mmol) of ninhydrin 300 ml of water was stirred for 30 min at 25°. The fluffy, yellow precipitate that formed was collected and dried under vacuum to yield 7.50 g (93%) of **5a**. An analytical sample, which did not melt below 340°, was prepared by recrystallization from ethanol: the ir and uv spectra were similar to those reported;[4] nmr (CD_3SOCD_3) τ 1.07 (s, 1, phenolic OH), 1.90–2.35 (m, 4, indanone H), 2.90 (d, 1, J = 8 Hz, H *meta* to NH), 3.37 (s, 1, NH), 3.65–4.08 (m, 2, H *ortho* and *para* to NH), and 4.70 (broad, 2, OH); the NH and OH protons disappeared upon addition of D_2O; nmr (CF_3CO_2H) τ 1.93–2.75 (m, 5, indanone H and H *meta* to NH) and 2.92–3.27 (m, 2, H *ortho* and *para* to NH); at 15° a broad peak at τ 1.16 appeared (NH or OH); tlc R_f 0.80 [1-butanol–water (86:14) on Avicel microcrystalline cellulose].

Anal. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20; mol wt, 269. Found: C, 67.18; H, 3.95; N, 4.84; mol wt, 269 (mass spectrum).

Acetylation of 5a.—A mixture of 2.0 g (7.5 mmol) of **5a**, 100 ml of acetic anhydride, and 2 ml of pyridine was heated at reflux, with stirring, for 5 days. The solvents were removed under vacuum and the red-brown residue was treated with methanol and filtered. The filtrate was decolorized with charcoal and evaporated. The residue was washed with water and then recrystallized from methanol–water to afford 1.10 g (34%) of crude acetylated product **5b**. An analytical sample, mp 194–196°, was prepared by multiple recrystallizations from methanol: ir (KBr) 5.68 (shoulder), 5.75 (shoulder), 5.81, 5.88 (shoulder), 6.25, and 6.67 μ; uv max (MeOH) 244 mμ (ϵ 20,000), 294 (6490); nmr (CD_3SOCD_3) τ 2.02 (s, 4, indanone H), 2.23 (d, 1, J = 9 Hz, H *meta* to $NCOCH_3$), 2.72–2.96 (m, 2, H *ortho* and *para* to $NCOCH_3$), 7.90 (s, 3, CH_3CO), 7.99 (s, 6, CH_3CO), and 8.25 (s, 3, CH_3CO); tlc R_f 0.62 (ethyl acetate).

Anal. Calcd for $C_{23}H_{19}NO_5$: C, 63.16; H, 4.39; N, 3.20; mol wt, 437. Found: C, 63.22; H, 4.25; N, 3.21; mol wt, 437 (mass spectrum).

Reaction of Ninhydrin with *m*-Anisidine. Formation of 5c.—The preparation was analogous with that conducted with *m*-hydroxyaniline. A crude yield of 92% was obtained. An analytical sample, mp 212–214° dec, was prepared by several recrystallizations from ethanol: ir (KBr) 2.92, 2.99, 3.14, 5.71, 5.84, 6.20, 6.28, 6.66, and 6.84 μ; uv max (MeOH) 224 mμ (ϵ 50,000), 244 (24,100), and 288 (4080); nmr (CD_3SOCD_3) τ 2.00 (s, 4, indanone H), 2.65 (d, 1, J = 8 Hz, H *meta* to NH), 3.23 (s, 1, NH), 3.60–3.95 (m, 2, H *ortho* and *para* to NH), 4.85 (broad, 2, OH), and 6.85 (s, 3, OCH_3); tlc R_f 0.68 [benzene–methanol (80:20)].

Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94; mol wt, 283. Found: C, 68.26; H, 4.71; N, 4.92; mol wt, 283 (mass spectrum).

Acetylation of 5c.—A mixture of 2.0 g (7.1 mmol) of **5c** and 65 ml of acetic anhydride were heated with stirring at 95° for 139 hr. The solvent was removed under vacuum and the residue was recrystallized from methanol to yield 0.80 g (28%) of crude **5d**. An analytical sample, mp 179–180°, was prepared by several recrystallizations from methanol: ir (KBr) 5.72, 5.80, 5.91, 6.23, 6.30 (shoulder), 6.67, and 6.83 μ; uv max (MeOH) 227 mμ (ϵ 46,200), 252 (27,500), and 290 (6720); nmr (CD_3SOCD_3) τ 2.12 (s, 4, indanone H), 2.25 (d, 1, J = 8 Hz, H *meta* to $NCOCH_3$), 2.95–3.20 (m, 2, H *ortho* and *para* to $NCOCH_3$), 6.88 (s, 3, OCH_3), and 7.97 (s, 9, CH_3CO); tlc R_f 0.90 (ethyl acetate).

Anal. Calcd for $C_{22}H_{19}NO_7$: C, 64.54; H, 4.68; N, 3.42; mol wt, 409. Found: C, 64.71; H, 5.04; N, 3.36; mol wt, 409 (mass spectrum).

Reaction of Ninhydrin with *m*-Phenylenediamine. Formation of 5e.—The preparation was analogous to that conducted with *m*-hydroxyaniline. A yield of 65% **5e**, as a yellow solid, was obtained. An analytical sample, which had no melting point below 300°, was prepared by several recrystallizations from acetone–water: ir (KBr) 2.86, 2.98, 3.10 (shoulder) 5.88, 6.15, and 6.80 μ; nmr (CD_3SOCD_3) τ 2.00–2.45 (m, 4, indanone H), 2.88 (s, 1, NH), 3.00 (d, 1, J = 8 Hz, H *meta* to NH), 3.90–4.20 (m, 4, H *ortho* and *para* to NH; NH_2 or OH), 4.85 (broad, 2 NH_2 or OH), and 7.82 (acetone); upon addition of D_2O, the peaks at τ 2.88 and 4.95 disappeared and the multiplet at τ 3.90–4.20 integrated as two protons; tlc R_f 0.55 (ethyl acetate).

Anal. Calcd for $C_{15}H_{12}N_2O_3$–C_3H_6O: C, 66.25; H, 5.56; N, 8.59. Found: C, 66.54; H, 5.66; N, 8.39.

Acetylation of 5e.—A mixture of 1.2 g of **5e**, 100 ml of acetic anhydride, and 10 ml of pyridine was heated at reflux under N_2 for 48 hr. The resulting red solution was evaporated to dryness under vacuum. The residue was washed with water and triturated with acetone. The insoluble, crystalline material was recrystallized several times from alcohol (once with charcoal) and then from chloroform–hexane. This afforded 0.1 g of **8** as a yellow powder: mp 236–237.5°; ir (KBr) 5.65, 5.80, 5.90, 6.18, and 6.90 μ; uv max (MeOH) 238 mμ (ϵ 33,000), 278 (18,800), 289 (13,600), 302 (13,500), and 359 (7120); nmr ($CDCl_3$) τ 2.10–3.15 (m, 7, aromatic H), 7.50 (s, 3, CH_3CO), and 7.65 (s, 6, CH_3CO); tlc R_f 0.91 (ethyl acetate).

Anal. Calcd for $C_{21}H_{16}N_2O_5$: C, 67.02; H, 4.28; N, 7.44; mol wt, 376. Found: C, 66.50; H, 4.27; N, 7.35; mol wt, 376 (mass spectrum).

Reaction of Ninhydrin with Urea. Formation of 6a.—The reaction was conducted according to the published procedure.[10] The ultraviolet spectrum of the product has been reported.[7] The product, **6a**, had the following additional properties: ir (KBr) 2.98, 3.05, 5.80, 5.92, and 6.33 μ; nmr (CD_3SOCD_3)

τ 1.99 (s, 1, NH), 2.08–2.60 (m, 5, indanone H and 1 NH), 3.45 (s, 1, OH), and 3.58 (s, 1, OH); tlc R_f 0.14 (ethyl acetate).

Anal. Calcd for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66; N, 12.72; mol wt, 220. Found: C, 54.41; H, 3.87; N, 12.84; mol wt, 220 (mass spectrum).

Acetylation of 6a.—A suspension of 2.0 g (9.1 mmol) of **6a** in 75 ml of acetic anhydride was heated with stirring, under N_2 for 3 hr. The temperature, initially 50°, was raised to 100° over this time. The mixture was poured into 500 ml of ice–water and allowed to stand for 16 hr. The mixture was extracted with an ether–benzene mixture, and the organic layer was washed several times with water and evaporated. The residue was washed with hot water, allowed to dry, and then crystallized from benzene–petroleum ether (bp 30–60°). A yield of 1.80 g (52%) of **6b** was obtained. An analytical sample, mp 186–188°, was prepared by recrystallization from benzene–petroleum ether: ir (KBr) 5.61, 5.70, 5.80, 6.22, and 6.82 μ; uv max (MeOH) 225 mμ (ϵ 8600), 250 (9000), and 286 (1000); nmr (CD_3SOCD_3) τ 1.95–2.40 (m, 4, indanone H), 7.62 (s, overlaps CD_2HSOCD_3 peak, $COCH_3$), 7.70 (s, 3, $COCH_3$), 7.97 (s, 3, $COCH_3$), and 7.99 (s, 3, $COCH_3$); tlc R_f 0.86 (ethyl acetate).

Anal. Calcd for $C_{13}H_{16}N_2O_8$: C, 55.67; H, 4.15; N, 7.21; mol wt, 388. Found: C, 55.98; H, 4.12; N, 7.43; mol wt, 388 (mass spectrum).

Reaction of Ninhydrin with 1,3-Dimethylurea. Formation of 6c.—A solution containing 2.42 g (13.6 mmol) of ninhydrin and 2.82 g (32 mmol) of 1,3-dimethylurea in 80 ml of 0.1 *N* H_2SO_4 was heated at 60° for 30 min. The reaction mixture was kept at 5° for 48 hr. The precipitate that formed was filtered, washed with water, and dried to afford 3.10 g (92%) of **6c**. An analytical sample, mp 259–261° dec, was prepared by recrystallization from methanol–chloroform: ir (KBr) 3.01, 3.20 (shoulder), 5.75, 5.95, 6.20, 6.74, and 6.83 μ (shoulder); uv max (MeOH) 248 mμ (ϵ 10,600) and 290 (1730); nmr (CD_3SOCD_3) τ 1.95–2.28 (m, 4, indanone H), 3.00 (s, 1, OH), 3.15 (s, 1, OH), 7.08 (s, 3, NCH_3), and 7.16 (s, 3, NCH_3); tlc R_f 0.49 (ethyl acetate).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.28; mol wt, 248. Found: C, 57.77; H, 4.63; N, 11.03; mol wt, 248 (mass spectrum).

Acetylation of 6c.—A mixture of 0.5 g (2.0 mmol) of **6c**, 40 ml of acetic anhydride, and a small amount of sodium acetate was heated at reflux with stirring under N_2 for 90 min. The reaction was worked up by the procedure used for **6b** to afford 0.3 g (45%) of **6d**. An analytical sample, mp 191–193°, was prepared by several recrystallizations from benzene–petroleum ether: ir (KBr) 3.38, 5.64, 5.80, 6.22, 6.82, and 6.95 μ; uv max (MeOH) 250 mμ (ϵ 10,800) and 290 (1500); nmr (CD_3SOCD_3) τ 1.91–2.30 (m, 4, indanone H), 7.10 (s, 3, NCH_3), 7.17 (s, 3, NCH_3), 7.85 (s, 3, $COCH_3$), 7.88 (s, 3, $COCH_3$); tlc R_f 0.90 (ethyl acetate).

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43; mol wt, 332. Found: C, 57.63; H, 4.81; N, 8.44; mol wt, 332 (mass spectrum).

Reaction of Ninhydrin with Guanidine.—A solution containing 1.78 g (10 mmol) of ninhydrin and 1.80 g (15 mmol) of guanidine carbonate in 150 ml of water was stirred at 25° for 30 min and kept at 5° for 16 hr. The precipitate that formed was filtered, washed with water, and dried under vacuum. This product, 2.0 g (91%), mp 215–218° dec, was used directly for analysis: ir (KBr) 2.90–4.0 (broad), 5.82, 5.90 (shoulder), 5.98, 6.02 (shoulder), 6.08 (shoulder), 6.12 (shoulder), 6.21, 6.40, and 6.86 μ; nmr (CF_3CO_2H) τ 2.30–2.80 (m, overlapping broad absorption, 5, indanone H + NH) and 3.50 (s, 2, NH). The mass spectrum showed numerous weak peaks beyond the expected molecular ion (m/e 219) up to about m/e 350.

Anal. Calcd for $C_{10}H_9N_3O_3$: C, 54.80; H, 4.14; N, 19.17. Found: C, 54.77; H, 4.12; N, 19.05.

Registry No.—**1**, 485-47-2; **2a**, 17438-16-3; **5a**, 22487-55-4; **5b**, 22433-31-4; **5c**, 22430-97-3; **5d**, 22430-98-4; **5e**, 22430-99-5; **6a**, 22431-00-1; **6b**, 22431-01-2; **6c**, 22431-02-3; **6d**, 22431-03-4; **7**, 22431-04-5; **8**, 22431-05-6; **9**, 22431-06-7.

Attempted Epoxidation of Triphenylcyclopropene[1a,b]

LOUIS E. FRIEDRICH[1c] AND RUSSELL A. CORMIER

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received May 5, 1969

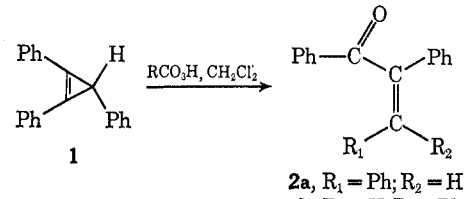
Treatment of triphenylcyclopropene (**1**) with both *p*-nitro- and *m*-chloroperbenzoic acid gave the two isomeric *cis*- and *trans*-α-phenylchalcones (**2a** and **2b**) in the approximate ratio of 82:18. No intermediates were detected when the progress of the reaction was monitored by nmr under buffered conditions. The possibility and significance of oxabicyclobutane intermediates is briefly discussed.

Oxabicyclobutanes have been postulated several times as intermediates in various thermal[2a,b] and photochemical[2c–h] reactions. In none of these cases, however, have oxabicyclobutanes been detected.

The report of Prinzbach and Fischer[2b] provides the most compelling choice for an oxabicyclobutane intermediate in chemical reactions. Peracetic acid oxidation of 1,2-dimethylcyclopropenecarboxylic acid methyl ester gave a 30% isolated yield of the two isomeric *cis*- and *trans*-β-acetylcrotonic acid methyl esters in a ratio of 1:4. If the expected oxabicyclobutanes were intermediates, thermal fragmentation of the bicyclo[1.1.0] ring system[3] would yield the observed products.

As part of a larger effort to synthesize oxabicyclobutanes and determine the chemistry of their ring-opening processes, we have studied the oxidation of triphenylcyclopropene with peracids.

Room-temperature treatment of a methylene chloride solution of triphenylcyclopropene (**1**) with 1.2 equiv of *p*-nitroperbenzoic acid in a flask wrapped with aluminum foil gave only the two isomeric *cis*- and *trans*-



1

2a, R_1 = Ph; R_2 = H
b, R_1 = H; R_2 = Ph

(1) (a) This work was supported by National Science Foundation Grant GP-8878. (b) NOTE ADDED IN PROOF.—A communication recently appeared in which the epoxidation of several alkyl-substituted cyclopropenes was reported: J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.*, **91**, 6534 (1969). (c) To whom inquiries should be addressed.

(2) (a) S. Marmor and M. M. Thomas, *J. Org. Chem.*, **32**, 252 (1967); (b) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967); (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (d) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965); (e) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966); (f) O. L. Chapman and W. R. Adams, *ibid.*, **90**, 2333 (1968); (g) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969); (h) N. Furutachi, Y. Nakadaira, and K. Nakanishi, *ibid.*, **91**, 1028 (1969).

(3) Substituted bicyclobutanes fragment into butadienes in an analogous fashion; see G. Closs and P. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).