

yield an additional 0.025 g. Both crops, 0.125 g. (86%), had the same m.p. 261–262° dec.; infrared spectrum (KBr), 6.00 (broad C=N + C=O), 7.10 (broad, *gem*-dimethyl), and 7.38 μ (acetyl-C-methyl).

Anal. Calcd. for C₁₅H₂₁IN₂O: C, 48.42; H, 5.69; N, 7.53. Found: C, 48.42; H, 5.83; N, 7.58.

1,3,3-Trimethyl-2-phenyl-4-acetylpiperazine Hydrochloride (XVI).—A solution of 0.16 g. (0.43 mmole) of methiodide XV in 25 ml. of 50:50 methanol-ethanol was swirled with 0.19 g. (0.005 mole) of sodium borohydride. An immediate exothermic reaction ensued which slowly subsided. After standing at room temperature for 4 hr., the solution was poured into 50 ml. of 3 *N* hydrochloric acid and washed with ether. After basification with solid potassium hydroxide, the aqueous solution was washed four times with ether. The combined ethereal extracts were dried, and the product was precipitated as the hydrochloride salt. Recrystallization from methanol-ether yielded 0.10 g. (80%) of white needles, m.p. 244–245° dec. A portion was recrystallized again from the same solvents for an analytical sample: m.p. 245–246° dec.; pK'_a 5.60 (50% methanol); infra-

red spectrum (KBr), 5.95 (C=O), 7.10 (*gem*-dimethyl), and 7.38 (acetyl-CH₃).

Anal. Calcd. for C₁₅H₂₃ClN₂O: C, 63.73; H, 8.20; N, 9.91. Found: C, 63.47; H, 8.47; N, 9.90.

1,3,3-Trimethyl-2-phenylpiperazine Dihydrochloride (XVII).—A solution of 0.065 g. (0.34 mmole) of piperazine acetate XVI in 10 ml. of ethanol and 10 ml. of 10% sodium hydroxide solution was refluxed for 48 hr. The reaction was cooled, poured into 30 ml. of concentrated sodium chloride solution, and washed with five 30-ml. portions of ether. After drying (sodium sulfate-potassium carbonate), the ethereal solution was reduced (*in vacuo*) to about 25 ml. in volume. The hydrochloride salt was precipitated in the usual fashion, and recrystallized from methanol-acetone. The first crop weighed 0.035 g., decomposed over 250°. A second crop (same decomposition point) brought the total yield to 0.050 g. (78%). A portion of the first crop served as an analytical sample: pK'_a 3.10, 8.30 (50% methanol); infrared spectrum (KBr), 6.35 (NH₃⁺), 7.11, and 7.23 μ (*gem*-dimethyl).

Anal. Calcd. for C₁₃H₂₂Cl₂N₂: C, 56.32; H, 8.00; N, 10.11. Found: C, 56.48; H, 8.09; N, 9.88.

Pyrolysis and Photolysis of 1-Methyl-3-diazooxindole. Base Decomposition of Isatin 2-Tosylhydrazone^{1,2}

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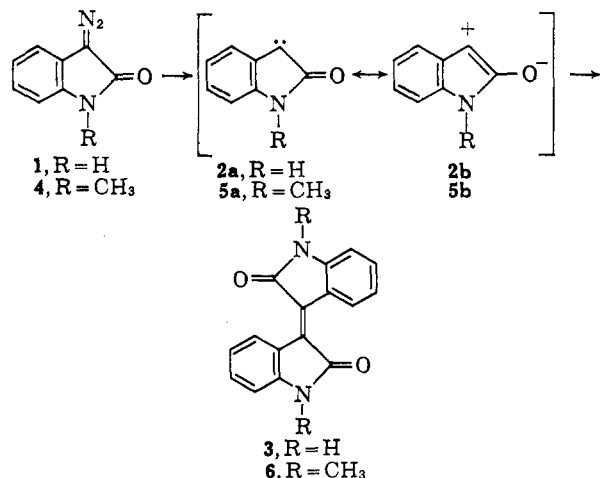
Received June 4, 1964

Pyrolysis of 1-methyl-3-diazooxindole (4) in refluxing ethanol led to 1,1'-dimethylisoinidigo (6) and 1,1'-dimethylisatinazine (16), and in the presence of pyridine *N*-oxide produced 6, 16, and 1-methylisatin (12). Photolysis of 4 in ethanol gave 3-ethoxy-1-methyloxindole (23); photolysis in cyclohexene led to two geometric cyclopropane isomers (24 and 25) resulting from *cis* addition to the cycloolefin, and in hexane solution containing 1,1-diphenylethylene produced the spirooxindole (26). Compounds 6, 12, 16, and 23–26 were probably formed by appropriate reaction with the pyrolytically and photolytically generated oxindolyne acting as a singlet (5a). This same oxindolyne also displayed triplet character (5c) in the e.s.r. spectrum at 4°K., in reaction with oxygen to form 12, and with photolytically generated Cl· atoms and Cl₃C· free radicals (from CCl₄) to yield 3-chloro-3-trichloromethyl-1-methyloxindole (28). At room temperature, 4 reacted with bromine and triphenylphosphine to form 3,3-dibromo-1-methyloxindole (17) and the phosphazine adduct (18), respectively. Pyrolysis of 18 led to the triphenylphosphine, 6 and 16, but no ylide. The mechanisms of these reactions are discussed. Base decomposition of isatin 2-tosylhydrazone (9) led to indigo blue (38), presumably *via* the unisolable 2-diazoindoxyl (36) and reactive indoxylene (37).

In 1916, Staudinger and Goldstein reported that a sealed-tube pyrolysis of 3-diazooxindole (1) at 200° in benzene afforded isoindigo (3).³ In 1955, Huisgen proposed that this reaction proceeded *via* the inter-

mediacy of a resonance-stabilized, "reaktionsträgen," carbene (2).⁴

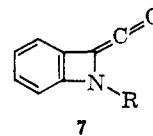
Our study of this system arose from our interest in the nature of 1⁵ and 2⁶ and the mode of formation of 3. Since the isatin lactam-lactim controversy is as yet unresolved,⁹ this variable could be eliminated by a study of the *N*-alkyl derivative. In this paper we report on the preparation of 1-methyl-3-diazooxindole (4), and its pyrolytic and photolytic decomposition in the presence of reagents which would react with carbene 5 in the sin-



(4) R. Huisgen, *Angew. Chem.*, **67**, 457 (1955).

(5) Possibility of diazoxide character: (a) L. Horner, E. Spietschka, and A. Gross, *Ann.*, **578**, 17 (1951); (b) P. Yates and E. Robb, *J. Am. Chem. Soc.*, **79**, 5760 (1957).

(6) Possible reaction paths as a singlet electrophile include stereospecific insertions, 1,3-dipolar additions *via* 2b,⁷ and rearrangement *via* ketene 7 to ring contraction products.⁸ As a triplet, 2 should undergo free-radical reactions.



(7) R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961).

(8) As in the thermolysis of naphthalene 1,2-diazooxide.⁵

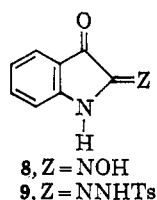
(9) Summarized by P. L. Julian, E. W. Meyer, and H. C. Printy in "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1952, p. 202; and W. C. Sumpter, *Chem. Rev.*, **34**, 398 (1944).

(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-62-18.

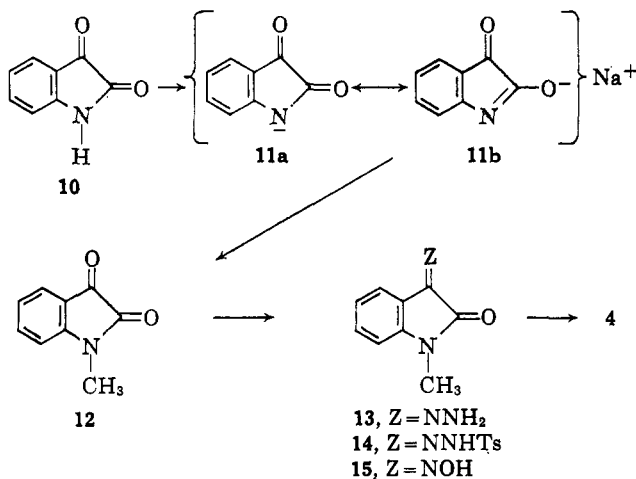
(2) Presented in part at the Organic Division of the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, Abstracts of Papers, p. 55S.

(3) H. Staudinger and J. Goldstein, *Ber.*, **49**, 1923 (1916).

plet or triplet state. In a parallel investigation we will also report briefly on the preparation and reactions of isatin 2-oxime (8) and 2-tosylhydrazone (9) as possible precursors of the 2-diazoindoxyl system (36).



1-Methyl-3-diazoindole (4).—Treatment of isatin (10) with sodium ethoxide led to the black-violet sodium salt 11; N-methylation of ambident anion 11 with methyl iodide afforded orange-red 1-methylisatin (12) in 90% yield. 1-Methyl-3-diazoindole (4) was prepared in two steps from 12 by three independent routes: (i) mercuric oxide oxidation of 1-methylisatin 3-hydrazone (13), (ii) aqueous base decomposition of 1-methylisatin 3-tosylhydrazone (14), and (iii) alkaline chloramine oxidation of 1-methylisatin 3-oxime (15). Over-all yields of 4 from 12 *via* each of these three methods were, respectively, 62, 84, and 58%. The infrared spectrum of dark red-brown 4 showed the expected intense diazo stretching absorption at 4.71 μ ; the amide carbonyl appear at 5.91 μ .¹⁰



Under reflux, pyrolysis of 4 in absolute ethanol over a 96-hr. period led to a 1.7% yield of violet 1,1'-dimethylisatin (6), 2.2% of orange-red 1,1'-dimethylisatinazine (16), and an 84% recovery of unreacted 4; in refluxing toluene, 4 deoxygenated pyridine N-oxide¹³ over a 48-hr. period to form 9% of 1-methylisatin (12), in addition to 6 and 16. At room temperature, 4 reacted with bromine in carbon tetrachloride to yield

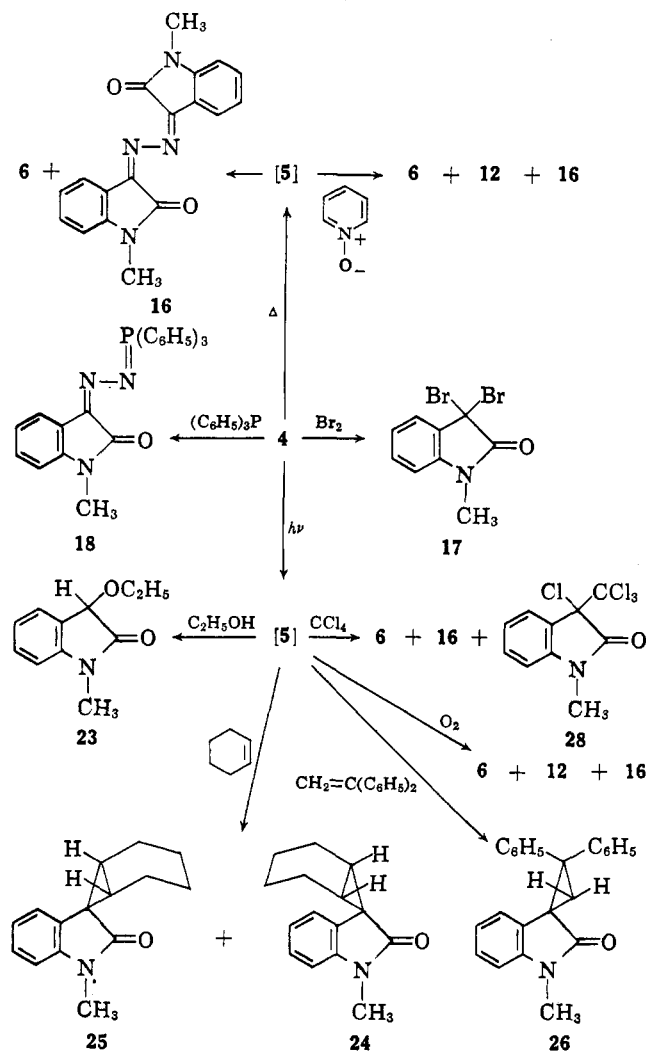
(10) This could be compared with similar strong bands (KBr wafer; in this work, 1 showed bands at 4.74 and 5.90 μ). In CH_2Cl_2 solution compound 1 shows strong bands at 4.78 and 5.87 μ .¹¹ Corresponding bands in the solution spectra of other compounds of the 1,2-diazoindole type are summarized.¹²

(11) M. P. Cava, R. L. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

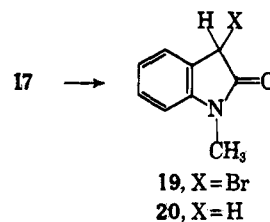
(12) D. G. Farnum and P. Yates, *ibid.*, **84**, 1399 (1962).

(13) E. E. Schweizer and G. J. O'Neill [*J. Org. Chem.*, **28**, 2460 (1963)] have demonstrated the singlet electrophilic nature of dichlorocarbene in their novel deoxygenation of pyridine N-oxide in methanol to produce pyridine and dimethyl carbonate; these authors also reported that 9-diazo fluorene with pyridine N-oxide in refluxing benzene gave fluorenone and fluorenoneazine, in contrast to the reaction of 9-diazo fluorene with benzene alone which gave the dimer, difluorene.

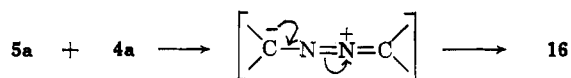
CHART I



89% of colorless 3,3-dibromo-1-methylisatin (17),^{14,15} and with triphenylphosphine in absolute ether to form the yellow, hygroscopic, phosphazine adduct 18 in 80% yield (see Chart I).



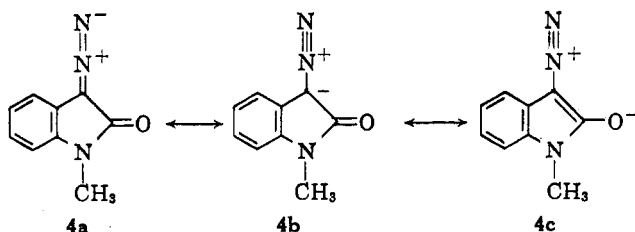
Plausibly 6 could result either from direct dimerization of two singlet oxindolylenes (two 5a \rightarrow 6), or reaction of 5a with 4b accompanied by expulsion of nitrogen; 16 could be obtained by singlet electrophilic attack of the carbene on the terminal, nucleophilic nitrogen in 4a.



The unusual stability of 4 with respect to 6 and 16 could be accounted for by a hybrid to which the diazo-

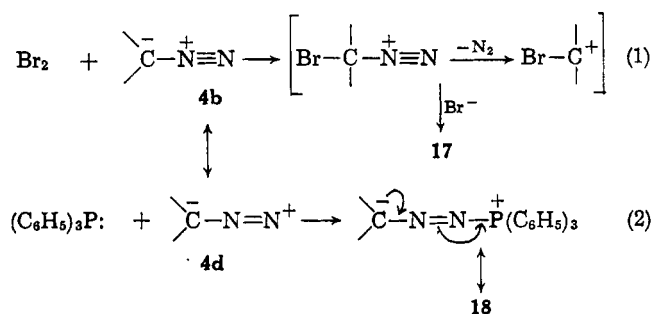
(14) E. Fischer and O. Hess, *Ber.*, **17**, 561 (1884).

(15) (a) Reduction of 17 with zinc dust and concentrated hydrochloric acid led to a compound reported as 3-bromo-1-methylisatin (19) in 33% yield and trace amounts of colorless 1-methylisatin (20); see Experimental. (b) H. G. Colman, *Ann.*, **248**, 115 (1888).

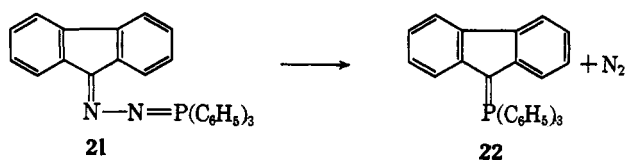


oxide structure (4c) makes a contribution comparable to 4a and 4b.

The formation of 6 and 16 and the deoxygenation of pyridine N-oxide to form 12 occurred slowly under pyrolysis conditions and in low yields. By contrast, 4 reacted rapidly at room temperature with bromine and triphenylphosphine to yield 17 and 18, respectively, in high yields. Clearly here, carbene 5 or its incipient development is not involved in either case, and the reaction pathway probably involves electrophilic displacement (reaction 1) and nucleophilic addition (reaction 2) according to the following simplified schemes.



One of the many Staudinger successes was the preparation of the phosphazine, (fluorenylhydrazono)triphenylphosphorane (21), from diazofluorene and triphenylphosphine, and its thermal decomposition at 220° to the first stable ylide, fluorenylidetriphenylphosphorane (22).¹⁶



Pyrolysis of a concentrated solution of our adduct 18, however, led to 6, 16, nitrogen, and triphenylphosphine, but no ylide. Thus, stepwise pyrolytic cleavage of the N-P bond (to 4) and the C-N bond (to 5) did occur, but their reaction rate to form 6 and 16 must be too rapid to permit condensation with the available triphenylphosphine.

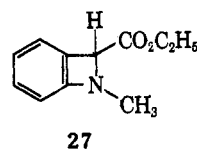
Photolysis of very dilute solutions¹⁷ of 4 under nitrogen¹⁸ with a 100-w., high-pressure mercury arc fitted with a Pyrex filter led to the following results: (i) in absolute ethanol, the colorless 3-ethoxy-1-methyloxindole (23) was isolated in 21–24% yields; (ii) in cyclohexene solutions, two colorless geometric isomers, tentatively assigned structures 24 and 25, were obtained in a total yield of 27%; and (iii) in a hexane solution with 1,1-diphenylethylene, the colorless spirooxindole 26 was obtained in 26% yield.

(16) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919).

(17) To decrease possibility for dimerization of 5a to 6.

(18) To prevent reaction with oxygen.

Compound 23 displayed two strong bands in the infrared at 5.77 (C=O) and 8.95 μ (C—O—C). Integration of its n.m.r. spectrum showed a proton ratio of 4:1:2:3:3, and, significantly, the two methylenic protons appeared as a quartet (centered at δ 3.82) characteristic of an ethyl ether. This information eliminated the carbene rearrangement product 2-carbethoxy-1-methylbenz[c]azetine (27) as a possible structure (*via* 5a → 7 (R = CH₃) → 27). Formation of 23 can be rationalized by electrophilic attack of 5a on ethanol to yield the dipolar species >C—OH—C₂H₅, followed by proton rearrangement to 23.

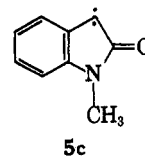


Products 24 and 25 had identical molecular formulas, C₁₅H₁₇NO. The low-melting (83–85°) isomer showed a strong carbonyl band in the infrared at 5.84 μ, and its n.m.r. spectrum displayed signals at δ 1.98 and 2.13 (as a broad methylene and methine resonance between two peaks, ten protons), a sharp singlet at 3.36 (N—CH₃, three protons), and an aromatic multiplet at 6.77–7.46 (four protons). The 137–139° isomer showed a strong infrared carbonyl at 5.81 μ, and its n.m.r. spectrum displayed two broad methylenic and methine proton signals at δ 1.62 and 2.17 (ten protons), a sharp singlet at 3.32 (N—CH₃, three protons), and an aromatic multiplet at 6.99–7.54 (four protons). Although this information did not suffice to distinguish between these isomers, compounds 24 and 25 have been depicted as *cis*-addition products of singlet carbene 5a to cyclohexene.¹⁹ In one isomer (24), the *cis* hydrogens at the ring fusion overlook the oxindole carbonyl group, while in 25, these same protons see the benzene ring.

Irradiation of 4 in the presence of 1,1-diphenylethylene in hexane at room temperature over a 20-hr. period led to the spirooxindole (26), m.p. 190–191.5°. The n.m.r. spectrum of 26 showed the expected signals for two rigid geminal cyclopropane ring protons (two doublets in an AB pattern centered at δ 2.42 and 2.72, *J* = 5 c.p.s.), a sharp singlet at 3.33 (N—CH₃, three protons), and an aromatic multiplet at 6.67–7.67 with a main peak at 7.42 (14 protons).

The reactions reported to this point support writing the carbene, generated both pyrolytically and photolytically from 4, as the singlet 5a. These include the formation of olefin 6,²⁰ azine 16, ether 23, *cis*-olefinic addition products 24–26, and 1-methylisatin (12) *via* deoxygenation.

However, irradiation of dilute solutions of 4 in hexane at room temperature in air over a 13-hr. period led to 1-methylisatin (12) in 42% yield, 1.1% of 16, and trace amounts of 6. This reaction with oxygen now provides good evidence of the biradical nature of 5 (schematically drawn as 5c), analogous to the results ob-



(19) A pyrazoline intermediate is not excluded but none was ever isolated.

tained with diphenylmethylene.²¹ Unlike the diphenylmethylene biradical, however, the methylene carbon in **5c** cannot achieve the linear divalency expected for optimum stability of a triplet form, and the bonds to C-3 in **5c** are probably bent.^{22a} One alternative to a triplet carbene reaction is the light-induced conversion of triplet oxygen to an excited singlet, and consequent reaction with singlet **5a**.^{22b}

However, the e.s.r. spectrum of **5c**, generated by irradiation of **4** with a high-pressure mercury lamp at 4°K., was clearly characteristic of a triplet in the ground state.^{23,24} In hexafluorobenzene solution, resonances were observed at about 500, 4439, 5456, and 7356 gauss [a single unpaired electron ($S = 1/2$) would absorb at 3345 gauss], and the spectrum remained after irradiation ceased. The D value (0.38 cm.⁻¹) was quite similar to that of phenylbenzoylmethylene and both are less than that of phenylmethylene ($D = 0.52$ cm.⁻¹).²⁵ This suggests significant delocalization of the triplet electrons by the adjacent carbonyl.

Finally, upon irradiation of **4** in carbon tetrachloride solvent, a small amount (1.8%) of a white crystalline material, m.p. 168–171°, was obtained, in addition to the expected products, **6** (11%) and **16** (2.7%). Analytical and spectral data suggest the 168–171° material to be 3-chloro-3-trichloromethyl-1-methyloxindole (**28**). Recently reported results demonstrate that the photolysis of carbon tetrachloride under comparable conditions produces in the primary step, $\text{Cl}_3\text{C}\cdot$ radicals and Cl atoms.²⁶ Thus **5** displays biradical properties (**5c**) in the ground state, in the formation of **28**, and probably in the reaction with oxygen to produce **12**. These results suggest that singlet (**5a**) and triplet (**5c**) structures have very similar energies and may be readily interconvertible.²⁷

Already noted was the absence in all reactions reported thus far of any ring contraction products, e.g., **27**. It is probable that the α -ketocarbene singlet **5a**, generated both pyrolytically and photolytically, undergoes intermolecular addition with nucleophiles at a greater rate than the rearrangement.²⁸ This relatively slow rearrangement process could be attributed to the poor migrating tendency of the amide link in **5a**. One obvious technique to weaken the N–C bond was to decrease the basicity of the amide nitrogen by the introduction of a strong electron-withdrawing group, e.g.,

(20) H. E. Zimmerman and D. H. Paskovich [*J. Am. Chem. Soc.*, **86**, 2149 (1964)] have suggested that, in sterically hindered divalent carbon species with bent geometry, two triplets also could bond to form olefin.

(21) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958); R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

(22) (a) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager *ibid.*, **86**, 2304 (1963). (b) Suggested by Dr. Richard W. Franck.

(23) We are grateful to Dr. E. Wasserman of Bell Telephone Laboratories, Murray Hill, N. J., for the spectrum and its interpretation.

(24) One must be reminded that knowledge of the triplet structure of resonance-stabilized carbene **5c** at liquid helium temperature is not necessarily a guide to the triplet structure of the reactive, transient species at pyrolytic temperatures and photolytic conditions ordinarily employed.

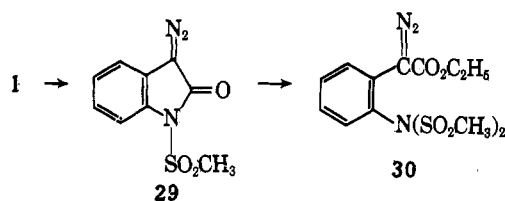
(25) (a) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964); (b) ref. 22a.

(26) B. C. Roquette and M. H. J. Wignen, *J. Am. Chem. Soc.*, **85**, 2053 (1963); E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).

(27) A referee has suggested the alternative interpretation of a free-radical chain mechanism for the reaction between **4** and CCl_4 based on the classical work of W. H. Urry and J. R. Eisner [*J. Am. Chem. Soc.*, **74**, 5822 (1952)] with the light-induced reaction of CH_2N_2 with CCl_4 .

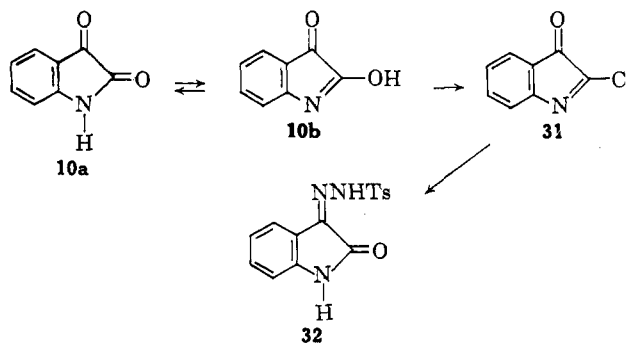
(28) Cf. S. Masamune *ibid.*, **86**, 735 (1964)] where an α -ketocarbene underwent an intramolecular addition to a double bond at a greater rate than the rearrangement.

$-\text{SO}_2\text{CH}_3$. Thus orange-colored 1-methanesulfonyl-3-diazooxindole (**29**) was prepared in 38% yield by treatment of 3-diazooxindole¹¹ with sodium ethoxide and methanesulfonyl chloride at room temperature. When a large excess of these reagents was used, the yellow α -diazophenylacetate **30** was obtained, un-



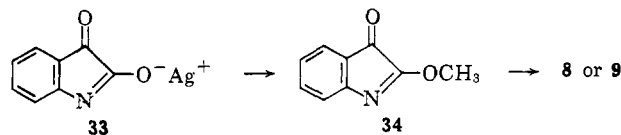
doubtedly *via* **29** since the amide linkage is reported to be labile to ring cleavage with dilute base.²⁹ Photolysis of **29** led to recovery of unreacted starting material and no product resembling compound **27**.

Isatin 2-Oxime (8) and **2-Tosylhydrazone (9)**.—Initial attempts to prepare **9** *via* treatment of 2-chloro-3-oxo-3H-indole (**31**) (isatin α -chloride in the older literature)^{9,30} with p -TsNHNH₂ led only to the yellow-colored isatin 3-tosylhydrazone (**32**) in 53% yield. The unstable cyclic imidyl chloride (**31**) was prepared by reaction of isatin in its lactim form (**10b**) with phosphorus pentachloride. The conversion of **31** to **32** instead of **9** is again clearly a reflection of the greater reactivity of the 3-oxo group in **31**. Thus, for example, **31** also reacts with aniline to form the 3-anil.³¹



Undoubtedly, hydrazone formation is accompanied or followed by hydrolysis of the imidyl chloride to the stable lactam **32**.

Ultimately **8** and **9** were prepared *via* the silver salt of isatin (**33**), O-methylation of which led to the blood red 2-methoxy-3-oxo-3H-indole (**34**); a substantial amount of the N-methylation product **12** was also obtained. Compound **34** was easily converted to yellow **8** in 90% yield with hydroxylamine hydrochloride, and orange-



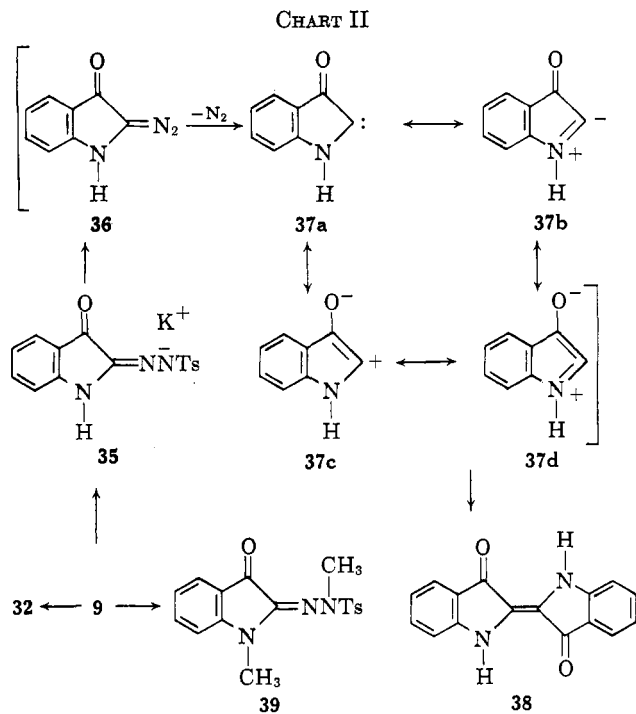
red **9** (84%) with p -TsNHNH₂. Yellow-brown isatin 2-hydrazone could also be obtained from **34** in 89% yield with 85% hydrazine hydrate.

Base decomposition of **9** in conventional fashion with excess 0.2 N potassium hydroxide at room temperature

(29) G. Heller, *Ber.*, **51**, 430 (1918).

(30) A. Baeyer, *ibid.*, **12**, 456 (1879).

(31) R. K. Callow and E. Hope, *J. Chem. Soc.*, 1191 (1929).



over a period of 96 hr. led to the yellow potassium salt **35**. When an aqueous solution of **35** was heated at 65–70° for several hours, a 62% yield of indigo blue (**38**) was obtained. An idealized reaction mechanism would lead successively through the unstable 2-diazoindoxyl (**36**), its breakdown to carbene **37**, and dimerization to **38**. It is tempting to consider **37** as a zwitterion-carbene hybrid³² ($37a \leftrightarrow 37b \leftrightarrow 37c \leftrightarrow 37d$), but no other evidence of its nucleophilicity³⁴ or its enhanced stabilization could be demonstrated. Its precursor (**36**) also could never be isolated. (See Chart II.)

Compound **9** showed the characteristics of an amidrazone, which on hydrolysis should lead to its components, an amide and a hydrazine. Acid-catalyzed hydrolysis of **9** in refluxing 50% ethanol led to **32**, most probably by a recombination of the hydrolysis products, the amide **10**, and the hydrazine *p*-TsNHNH₂, in conventional fashion.

Alkylation of **9** with methyl iodide in excess sodium ethoxide led to an 88% yield of the dimethyl derivative **39** as brilliant red plates.

One final attempt to prepare **36** was made by alkaline chloramine oxidation of the amidoxime³⁵ **8**. Since only dark yellow-brown intractable material was obtained, this approach too was abandoned.

Experimental³⁶

Sodium Salt of Isatin (11).—Treatment of a suspension of **10** (K and K) in absolute ethanol with an alcoholic solution of sodium ethoxide at room temperature quantitatively led to **11** as a fine black-violet powder.³³ Infrared spectrum showed λ_{\max}^{KBr} 5.79 μ (C=O).

1-Methylisatin (12).—A mixture of 30 g. (0.177 mole) of **11** and a large excess of methyl iodide (88 ml., 1.42 moles) was heated at

reflux for 68 hr. Evaporation of the excess methyl iodide (Rinco) left a residue which was washed well with water yielding 25.5 g. (90%) of **12**. One recrystallization from water afforded pure **12** as tiny orange-red needles, m.p. 131–133.5°, lit.³⁸ m.p. 131°. Infrared spectrum showed λ_{\max}^{KBr} 5.77 and 5.82 μ (C=O); n.m.r. showed δ 3.33 (N-CH₃, three protons) and 6.99–7.99 (aromatic multiplet, four protons).

1-Methylisatin 3-hydrazone (13), m.p. 104–106°, lit.³⁹ m.p. 107–108°, was obtained as lustrous yellow plates from 50% ethanol. Infrared spectrum showed λ_{\max}^{KBr} 5.93 μ (C=O).

1-Methylisatin 3-oxime (15), m.p. 193–197°, lit.^{15b} m.p. 180–183°, was obtained as straw-like, yellow needles from water. Infrared spectrum showed λ_{\max}^{KBr} 5.81 μ (C=O).

1-Methylisatin 3-Tosylhydrazone (14).—To a warm solution of 3.22 g. (0.020 mole) of **12** in 75 ml. of absolute methanol was added 3.72 g. (0.020 mole) of *p*-toluenesulfonylhydrazine with rapid stirring at room temperature. The solution was then heated gently with stirring for 1 hr. The reaction mixture was cooled overnight and filtered; the yellow residue was washed with a small amount of chilled absolute methanol to yield 6.17 g. (93%) of crude **14**. Recrystallization from absolute ethanol led to pure **14** as yellow plates, m.p. 192–195° dec. Infrared spectrum showed λ_{\max}^{KBr} 5.88 μ (C=O).

Anal. Calcd. for C₁₆H₁₆N₂O₂S: C, 58.35; H, 4.59. Found: C, 58.59; H, 4.66.

Preparation of 1-Methyl-3-diazoindole (4). (i) **From 13.**—A solution of 1.50 g. (0.0086 mole) of **13** and 1.95 g. (0.0090 mole) of yellow mercuric oxide in 150 ml. of thiophene-free benzene was stirred at room temperature for 5 hr. The mercury residue was filtered and washed with 50 ml. of warm benzene. The combined filtrates were twice refiltered and then evaporated to dryness in air to yield 1.37 g. (93%) of crude **4**. Recrystallization from 50 and 95% ethanol led to pure **4**, m.p. 88–90°, as dark, reddish brown rods-plates. Infrared spectrum showed λ_{\max}^{KBr} 4.71 μ (C=N₂) and 5.91 μ (C=O); ultraviolet spectrum showed $\lambda_{\max}^{65\% EtOH}$ 262 m μ (ϵ 24,300), 265 (24,200), 301 (9600); n.m.r. gave δ 3.40 (N-CH₃, three protons) and 6.98–7.50 (aromatic multiplet, four protons). T.l.c. of this material showed only a single compound.

Anal. Calcd. for C₈H₇N₃O: C, 62.42; H, 4.07. Found: C, 62.72, 62.22; H, 4.04, 4.30.

(ii) **From 14.**—A solution of 1.50 g. (0.00456 mole) of **14** in 120 ml. of methylene chloride was stirred with 50 ml. of 0.1 *N* sodium hydroxide (0.0050 mole) at room temperature for 2 hr. The reaction mixture was then heated gently for 2.5 hr. while maintaining the volume of methylene chloride at ca. 120 ml. Evaporation of the organic layer to dryness in air left 0.726 g. (92%) of crude **4**, m.p. 84–90°.

(iii) **From 15.**—A solution of 0.50 g. (0.00254 mole) of **15** in 20 ml. of water and 3 ml. of 1 *N* sodium hydroxide (0.0030 mole) was cooled to 0° in an ice-salt bath. Concentrated ammonium hydroxide (1 ml., 0.015 mole) was then added with stirring and cooling (10°), followed by the addition of 14 ml. of 5.25% (0.010 mole) sodium hypochlorite solution dropwise over a period of 10 min. Stirring and cooling at 0° was continued for an additional 15 min. and then at room temperature for 1 hr. Crude **4** (0.313 g., 64%) precipitated.

Pyrolysis of 1-Methyl-3-diazoindole (4) in Absolute Ethanol.—A solution of 0.500 g. (0.0029 mole) of **4** in 30 ml. of absolute ethanol was refluxed for 96 hr. The reaction mixture was evaporated to dryness (Rinco) and the residue was extracted with 250 ml. of petroleum ether (b.p. 30–60°); evaporation of the solution to dryness in air led to recovery of 0.420 g. (84%) of unreacted **4**.

(36) Melting points are corrected. Boiling points are uncorrected. The infrared spectra were run on Perkin-Elmer Models 21 and 137 spectrophotometers; ultraviolet spectra were determined on a Cary 15 spectrophotometer; the n.m.r. spectra were obtained on a Varian A-60 spectrometer³⁷ using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. The irradiation experiments were conducted with a Hanovia 100-w., high-pressure, quartz, mercury vapor arc. Both Vycor (absorbs all radiations below 220 m μ) and Pyrex (absorbs all radiations below 350 m μ) filters were used. In experiments excluding oxygen, solutions were first degassed by heating and purging with nitrogen. The entering nitrogen flow was first passed through an alkaline solution of pyrogallol and then through Drierite.

(37) We acknowledge with pleasure the assistance of a National Science Foundation Grant GP-1482 to the Department of Chemistry toward the purchase of this instrument.

(38) G. Heller, *Ber.*, **40**, 1295 (1907).

(39) W. Borsche and R. Meyer, *ibid.*, **54**, 2852 (1921).

(32) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

(33) R. A. Olofson, W. R. Thompson, and J. S. Mickelman, *ibid.*, **86**, 1865 (1964).

(34) H. M. Blatter, Abstracts of Papers presented at the Division of Organic Chemistry, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 48C.

(35) R. Roger and D. Neilson, *Chem. Rev.*, **61**, 179 (1961).

The petroleum ether insoluble material was dissolved in chloroform, adsorbed on a 4 × 8 in. plate of silica gel G, and developed once with benzene to lead to two well-separated bands. Both bands were eluted with either chloroform or absolute ethanol. The first, dark red-brown band yielded 7 mg. (1.7%) of 1,1'-dimethylisoidigo (6), m.p. 275–275.5° (sublimes), lit.⁴⁰ m.p. 265°, as long, thin, red-brown to violet needles from absolute ethanol. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.90 μ (C=O). N.m.r. gave δ 3.28 (N—CH₃, six protons) and 6.67–7.51 (aromatic multiplet, eight protons). The infrared and n.m.r. spectra were superimposable with an authentic sample of 6 prepared in 41% yield by treatment of 1-methyloxindole (20)⁴¹ with *p*-nitrosodimethylaniline in glacial acetic acid⁴⁰; a 43% yield of 6 could also be obtained by an acid-catalyzed condensation of 12 with 20 (*vide infra*).

Anal. Calcd. for C₁₈H₁₄N₂O₂: C, 74.46; H, 4.86. Found: C, 74.52; H, 4.92.

The second orange band led to 10 mg. (2.2%) of 1,1'-dimethylisatinazine (16), m.p. 272–275.5° dec., lit.³⁹ m.p. 240–245° dec., as tiny orange-red needles from glacial acetic acid. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.80 μ (C=O); n.m.r. gave δ 3.39 (N—CH₃, six protons) and 6.92–8.03 (aromatic multiplet, eight protons). The infrared and n.m.r. spectra were superimposable with an authentic sample of 16 prepared in 93% yield by the acid-catalyzed condensation of 12 with 13.³⁹

Preparation of 1,1'-Dimethylisoidigo (6).—To a solution of 0.735 g. (0.0050 mole) of 1-methyloxindole (20) and 0.805 g. (0.005 mole) of 12 in 25 ml. of 95% ethanol, was added 2 drops of concentrated hydrochloric acid, and the solution was refluxed for 18 hr. Refrigeration of this mixture for 2 hr. precipitated 6 (0.616 g., 43%), m.p. 275–275.5° (from absolute ethanol).

3,3-Dibromo-1-methyloxindole (17).—To a stirred solution of 0.500 g. (0.0029 mole) of 4 in 25 ml. of carbon tetrachloride was added dropwise excess bromine (1 ml., 0.02 mole) in 20 ml. of carbon tetrachloride at room temperature. The mixture was stirred for an additional 30 min., and then evaporated to dryness in air. The residue was washed with 15 ml. of chilled 95% ethanol to yield 0.787 g. (89%) of crude 17. Two recrystallizations from 95% ethanol gave 17 as white plates, m.p. 200–203° dec., lit.¹⁴ m.p. 204°. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.76 μ (C=O); n.m.r. gave δ 3.34 (N—CH₃, three protons) and 6.88–7.82 (aromatic multiplet, four protons). The infrared and n.m.r. spectra were identical with an authentic sample of 17 prepared in a three-step reaction sequence¹⁴: α -methyl- α -phenylhydrazone of pyruvic acid (yellow plates, m.p. 82.5–85°, lit.¹⁴ m.p. unrecorded) → 1-methylindole-2-carboxylic acid (white needles, m.p. 209–211.5°, lit.¹⁴ m.p. 212°) → 17 (in an over-all yield of 51%).

Reduction of 3,3-Dibromo-1-methyloxindole (17).—Compound 17 in absolute ethanol was reduced with zinc dust and concentrated hydrochloric acid.^{15b} 3-Bromo-1-methyloxindole (19) was obtained in 33% yield as tiny white leaflets (from water), m.p. 125–129°, lit.^{15b} m.p. 132–134°. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.81 μ (C=O). Trace amounts of 1-methyloxindole (20) were also obtained.

Pyrolysis of 4 in Presence of Pyridine N-Oxide.—A solution of 0.500 g. (0.0029 mole) of 4 and 0.414 g. (0.00435 mole) of pyridine N-oxide in 20 ml. of toluene was refluxed for 48 hr. The residue remaining after evaporation to dryness in air, was redissolved in 50 ml. of absolute ethanol and filtered. The insoluble material was a mixture of 6 and 16. Excess 2,4-dinitrophenylhydrazine reagent was added to the ethanolic filtrate to yield ultimately 0.089 g. (9%) of 1-methylisatin 3-(2,4-dinitrophenyl)hydrazone, m.p. 332.5–334.5° dec., as orange-red needles from glacial acetic acid. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.79 μ (C=O).

Anal. Calcd. for C₁₅H₁₁N₅O₃: C, 52.73; H, 3.24; N, 20.61. Found: C, 52.95; H, 3.55; N, 20.30.

(40) R. Stollé, R. Bergdoll, M. Luther, A. Auerholm, and W. Wacker, *J. prakt. Chem.*, [2] **123**, 1 (1930).

(41) A number of unsuccessful attempts to prepare 20 were made: (i) ring closure of *N*-methylchloroacetanilide with anhydrous AlCl₃⁴⁰; (ii) thermal decomposition of 16³⁹; and (iii) reduction of 3,3-dibromo-1-methyloxindole (17) leading only to trace amounts of 20^{15b} (*vide infra*). Ultimately 20, m.p. 90–92°, lit.⁴² m.p. 89°, was obtained as long, thin white needles (from 60–75° petroleum ether) in 75% yield by hydrochloric acid hydrolysis of *N*-methylindole-2-sulfonic acid sodium salt in boiling water. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.85 μ (C=O); n.m.r. gave δ 3.31 (N—CH₃), 3.62 (CH₂), and 6.87–7.72 (aromatic multiplet).

(42) O. Hinsberg and J. Rosenweig, *Ber.*, **27**, 3256 (1894).

The infrared spectrum was identical with that of an authentic sample prepared from 12 and 2,4-DNP in the usual manner.

(1-Methyloxindol-3-yl-hydrazono)triphenylphosphorane (18).—To a stirred solution of 0.500 g. (0.0029 mole) of 4 in 30 ml. of anhydrous ether was added 0.786 g. (0.0030 mole) of triphenylphosphine at room temperature and the mixture, protected from moisture, was stirred for 4 hr. The precipitate was filtered, washed with 50 ml. of anhydrous ether, and dried in air to give 1.076 g. (86%) of 18. Recrystallization from absolute ethanol gave pure 18 as dull yellow, hygroscopic plates, m.p. 121–126° dec. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.92 μ (C=O); C=N₂ absorption at 4.71 μ absent.

Anal. Calcd. for C₂₇H₂₂N₃OP: C, 74.47; H, 5.09; N, 9.65. Found: C, 74.26; H, 5.14; N, 9.61.

Pyrolysis of 18.—The adduct 18 (1.50 g., 0.00345 mole) was heated in a Wood's metal bath at 200–210° over a period of 15 min. Cooling of the dark red-brown melt to room temperature led to a tarry residue which was dissolved in 50 ml. of benzene and deposited upon a 2.5 × 25 cm. column of aluminum oxide (Woelm's neutral, activity grade II). After washing well with benzene, elution of the first, colorless band with benzene gave 0.580 g. (64%) of triphenylphosphine. Elution of the second, broad blood red band with benzene led to 0.070 g. (7%) of 1,1'-dimethylisoidigo (6). Elution of the remainder of the column with 95% ethanol led to 0.230 g. (21%) of crude 1,1'-dimethylisatinazine (16).

Photolysis of 4 in Air.—A rapidly stirred solution of 1.00 g. (0.00577 mole) of 4 in 400 ml. of hexane was irradiated (Pyrex filter) for 13 hr. in air. The volume of solution was maintained by continual addition of hexane. At 5-hr. intervals, the immersion well was washed with acetone to remove the insoluble material that collected, and then the combined acetone washings were evaporated to dryness (Rinco). Finally, the irradiated solution was filtered, and the insoluble material was combined with the residue obtained from the acetone washings.

The filtrate was evaporated to dryness in air and the resulting tar was dissolved in 15 ml. of warm absolute ethanol, to which was added excess 2,4-DNP reagent. On cooling, 0.740 g. (38%) of 1-methylisatin 3-(2,4-dinitrophenyl)hydrazone precipitated. Crystallization of the crude tar directly from water gave 12 as orange-red needles, m.p. 131–132°.

The hexane-insoluble, red-brown residue was dissolved in chloroform and deposited upon two 4 × 8 in. plates of silica gel G. Development of the plates (five times) with benzene led to four well-separated bands, each eluted from the plates with 95% ethanol: (i) a sharp, red-brown band which led to trace amounts of 6; (ii) a broad, orange-yellow band which produced 0.035 g. (3.7%) of 12; (iii) a sharp, orange-red band which gave 0.010 g. (1.1%) of 16; and (iv) a broad, dark brown band which led to 0.086 g. of a dark brown, unidentified product, m.p. >300° dec.

Photolysis of 4 in Absolute Ethanol.—A stirred solution of 1.00 g. (0.00577 mole) of 4 in 250 ml. of absolute ethanol was irradiated at room temperature for 18 hr. under nitrogen. The solution was evaporated to dryness (Rinco) on a steam bath, and the resulting residue was dissolved in 15 ml. of chloroform. The solution was deposited on a 2.5 × 20 cm. column of aluminum oxide (Woelm's neutral, activity grade II), and the column was washed with carbon tetrachloride. Elution of the first colorless nonfluorescent band with carbon tetrachloride, followed by evaporation of the eluate to dryness (Rinco), afforded a pale yellow oil which ultimately crystallized to give 0.268 g. (24%) of crude 23, m.p. 49–58°. One recrystallization from 30–60° petroleum ether gave pure 3-ethoxy-1-methyloxindole (23), m.p. 57–58°, as compact, white needles. Infrared spectrum showed $\lambda_{\max}^{\text{KBr}}$ 5.77 (C=O) and 8.95 μ (C—O—C); n.m.r. gave δ 1.13, 1.24, 1.37 (triplet, CH₃, three protons), 3.14 (N—CH₃, three protons), 3.68, 3.79, 3.88, 3.99 (quartet, CH₂, two protons), 4.72 (CH, one proton), and 6.67–7.50 (aromatic multiplet, four protons).

Anal. Calcd. for C₁₁H₁₃NO₂: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.35; H, 6.95; N, 7.45.

Further elution of the column with benzene, benzene-chloroform (1:1), and chloroform led only to small amounts of tars.

Photolysis of 4 in Cyclohexene.—A rapidly stirred solution of 1.00 g. (0.00577 mole) of 4 in 250 ml. of freshly distilled cyclohexene was irradiated at room temperature for 20 hr. under a nitrogen atmosphere. Evaporation of the solution to dryness (Rinco) led to an orange-yellow oily residue which was dissolved in 30 ml. of carbon tetrachloride and adsorbed on a 2.5 × 25

cm. alumina-packed column (Woelm's neutral aluminum oxide, activity grade II) and washed with ca. 50 ml. of carbon tetrachloride. The first band (fluorescent) was eluted with ca. 60 ml. of carbon tetrachloride. Evaporation to dryness (Rinco) of this eluate led to a pale yellow-green crude oil. Further elution of the column (nonfluorescent band) with an additional 300 ml. of carbon tetrachloride gave an eluate which on evaporation to dryness (Rinco) left a faint yellow oil. This oil crystallized within a few minutes on standing in air. One recrystallization from 30–60° petroleum ether gave 0.240 g. (18%) of 24–25 as tiny white needles and plates, m.p. 137–139°.

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.25; H, 7.54; N, 6.16; mol. wt., 227. Found: C, 79.52; H, 7.61; N, 6.29; mol. wt., 237.

The pale, yellow-green crude oil (first eluted from the column) failed to crystallize. It was dissolved in 20 ml. of petroleum ether (b.p. 60–75°) and adsorbed on a 2.5 × 15 cm. alumina-packed column (Woelm's neutral aluminum oxide, activity grade II). The column was developed by washing with petroleum ether (b.p. 60–75°) and eluted with 750 ml. of petroleum ether (b.p. 60–75°). Evaporation of the eluate to dryness (Rinco) led to a colorless oil which crystallized immediately to yield 0.197 g. (15%) of crude material. Recrystallization from petroleum ether (b.p. 30–60°) finally gave 0.120 g. (9%) of pure 25–24 as white, crystalline plates, m.p. 83–85°.

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.25; H, 7.54; N, 6.16; mol. wt., 227. Found: C, 79.33; H, 7.36; N, 6.39; mol. wt., 235.

Photolysis of 4 in the Presence of 1,1-Diphenylethylene.—A rapidly stirred solution of 1.00 g. (0.00577 mole) of 4 and 48 ml. of 1,1-diphenylethylene (0.277 mole) (Eastman) in 200 ml. of hexane was irradiated at room temperature for 20 hr. under a nitrogen atmosphere. The hexane was evaporated (Rinco) on a steam bath and the resulting solution was reduced in volume to 3–5 ml. by distilling the 1,1-diphenylethylene under vacuum (b.p. 105–106° at 2 mm.). The residue was dissolved in 25 ml. of benzene and deposited on a 2.5 × 25 cm. alumina-packed column (Woelm's neutral aluminum oxide, activity grade II). The column was washed and eluted with 200 ml. of petroleum ether (b.p. 60–75°), followed by 350 ml. of carbon tetrachloride. The combined eluates ultimately gave crude 1,1-diphenylethylene. Elution with the first 100 ml. of benzene led to a tarry residue which was dissolved in chloroform and placed upon a 4 × 8 in. plate of silica gel G and developed with benzene. Removal of the broad, colorless (faint blue fluorescent) band with chloroform ultimately gave 0.030 g. of crude 26. Further elution of the column with 250 ml. of benzene ultimately afforded a tan-colored oily residue which crystallized to yield an additional 0.465 g. of 26, m.p. 167–181°. The over-all yield of crude material was 26%. One recrystallization from absolute ethanol gave pure 26 as tiny white plates, m.p. 190–191.5°. Infrared spectrum showed λ_{\max}^{KBr} 5.79 μ (C=O).

Anal. Calcd. for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30. Found: C, 84.93; H, 5.79; N, 4.54.

Photolysis of 4 in Carbon Tetrachloride.—A rapidly stirred solution of 1.50 g. (0.00867 mole) of 4 in 180 ml. of carbon tetrachloride was irradiated (Vycor filter) at room temperature for 14 hr. under a nitrogen atmosphere. The brown insoluble material that collected on the surface of the immersion well during the irradiation was washed off with acetone after 4, 8, and 12 hr. Finally, the photolyzed solution was filtered to remove additional insoluble brown material, and the blood red filtrate was adsorbed on a 2.5 × 25 cm. column of neutral alumina (Woelm's, activity grade II) and washed well with carbon tetrachloride. The first, colorless, nonfluorescent band was eluted with carbon tetrachloride and led to a small amount of a white material which after one recrystallization from 95% ethanol gave 0.037 g. (1.8%) of 3-chloro-3-trichloromethyl-1-methyloxindole (28), m.p. 160–168°. A second recrystallization from absolute ethanol afforded pure 28 as white hexagonal plates, m.p. 168–171°. Infrared spectrum showed λ_{\max}^{KBr} 5.74 μ (C=O).

Anal. Calcd. for $C_{10}H_7Cl_4NO$: C, 40.16; H, 2.38; N, 4.68. Found: C, 39.83; H, 2.46; N, 4.46.

Elution of the second band with carbon tetrachloride led to the recovery of 0.288 g. (19%) of 4. The third band was eluted with 100 ml. of 1:1 carbon tetrachloride–benzene, and 350 ml. of benzene to yield 0.140 g. (11%) of 6. The fourth band was eluted with 500 ml. of 1:1 benzene–chloroform and on evaporation of the eluate to dryness (Rinco) left a residue which was dissolved in chloroform and placed upon a plate of silica gel G (4 × 8 in.).

Elution of the plate (five times) with benzene led to (i) a sharp reddish brown band which was determined to be a trace amount of 6, and (ii) a very broad orange-brown band, which was removed with chloroform and replaced upon a second silica gel G plate. Elution of this plate twice with chloroform and removal of the main broad orange-red band with chloroform led to 0.030 g. (3%) of 16. Elution of the remainder of the alumina column with 95% ethanol afforded a dark brown residue, m.p. >300° dec., which was not further investigated.

3-Diazoindole (1).—Treatment of isatin 3-tosylhydrazine (32) with 0.2 N sodium hydroxide at room temperature led to an 86% yield of 1, m.p. 171–173.5° dec., lit.^{29,30} m.p. 168° dec., as dark red-brown plates and prisms from benzene. Infrared spectrum showed λ_{\max}^{KBr} 4.74 (C=N₂) and 5.90 μ (C=O).

1-Methanesulfonyl-3-diazoindole (29).—To 4.00 g. (0.0251 mole) of 1 was added a solution of 0.577 g. (0.0251 g.-atom) of sodium in 100 ml. of absolute ethanol, and the resulting solution was stirred at room temperature for 15 min. Methanesulfonyl chloride (4 ml., 0.053 mole) was then added with cooling in an ice-salt bath. The reaction mixture was stirred for 1 hr. at room temperature after the addition, refrigerated overnight, and filtered, and the light orange residue was washed well with water to yield 2.26 g. (38%), m.p. 125–129°, of crude 29. One recrystallization from 95% ethanol gave pure 29 as light orange, silken needles, m.p. 138–140° dec. Infrared spectrum showed λ_{\max}^{KBr} 4.71 (C=N₂), 5.89 (C=O), and 8.56 μ (SO₂); n.m.r. gave δ 3.57 (S-CH₃) and 7.32–7.50 (aromatic multiplet).

Anal. Calcd. for $C_9H_7N_3O_2S$: C, 45.58; H, 2.97. Found: C, 45.50; H, 2.97.

Ethyl *o*-(N,N-Bismethanesulfonyl)amino- α -diazophenylacetate (30).—To a cooled solution (5–10°) of 30 ml. of 1 N sodium ethoxide (0.030 mole) and 1.59 g. (0.01 mole) of 1 was added (dropwise) 5 ml. of methanesulfonyl chloride (0.066 mole). The reaction mixture was refrigerated overnight and filtered to remove the crude yellow precipitate. The crude material was extracted with ether and filtered; the filtrate was evaporated to dryness in air yielding 1.14 g. (32%) of 30, m.p. 97–99°, as yellow plates from absolute ethanol. Infrared spectrum showed λ_{\max}^{KBr} 4.71 (C=N₂), 5.87 (C=O), and 8.59 μ (SO₂).

Anal. Calcd. for $C_{12}H_{15}N_3O_5S_2$: C, 39.89; H, 4.02. Found: C, 39.99; H, 4.05.

Attempted Photolysis of 29.—A stirred solution of 0.500 g. (0.00211 mole) of 1-methanesulfonyl-3-diazoindole (29) in 250 ml. of absolute ethanol was irradiated at room temperature for 14 hr. under a nitrogen atmosphere. Upon evaporation to dryness (Rinco), the residue was dissolved in 20 ml. of chloroform and adsorbed on a 2.5 × 15 cm. alumina-packed (Woelm's neutral aluminum oxide, activity grade II) column which was then washed and eluted with 500 ml. of benzene. Evaporation of the eluate to dryness (Rinco) led to an orange-yellow oil, which crystallized to give unreacted 29. Further elution of the column with chloroform (100 ml.) and ethyl acetate (100 ml.) led to no discernible products.

2-Chloro-3-oxo-3H-indole (31).—Treatment of isatin (10) with phosphorus pentachloride in warm, dry, thiophene-free benzene ultimately gave 31 in 36% yield as a light brown powder, m.p. 155–160° dec., lit.³⁰ m.p. 180° dec. Compound 31 resisted purification by conventional techniques and decomposed completely on standing overnight in air. Zinc dust treatment of 31, as reported,³⁰ led to indigo.

Reaction of 31 with *p*-Toluenesulfonylhydrazine.—To a stirred solution of 1.00 g. (0.00606 mole) of 31 in 100 ml. of absolute ethanol under nitrogen was added a solution of 1.127 g. (0.00606 mole) of *p*-toluenesulfonylhydrazine in 50 ml. of absolute ethanol dropwise over a period of 10 min. The solution was cooled to room temperature, refrigerated for 1 hr., and filtered to yield 1.00 g. (53%) of isatin-3-tosylhydrazone (32), m.p. 190–200° dec. (from absolute methanol), lit.¹¹ m.p. 190–200° dec. The infrared spectrum was superimposable with that of authentic 32 prepared in 98% yield by reaction of 10 with *p*-toluenesulfonylhydrazine.

Silver Salt of Isatin (33).—Treatment of the sodium salt of isatin (11) in water with silver nitrate at room temperature quantitatively converted it to 33 as a violet powder⁴⁴; alternatively, 33 could be prepared in 70% yield by direct reaction between 10 and silver acetate. Infrared spectrum showed λ_{\max}^{KBr} 5.80 μ (C=O).

(43) Spectrum amplification too high for proper integration.

(44) G. Heller, *Ber.*, **40**, 1295 (1907).

2-Methoxy-3-oxo-3H-indole (O-Methylisatin, 34).—A heterogeneous mixture of 7.62 g. (0.030 mole) of **33** (finely powdered and vacuum dried), 3.6 ml. of methyl iodide (0.060 mole), and 25 ml. of anhydrous ether in a 125-ml. erlenmeyer flask (wrapped with aluminum foil) was allowed to stand for 3 days at room temperature in the dark. The mass was extracted with 4 × 20 ml. of dry benzene; an equal volume of petroleum ether (b.p. 90–100°) was added to the combined extracts. The benzene-petroleum ether solution was evaporated (Rinco), and the resulting orange precipitate of 1-methylisatin (**12**) was filtered. Evaporation of the filtrate to dryness (Rinco) on a steam bath gave a liquid which solidified on cooling. One recrystallization of this solid from the minimum amount of benzene led to 1.53 g. (32%) of **34**, m.p. 95–100°. Sublimation of this material at 60–65° at 6 mm. led to pure O-methylisatin (**34**), m.p. 102–104°, lit.⁴⁵ m.p. 101–102°, as blood red prisms. Infrared spectrum showed $\lambda_{\text{max}}^{\text{KBr}}$ 5.76 μ (C=O).

Anal. Calcd. for $\text{C}_9\text{H}_7\text{NO}_2$: C, 67.07; H, 4.38. Found: C, 67.30; H, 4.46.

Isatin 2-Tosylhydrazone (9).—To a warm, stirred solution of 1.00 g. (0.0062 mole) of **34** in 50 ml. of dry benzene was added 1.155 g. (0.0062 mole) of *p*-toluenesulfonylhydrazine. The reaction mixture was heated gently for an additional 30 min., cooled to room temperature, and filtered; the residue was washed with 50 ml. of benzene. Upon drying in air, 1.64 g. (84%) of isatin 2-tosylhydrazone (**9**) was obtained as a chalky orange powder, m.p. 178–184° dec. Two recrystallizations from absolute methanol gave pure **9** as orange-red plates, m.p. 185–187° dec. Infrared spectrum showed $\lambda_{\text{max}}^{\text{KBr}}$ 5.83 (C=O) and 6.19 μ (C=N).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_5\text{S}$: C, 57.14; H, 4.15. Found: C, 57.29; H, 4.43.

Acid-Catalyzed Hydrolysis of Isatin 2-Tosylhydrazone (9) to Isatin 3-Tosylhydrazone (32).—A mixture of 0.180 g. (0.00057 mole) of **9** and 2 drops of concentrated hydrochloric acid in 20 ml. of 50% ethanol was refluxed for 3 hr. The solution was cooled to room temperature, refrigerated for 2 hr., and filtered to give 0.102 g. (57%) of **32**.

Base Decomposition of Isatin 2-Tosylhydrazone (9).—A mixture of 0.500 g. (0.0016 mole) of **9** and a threefold excess of 0.2 *N* potassium hydroxide (24 ml., 0.0048 mole) was stirred at room temperature for 96 hr. Filtration led to 0.505 g. of the potassium salt (**35**). Acidification of the filtrate with 1 *N* hydrochloric acid led to recovery of 0.015 g. of unreacted **9**.

An aqueous solution of the potassium salt was heated at 65–70° for 2 hr. with stirring. The resulting blue-black reaction mass was cooled to room temperature and filtered to yield 0.130 g. (62%) of indigo blue (**38**) as a blue-black powder, m.p. >350° (sublimes), lit.⁴⁶ m.p. >300°. The crude indigo sublimed partially as a blue-black powder and partially as a violet crystalline material with a coppery luster. The infrared spectra of both materials proved to be identical with an authentic sample of indigo blue (Eastman): $\lambda_{\text{max}}^{\text{KBr}}$ 6.14 μ (C=O). Acidification of the

(45) A. Baeyer and S. Oekonomides, *Ber.*, **15**, 2093 (1882).

(46) U. Weinstein, *J. Am. Chem. Soc.*, **78**, 4010 (1956).

aqueous filtrate with 1 *N* hydrochloric acid led to the recovery of an additional 0.015 g. of unreacted **9**.

When equimolar quantities of sodium ethoxide in ethanol were used (instead of aqueous base) over a 95-hr. period at room temperature, **9** was converted to **38** in only 17% yield.

Treatment of 9 with 1 *N* Sodium Ethoxide and Excess Methyl Iodide.—A solution of 10 ml. of 1 *N* sodium ethoxide (0.01 mole) and 0.50 g. (0.0016 mole) of **9** was allowed to stand at room temperature for 2 days, and then evaporated to dryness in air. Addition of 10 ml. of methyl iodide (0.16 mole) resulted in a deep blood red solution which was allowed to stand at room temperature overnight. Evaporation to dryness in air, followed by copious water washing of the crude red residue gave 0.48 g. (88%) of the dimethyl derivative (**39**) of isatin 2-tosylhydrazone, m.p. 233–235° dec., as brilliant red plates from acetone. Infrared spectrum showed $\lambda_{\text{max}}^{\text{KBr}}$ 5.79 μ (C=O).

Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_5\text{S}$: C, 59.49; H, 4.99. Found: C, 59.71; H, 5.22.

Isatin 2-Oxime (8).—Treatment of **34** with hydroxylamine hydrochloride at room temperature gave **8** in 90% yield, m.p. 198–200.5° (sublimes), as yellow needles; lit.⁴⁷ m.p. 198–200°. Infrared spectrum showed $\lambda_{\text{max}}^{\text{KBr}}$ 5.80 μ (C=O).

Attempted Reactions of Isatin 2-Oxime (8). (i) **With Chloramine.**—To a stirred solution of 0.500 g. (0.0031 mole) of **8** in 175 ml. of water and 4 ml. of 1 *N* sodium hydroxide (0.004 mole) at 0° (ice-salt bath) was added 1 ml. of concentrated ammonium hydroxide, followed by the immediate dropwise addition of 21 ml. of 5.25% sodium hypochlorite solution (0.015 mole) over a period of 5 min. The solution was stirred for an additional 30 min. at 0° and then at room temperature for 2 hr. Repeated extraction with large volumes of conventional organic solvents (ether, benzene, and methylene chloride) invariably led to a small amount of a crude, dark yellow-brown residue which could not be identified. Acidification with 0.1 *N* hydrochloric acid, followed by similar extractions, again led to a small amount of crude intractable residue. No starting material could be isolated.

(ii) **With Dilute Base.**—A solution of 0.500 g. (0.0031 mole) of **8** in 20 ml. of water and 4 ml. of 1 *N* sodium hydroxide (0.004 mole) was stirred at room temperature for 3 hr. Acidification with 0.1 *N* hydrochloric acid gave 0.340 g. (68%) of unreacted **8**. The acidic filtrate was extracted with 500 ml. of ether. The ether extracts were dried over anhydrous sodium sulfate, filtered, and upon evaporation to dryness in air led to the recovery of an additional 0.150 g. (30%) of unreacted **8**.

Isatin 2-Hydrazone.—To a solution of 1.00 g. (0.0062 mole) of **34** in 20 ml. of benzene was added 0.36 ml. of 85% hydrazine hydrate (0.0062 mole) in 2 ml. of water with stirring at room temperature. The reaction mixture was stirred an additional 30 min. and filtered to give 0.891 g. (89%) of isatin 2-hydrazone, m.p. 183–186° dec., as dark yellow-brown plates from absolute ethanol. Infrared spectrum showed $\lambda_{\text{max}}^{\text{KBr}}$ 5.96 μ (C=O).

Anal. Calcd. for $\text{C}_8\text{H}_7\text{N}_3\text{O}$: C, 59.62; H, 4.37; N, 26.07. Found: C, 59.81; H, 4.64; N, 25.90.

(47) G. Heller, *Ber.*, **49**, 2757 (1916).

A New Route to the 13H-Indolo[2,3-*a*]acridizinium System¹

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Using bromoacetone instead of chloroacetaldehyde, we have confirmed the observation of Stevens that quaternization of 2-(2'-pyridyl)indoles is accompanied by cyclization on nitrogen, affording indolo[2,1-*a*]-2-azaquinolizinium salts, and also that quaternization of 1-alkyl-2-(2'-pyridyl)indoles affords a 12-alkyl-12H-indolo[2,3-*a*]-quinolizinium system. Extension of the latter method to 1-methyl-2-(3-isoquinolyl)indole has made possible the synthesis of 8,13-dimethyl-13H-indolo[2,3-*a*]acridizinium bromide. The ultraviolet absorption spectrum of the new salt is in agreement with that of the 13H-indolo[2,3-*a*]acridizinium salts of Bradsher and Umans.

The indolo[2,3-*a*]acridizinium nucleus (I) may be regarded as the aromatic parent system of the yohimbine, reserpine, and alstoniline alkaloids.² The syn-

thesis of this aromatic system (by dehydrogenation of the 7,8-dihydro derivative) was first claimed by Swan,³ but the validity of this claim appeared questionable on

(1) This research was supported by U. S. Public Health Service Research Grant No. HE-2170 from the National Heart Institute.

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(3) G. A. Swan, *J. Chem. Soc.*, 2038 (1958).