Benz[f]isoindole

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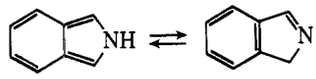
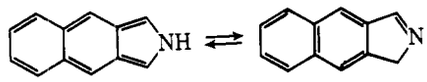
A new class of nitrogen-bridged anthracenes has been prepared by reaction of 1-(phenylmethyl)pyrrole and also *tert*-butyl pyrrole-1-carboxylate with 2,3-didehydronaphthalene (**10**) to give 11-(phenylmethyl)-1,4-dihydroanthracen-1,4-imine (**11**) and *tert*-butyl 1,4-dihydroanthracen-1,4-imine-11-carboxylate (**13**), respectively. Hydrogenation of **11** provides 11-(phenylmethyl)-1,2,3,4-tetrahydroanthracen-1,4-imine (**12**), which on hydrogenolysis yields 1,2,3,4-tetrahydroanthracene. Hydrogenation of **13** followed by acidic cleavage of the *tert*-butyloxycarbonyl group affords 1,2,3,4-tetrahydroanthracen-1,4-imine (**9**), which yields benz[*f*]isoindole (**3** ⇄ **5**) on retro-Diels–Alder thermolysis. The properties of the latter compound, which heretofore resisted isolation, are discussed. Unlike the parent isoindole (**1** ⇄ **6**) and 4,5,6,7-tetrafluoroisoindole, benz[*f*]isoindole exists, on the basis of spectroscopic examination, predominantly in the benzenoid (1*H*-benz[*f*]isoindole) tautomeric form (**5**). However, the formation of a Diels–Alder adduct, **8**, with *N*-phenylmaleimide suggests the presence of a trace amount of the *o*-quinonoid tautomer (2*H*-benz[*f*]isoindole) (**3**).

The recent review of nitrogen-bridged six-membered ring systems[1] and the continuing interest in the chemistry of *o*-quinonoid heteroaromatic compounds[2,3] prompt us to report the first isolation of benz[*f*]isoindole (**3** ⇄ **5**). The preparation involved several anthracen-1,4-imine intermediates which constitute a new class of nitrogen-bridged compounds.

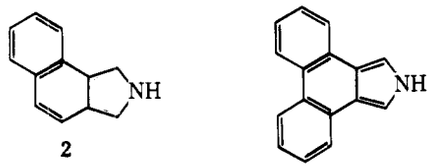
The annelation of one or two benzenoid rings to the parent isoindole (**1**) gives rise to three different structures (**2, 3,** and **4**). Of these possibilities, only benz[*e*]isoindole (**2**)[3a] and dibenz[*e,g*]isoindole (**4**)[3b] have been isolated. Benz[*f*]isoindole



1 **6**



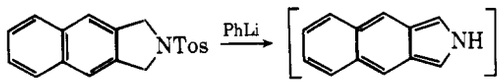
3 **5**



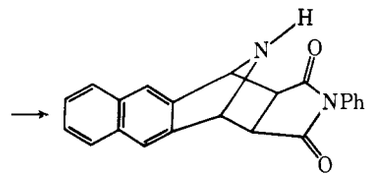
2 **4**

(**3**) until now has resisted isolation, although its formation in solution has been demonstrated[4] by trapping it as an adduct with *N*-phenylmaleimide. As in the case of the unsubstituted parent compound (**1**), benz[*f*]isoindole may be represented by two tautomeric forms; one is *o*-quinoid and the other has the benzenoid structure (**5**).

The transient formation of benz[*f*]isoindole (**3**) was demonstrated in 1967 by Shields and Bornstein,[4] who treated an



7 **3**



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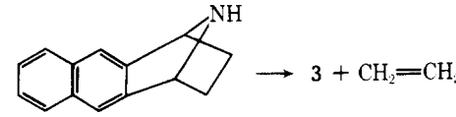
ethereal suspension of 2-(*p*-toluenesulfonyl)benz[*f*]isoindoline (**7**) with excess phenyllithium. Hydrolysis of the reaction mixture afforded an ethereal solution of benz[*f*]isoindole (**3**) as shown. Although they were unable to isolate **3** or its maleic anhydride adduct, the exo-adduct **8** with *N*-phenylmaleimide was obtained, and its identification served to prove the presence of benz[*f*]isoindole (**3**). From the results of this work, Shields and Bornstein concluded that benz[*f*]isoindole (**3**) was even more reactive than its simpler congener isoindole (**1**).

Results and Discussion

In view of the previous failure[1] to isolate benz[*f*]isoindole (**3**) from solution, it seemed essential that any further attempts at the preparation of this reactive compound should avoid the use of solvents. Accordingly, flash vacuum thermolysis was investigated. This method has been used in the past in our laboratory for the preparation of other highly reactive compounds.[5,6] Success in this undertaking would not only afford the first isolable specimen of benz[*f*]isoindole, but would further demonstrate the generality and scope of flash vacuum thermolysis as a route to isoindoles.

In the case of isoindole (**1**), thermolysis of 1,2,3,4-tetrahydronaphthalen-1,4-imine[5] afforded compound **1** and ethylene in essentially quantitative yield. By direct analogy, the thermolysis of 1,2,3,4-tetrahydroanthracen-1,4-imine (**9**) was expected to yield benz[*f*]isoindole (**3**).



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The 1,2,3,4-tetrahydronaphthalen-1,4-imines, which we have found to be important intermediates in the synthesis of isoindole (**1**) and its derivatives, have been well documented.[1] However, the related anthracen-1,4-imines have not been previously reported, although a few isomers bearing the imine bridge at the 9,10 positions have been made.[1] Since Rees and Storr[7] had succeeded in preparing an oxygen-bridged 1,4-dihydroanthracene by the addition of 2,3-didehydronaphthalene (**10**) to furan, we felt this route could be extended to the synthesis of **9**. Addition of compound **10** to an N-protected pyrrole presumably would result in the formation of the desired precursor to 1,2,3,4-tetrahydroanthracen-1,4-imine (**9**).

As expected, thermal decomposition of 2-naphthalenediazonium 3-carboxylate generated 2,3-didehydronaphthalene

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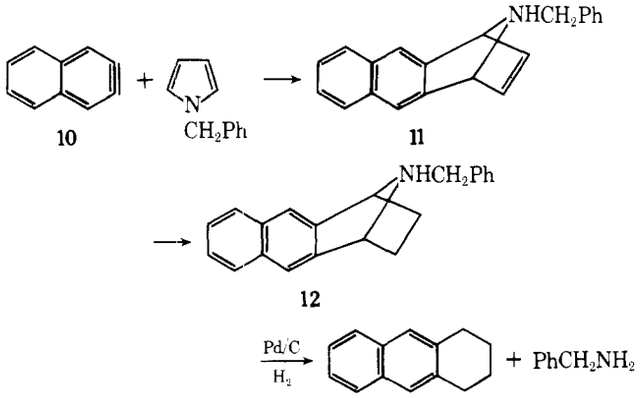
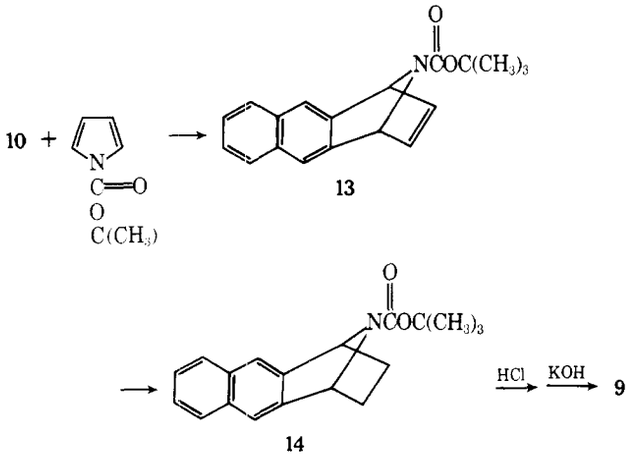
Table I

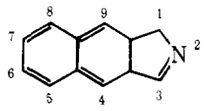
2-vinylnaphthalene, max, nm (95% EtOH)	Benz[f]isoindole, max, nm (95% EtOH)	Benz[f]isoindole, max, nm (hexane)
339	340	337
331		328
323	324	322
		314
296	298	298
283	288	285
273	278	275
265		265

(10), which reacted with 1-(phenylmethyl)pyrrole to afford adduct 11. Hydrogenation of imine 11 in methanol in the presence of 10% palladium–charcoal gave 11-(phenylmethyl)-1,2,3,4-tetrahydroanthracen-1,4-imine (12). An attempt to convert 12 to compound 9 by selective hydrogenolysis failed; only 1,2,3,4-tetrahydroanthracene and benzylamine were recovered. Accordingly, an alternate route to 9 was investigated. Treatment of 10 with *tert*-butyl pyrrole-1-carboxylate in 1,4-dioxane yielded adduct 13, which was smoothly reduced by hydrogen and 10% palladium–charcoal to *tert*-butyl 1,2,3,4-tetrahydroanthracen-1,4-imine-11-carboxylate (14). The protective *tert*-butyloxycarbonyl group was removed by reaction with dry hydrogen chloride in nitromethane; the resultant hydrochloride was transformed to the corresponding free base 9 with aqueous potassium hydroxide.





Flash vacuum thermolysis of 9 in the usual apparatus[5,6] at 600 °C (0.05 mm) effected the desired retro-Diels–Alder reaction and gave both benz[f]isoindole (3) and its coproduct, ethylene, in essentially quantitative yield. Both compounds were collected in a trap cooled in liquid nitrogen. The ethylene was removed by vaporization and identified by conversion to its 1,2-dibromo derivative.[5] The product which remained was a cream-colored solid. Although neat benz[f]isoindole was



relatively stable at dry ice temperature it resinified immediately upon being warmed to room temperature. In contrast, the compound was sufficiently stable in dilute solution to allow absorption spectra to be measured at room temperature. The UV spectrum showed no absorption above 337 nm, which is consistent with the benzenoid structure 5 rather than the *o*-quinonoid form 3. Indeed, 2-methylbenz[f]isoindole,[8] which can exist only in the *o*-quinonoid form, shows absorption well above 337 nm. It is interesting to note that the UV spectrum of our specimen of benz[f]isoindole was strikingly similar to that of 2-vinylnaphthalene[9] (Table I).

The NMR spectra of the thermolysis product offered no evidence for the presence of the *o*-quinonoid tautomer, 2*H*-benz[f]isoindole (3). Unlike the spectrum of the parent isoindole (1), which exhibited a clearly recognizable N–H resonance at δ 12,[5] no similar resonance characteristic of 3 could be detected even though the scan was extended downfield as far as δ 16. From these observations, it appeared that only 1*H*-benz[f]isoindole (5) was present. The NMR study was carried out at −40 °C with solutions of the product in acetone-d_6 and chloroform-d_1. These solutions appeared to be stable at −40 °C for approximately 1 h, after which time spectral changes were observed which suggested decomposition of the sample. This decomposition, possibly due to polymerization, was indicated by decreased signal intensity, broadening of the aromatic resonances, and loss of resolution. Evidence for the benzenoid tautomer 5 was clearly furnished by the NMR spectrum, which displayed a one-proton multiplet at δ 8.70 and a two-proton doublet at δ 4.95 assigned to the protons at C-3 and C-1, respectively. The appearance and chemical shifts of these two resonances were very similar to those observed in the NMR spectrum of the benzenoid tautomer 6 of the parent isoindole. As in the case of 6, the cross ring spin coupling of the protons at C-1 and C-3 was established by spin decoupling of the protons at these positions. The general appearance of the aromatic region of the spectrum, δ 7.3–8.2, was similar to that of anthracene. A broad singlet at δ 8.1 was assigned to the protons at C-4 and C-9 and, in addition, two multiplets centered at δ 7.9 and 7.5 were consistent with the protons bonded to C-5 and C-8 and to C-6 and C-7 of 5, respectively. There was no change in the NMR spectrum when D_2O was added to a solution of the thermolysis product in acetone-d_6 at −25 °C. The resonances for the hetero-ring protons were still apparent, although the resolution of their splitting patterns was severely diminished.

Benz[f]isoindole slowly gave a positive Ehrlich test for the pyrryl nucleus. Initially, a ruby-red color formed which became deep blue when the solution was set aside overnight. The pine splint test was also positive, imparting a magenta coloration to the wood. The melting point of the compound could not be determined owing to progressive decomposition of the solid as it was allowed to warm to room temperature.

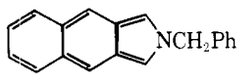
Benz[f]isoindole and *N*-phenylmaleimide slowly reacted in ether solution at low temperature to form Diels–Alder adduct 8 in low yield. The fact that 8 was obtained suggests that a small amount of the *o*-quinonoid tautomer 3 was present in solution. The melting point of adduct 8 corresponded with the value reported in the literature[4] and the mixture melting point with an authentic specimen exhibited no depression. The NMR spectrum of the adduct in dimethyl-d_6 sulfoxide indicated that 1,4-addition across the hetero ring had occurred to yield exo structure 8; further confirmation was provided by IR spectroscopy and elemental analysis.

An interesting feature of the flash vacuum thermolysis route is that apparently only the benzenoid form 5 is observed. This

tautomer is, according to molecular orbital calculations,[10] the less stable form of benz[f]isoindole. Clearly, when our product is dissolved in solution, there must be tautomeric equilibration leading to the formation of some of the *o*-quinonoid tautomer **3**. This would account for the isolation of adduct **8** on treatment with *N*-phenylmaleimide. In this connection, it is worth noting that a similar situation has been encountered by Smith and Wikman[11] in the case of 1-benzalphthalan. These investigators inferred that in solution the tautomer, 1-benzylisobenzofuran, was present, since a Diels–Alder adduct of the latter could be prepared. Yet using UV and NMR spectroscopy they failed to detect the presence of the *o*-quinonoid tautomer. Subsequent investigation[12] corroborated the existence of a tautomeric equilibrium between these two compounds.

From the observations of Rettig and Wirz,[8] who recently described the preparation and isolation of 2-methylbenz[f]isoindole, it appears that this compound is substantially less reactive than our benz[f]isoindole. Similarly, decreased reactivity resulting from substitution on the hetero atom has been found in the case of the simpler nonbenzannelated compounds, isoindole and 2-methylisoindole. The latter compound shows considerably less reactivity than the parent. This decrease presumably results from the inability of the nitrogen-substituted isoindoles to tautomerize to a benzenoid (isoindolenine) form, which would display a greater tendency to polymerize.[8,10,13]

Prompted by our success with flash vacuum thermolysis as a technique for the preparation of isoindoles,[5,6] it was of interest to apply this method to the synthesis of 2-(phenylmethyl)benz[f]isoindole (**15**), whose precursor **12** was already



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in hand as noted above. Accordingly, 11-(phenylmethyl)-1,2,3,4-tetrahydroanthracen-1,4-imine (**12**) was pyrolyzed under the usual conditions. Surprisingly, none of the expected 2-(phenylmethyl)benz[f]isoindole (**15**) was detected. A small amount of white solid was obtained in the collection trap. However, this material, which gave a positive test with Ehrlich's reagent, failed to give an adduct with *N*-phenylmaleimide. Subsequent analysis of **12** by the pyrolysis–GC–MS technique[14] gave evidence for the formation of some benz[f]isoindole and other compounds. These results indicate that cleavage of the phenylmethyl group accompanied the retro-Diels–Alder reaction, a phenomenon which was not observed previously in the preparation by flash vacuum thermolysis of 2-(phenylmethyl)-4,5,6,7-tetrafluoroisoindole.[6]

Experimental Section

Melting points were determined by the capillary method in a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. and Midwest Microlab, Ltd., Indianapolis, Ind. For TLC, Eastman 6060 silica gel plates with fluorescent indicator were used. Mass spectra were obtained on a Perkin-Elmer Hitachi RMS-4 mass spectrometer. NMR spectra were recorded with a Varian Associates HA-100 and a JEOL-MH-100 spectrometer. Chemical shifts are reported as parts per million relative to tetramethylsilane. Ultraviolet spectra were obtained on a Cary Model 17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer. The apparatus used for flash vacuum thermolysis was modeled after that previously described.[13]

11-(Phenylmethyl)-1,4-dihydroanthracen-1,4-imine (11). A slurry of 2-naphthalenediazonium 3-carboxylate[15] (1.35 g, 6.81 mmol) in 100 mL of dried 1,2-dimethoxyethane was added in portions over a period of 30 min to a refluxing solution of 1-(phenylmethyl)pyrrole (2.13 g, 13.5 mmol) in 50 mL of 1,2-dimethoxyethane. Reflux was continued 10–15 min after addition of the reactants had been completed. The reaction mixture was concentrated in vacuo to give a dark red-brown oil. Excess 1-(phenylmethyl)pyrrole was removed from the oil by distillation [60–80 °C (0.1 mm)]. The solid residue was chromatographed on alumina with chloroform as eluent. The product fraction (TLC, single spot, R_f 0.5, silica gel/$CHCl_3$) was sublimed [125–130 °C 0.03 mm)] and the sublimate was recrystallized from methanol to yield 1.69 g (26.6%) of product, mp 127–128 °C. Further recrystallization from acetone–water (1:1) gave an analytical sample: mp 127.5–128.5 °C; IR (KBr) 3050, 2980, 2910, 2870, 2830, 1605, 1600, 1490, 1450, 809, 740, 700, and 695 cm^{-1}; NMR ($CDCl_3$) δ 7.55 (m, 6 H, naphthyl), 7.25 (s, 5 H, phenyl), 6.80 (m, 2 H, olefinic), 4.60 (m, 2 H, bridgehead), and 3.45 (s, 2 H, benzyl).

Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.10; H, 6.09; N, 4.98.

11-(Phenylmethyl)-1,2,3,4-tetrahydroanthracen-1,4-imine (12). A solution of **11** (0.90 g, 3.17 mmol) in 75 mL of absolute methanol containing 0.1 g of 10% palladium–charcoal was heated to boiling and shaken while warm (approximately 45 °C) with hydrogen at 50 psi for 30 min. TLC of the reaction mixture (silica gel/$CHCl_3$) gave a single spot with the same R_f value (0.5) as the starting material, but with different appearance when illuminated with an ultraviolet lamp. Filtration of the hydrogenation mixture to remove catalyst followed by evaporation in vacuo of the solvent afforded 0.89 g (90.5%) of white crystals, mp 118–120 °C. Recrystallization from methanol provided an analytical sample: mp 119.5–120.0 °C; IR (KBr) 3050, 2990, 2975, 2965, 2940, 2910, 2870, 2830, 1495, 1455, 1284, 886, 845, 753, 746, 738, and 695 cm^{-1}; NMR ($CDCl_3$) δ 7.60 (m, 6 H, naphthyl), 7.25 (s, 5 H, phenyl), 4.23 (m, 2 H, bridgehead), 3.80 (s, 2 H, benzyl), 2.25 (m, 2 H, exo protons), and 1.30 (m, 2 H, endo protons).

Anal. Calcd for $C_{21}H_{19}N$: C, 88.33; H, 6.71; N, 4.91. Found: C, 88.38; H, 6.81; N, 4.94.

Attempted Preparation of 1,2,3,4-Tetrahydroanthracen-1,4-imine (9) by Hydrogenolysis of 11-(Phenylmethyl)-1,2,3,4-tetrahydroanthracen-1,4-imine (12). Formation of 1,2,3,4-Tetrahydroanthracene. A slurry of 0.2 g of 10% palladium–charcoal in 50 mL of absolute ethanol was shaken with hydrogen at 50 psi for 20 min. A boiling solution of **12** (0.5 g, 1.76 mmol) in 100 mL of absolute ethanol was then added to this preconditioned catalyst and the hydrogenation was resumed at 65 °C. The colorless, oily residue obtained after removal of the catalyst by filtration followed by evaporation of the solvent in vacuo was chromatographed on alumina with hexane as eluent. The major product, 1,2,3,4-tetrahydroanthracene, was purified by two recrystallizations from ethanol; the colorless plates had: mp 98.5–99.0 °C [lit.[16] mp 103–105 °C]; NMR (CCl_4) δ 7.80 (m, 6 H, naphthyl), 3.05 (m, 4 H, C-1, C-4 protons), and 1.94 (m, 4 H, C-2, C-3 protons).

Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.81.

The picrate of 1,2,3,4-tetrahydroanthracene was prepared by refluxing an ethanolic solution of the compound with a saturated ethanolic solution of picric acid for 1 h. The solution deposited long reddish needles after being set aside several days at room temperature; mp 115–116 °C (lit.[16] mp 116–117 °C).

***tert*-Butyl 1,4-Dihydroanthracen-1,4-imine-11-carboxylate (13).** A slurry of 2-naphthalenediazonium 3-carboxylate (1.61 g, 8.13 mmol) in 125 mL of dry 1,4-dioxane was added in portions during 30 min to a refluxing solution of *tert*-butyl pyrrole-1-carboxylate (1.7 g, 10.2 mmol) in 50 mL of dry 1,4-dioxane. Reflux was maintained for 1 h after completion of the addition. The resulting deep red-orange solution was concentrated in vacuo to give a viscous red oil which partially crystallized. This residue was dissolved in 50 mL of boiling absolute methanol, treated with 2 g of activated charcoal, and filtered. The light brown filtrate was reduced in volume and the light tan crystals which separated (1.33 g, 56%) had mp 158–159 °C. This material on sublimation [130 °C (0.05 mm)] afforded 1.17 g of a white powder: mp 160.0–160.5 °C; IR (KBr) 3040, 2960, 2920, 1680, 1360, 1290, 1250, 1165, 1085, 870, and 825 cm^{-1}; NMR (acetone-d_6) δ 8.0 (m, 6 H, naphthyl), 7.35 (m, 2 H, olefinic), 5.88 (m, 2 H, bridgehead), and 1.40 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.78. Found: C, 77.88; H, 6.52; N, 4.73.

***tert*-Butyl 1,2,3,4-Tetrahydroanthracen-1,4-imine-11-carboxylate (14).** A sample of **13** (2.3 g, 7.8 mmol) was dissolved in 100 mL of absolute ethanol to which 0.1 g of 10% palladium–charcoal had been added. The mixture was shaken with hydrogen at 50 psi at room temperature for 2 h. The reaction mixture was filtered to remove catalyst and the filtrate was concentrated to yield 1.94 g (83.7%) of colorless crystals, mp 118–119 °C. Recrystallization from absolute methanol gave an analytical sample with melting point unchanged: NMR ($CDCl_3$) δ 8.1 (m, 6 H, naphthyl), 5.6 (m, 2 H, bridgehead), 2.4 (m, 2 H, exo protons), and 1.5 (m, 11 H, endo and *tert*-butyl protons).

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.43; H, 7.14; N, 4.68.

1,2,3,4-Tetrahydroanthracen-1,4-imine Hydrochloride. A solution of **14** (1.94 g, 6.62 mmol) in 75 mL of nitromethane was cooled to 5 °C in an ice bath and dry hydrogen chloride was bubbled into this stirred solution for 2 h. Addition of 100 mL of ether to the cold nitromethane solution precipitated 1.25 g (85%) of the hydrochloride as fine white crystals, mp 275–277 °C. Sublimation [165 °C (0.05 mm)] gave an analytical sample, mp 276–277 °C.

Anal. Calcd for $C_{14}H_{14}ClN$: C, 72.56; H, 6.09; Cl, 15.30; N, 6.04. Found: C, 72.52; H, 6.61; Cl, 15.12; N, 6.14.

1,2,3,4-Tetrahydroanthracen-1,4-imine (9). Addition of the hydrochloride of **9** (1.25 g, 5.41 mmol) to an excess of 10% aqueous potassium hydroxide followed by extraction with two 50-mL portions of ether gave, after drying over anhydrous magnesium sulfate and concentration of the solution, a white solid (1.02 g, 96%), mp 105–108 °C. Sublimation of this material [65 °C (0.02 mm)] gave white crystals: mp 108–109 °C; UV (95% ethanol) 319 (log ϵ 3.76), 3.06 (3.75), 284 (4.55), 274 (4.74), and 265 nm (4.71); IR (KBr) 3285, 3054, 3004, 2980, 2960, 2944, 2905, 2860, 1607, 1498, 1339, 1279, 1035, 906, 871, 848, 809, 745, 565, and 475 cm^{-1}; NMR (CCl_4) δ 7.50 (m, 6 H, naphthyl), 4.45 (m, 2 H, bridgehead), 2.30 (s, 1 H, NH, exchanges with D_2O), 1.90 (m, 2 H, C-2, C-3 exo protons), and 1.25 (m, 2 H, C-2, C-3 endo protons); mass spectrum *m/e* (rel intensity) 195 (5), 167 (100), 140 (13), 139 (14), 83.5 (18).

Anal. Calcd for $C_{14}H_{13}N$: C, 86.11, H, 6.71; N, 7.17. Found: C, 85.89; H, 6.81; N, 7.01.

Benz[*f*]isoindole (5). Compound **9** (200 mg, 1.03 mmol) was subjected to flash vacuum thermolysis in a quartz reactor tube at 600 °C (0.05 mm). The thermolysis required 10 min. The product was deposited as a cream-colored solid in essentially quantitative yield on a cold finger cooled by liquid nitrogen. The coproduct ethylene was removed by low temperature volatilization, effected by replacement of the liquid nitrogen coolant with dry ice–acetone while maintaining the low pressure. The olefin was characterized as its dibromide in the usual way.[5] The product, benz[*f*]isoindole, exhibited the following spectral data: UV (95% ethanol) 340, 324, 298, 288, 278, and 245 nm; UV (hexane) 337, 328, 322, 314, 298, 285, 275, and 265 nm; mass spectrum *m/e* (rel intensity) 167 (57), 166 (100), 153 (30), 140 (82), 139 (67), and 83.5 (60); NMR ($CDCl_3$, −40 °C) δ 8.70 (m, 1 H, C-3 proton) 8.10 (s, br, C-4, C-9 protons) 7.90 (m, C-5, C-8 protons) 7.50 (m, C-6, C-7 protons), and 4.95 (d, 2 H, C-1 protons).

***N*-Phenylmaleimide Adduct (8) of Benz[*f*]isoindole.** A 201-mg sample (1.03 mmol) of **9** was converted to **5** by the method described above. A solution of 200 mg (1.16 mmol) of *N*-phenylmaleimide in chloroform was added to the product on the cold finger, which was maintained at the temperature of liquid nitrogen. The reaction mixture was warmed sufficiently to permit its transfer to a flask and the mixture was kept at −10 °C for 48 h. The solvent was removed in vacuo and the resulting brown solid was chromatographed on silica gel, first with dichloromethane and then with chloroform as eluents. The product fraction yielded a tan solid (0.165 g, 47.2%), mp 220–238 °C dec. Recrystallization from absolute ethanol after treatment with activated charcoal gave 98 mg (28%) of colorless plates, mp 242–244 °C dec (lit.[4] mp 241.4–242 °C dec). A second recrystallization from hexane–benzene (1:1) provided an analytical sample: mp 243–244 °C dec; UV (95% ethanol) 325 (log ϵ 3.08), 310 (2.97), 286 (3.57), 275 (3.80), and 265 (3.87) nm; NMR (Me_2SO-d_6) δ 8.0–7.2 (m, 11 H, aromatic), 4.9 (s, 2 H, bridgehead), 3.9 (s, br, 1 H, NH, exchanges with D_2O), and 3.2 (s, 2 H, α to imide carbonyl).

Anal. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.42; H, 4.86; N, 8.09.

Registry No.—**5**, 268-49-5; **8**, 18009-78-4; **9**, 57833-62-2; **9** HCl, 67598-14-5; **11**, 67598-15-6; **12**, 57833-63-3; **13**, 67598-16-7; **14**, 67598-17-8; 2-naphthalenediazonium 3-carboxylate, 30013-85-5; 1-(phenylmethyl)pyrrole, 2051-97-0; 1,2,3,4-tetrahydroanthracene, 2141-42-6; *tert*-butyl pyrrole-1-carboxylate, 5176-27-2; *N*-phenylmaleimide, 941-69-5.

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Reactions of Acylaminoquinone Tosylhydrazones. 4.[1] A New Synthesis of Pyrrolo[1,2-*a*]indoloquinone and Related Compounds via Benzoxazoline by Thermolysis and Photolysis

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In our synthetic studies on mitomycin antibiotics, recently we reported that the thermolysis of acetylaminoquinone tosylhydrazones (**1**) gave the pyrrolo[1,2-*a*]indoloquinones and related compounds (**8**) in a one-step synthesis. These results suggested tentatively the existence of carbenes as the reaction intermediates. In this paper, however, we wish to describe the isolation of the unstable benzoxazoline intermediates (**5**) by the carefully controlled thermolysis and photolysis of **1** in good yields. Compounds **5** then turned into **8** via the dihydro compounds **7**. We also examined the solvent effects in the thermolysis and photolysis of **1**. This stepwise procedure via the benzoxazoline appears to be distinctly more versatile than the original procedure, which also afforded indazoloquinones and indazoles as the minor products, for the synthesis of pyrrolo[1,2-*a*]indoloquinones and related compounds.

During our course of synthetic studies on mitomycin antibiotics,[2] we have reported[3] that the thermolysis of acetylmono-**1a** and diaminoquinone tosylhydrazones **1d** gave the pyrrolo[1,2-*a*]indoloquinones **8a** and **8d**, respectively, both of which involve the parent skeleton of the mitomycins. Analogous products **8b,c,e,f** have also been obtained from the corresponding tosylhydrazones **1b,c,e,f** by the improved one-flask operation. These results suggested tentatively the

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