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(12) All melting points and boiling points are uncorrected. Ir spectra were recorded using a Perkin-Elmer Infracord using NaCl disks or KBr pellets. Nmr spectra were recorded on a Varian A-60 instrument and are reported as δ units (TMS = 0) in $CDCl_3$. Uv spectra were run using a Cary 14 recording spectrophotometer. The phrase "worked up in the usual way" means that an ether–benzene solution of the products was washed with dilute acid and/or base, with saturated NaCl solution. The ether–benzene solution was then filtered through a cone of $MgSO_4$ and the solvent was removed on a rotary evaporator.
(13) Used as obtained from the Chemical Samples Co., Columbus, Ohio.
(14) Obtained from the Aldrich Chemical Co., Milwaukee, Wis.
(15) If desired the crude product may be purified by distillation to yield 7 bp 90° (0.3 mm), in 95% yield. However, the yield of 8 is the same if the crude product is used.
(16) In a similar experiment at 125° a very low yield of adduct 7 was obtained.
(17) Venus 44-F, obtained from the U. S. Bronze Powders, Inc., Flemington, N. J. In a similar experiment in which the copper was omitted, the yield was 81%. Hence studies in which copper is replaced by other solids may be of interest.
(18) J. Meisenheimer, R. Haussen, and A. Wachterowitz, *J. Prakt. Chem.*, [2] **119**, 315 (1928).
(19) All analyses by Chemalytics, Inc., Tempe, Ariz.
(20) Methyltricaprylammonium chloride, obtained from General Mills Chemicals, Kankakee, Ill.
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Mechanistic Aspects of 2,3-Benzofulvene Formation from Sensitized Irradiation of 7-Azabenzonorbornadienes

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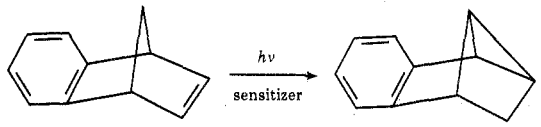
Received September 10, 1973

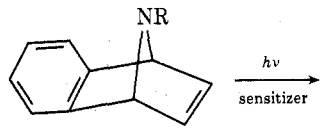
The singlet and triplet photochemistry of 7-*tert*-butoxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (**3c**) has been studied. While direct excitation of **3c** at 300 nm affords *tert*-butyl 3-benzazepine-3-carboxylate (**6c**) with low efficiency (Φ = 0.05), acetone-sensitized irradiation yields 5-*tert*-butoxycarbonyl-5-azatetracyclo[5.4.0.$0^{2,4}$.$0^{3,6}$]undeca-1(7),8,10-triene (**7c**) in high synthetic yield (93%) and with high efficiency (Φ = 0.93). The structure assignment for **7c** is supported by spectroscopic data and its hydrogenation and acid-catalyzed rearrangement reactions. The general mechanism for 2,3-benzofulvene formation from triplet-sensitized rearrangement of 7-azabenzonorbornadienes is discussed.

The photochemical rearrangement of various benzonorbornadiene derivatives to tetracyclic products *via* the di-π-methane reaction is well characterized (*i.e.*, 1 → 2).[2]

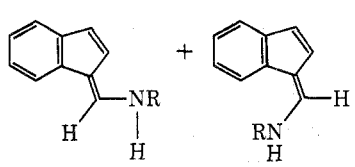


1 2

However, a photochemical study of the 7-aza derivative **3a** did not afford tetracyclic products analogous to **2**, but instead benzofulvene derivatives **4** and **5**.[3] We wish



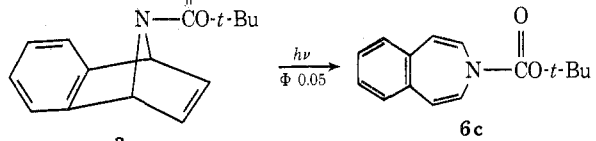
3a, R = CO_2CH_3
b, R = NTs
c, R = CO-*t*-Bu



4 5

to report here the details of the direct and photosensitized rearrangement of **3c** and the establishment of one mechanistic pathway for the production of benzofulvene derivatives from sensitized irradiation of 7-azabenzonorbornadienes.

Irradiation of 7-*tert*-Butoxycarbonyl-7-azabenzonorbornadiene (3c). Direct irradiation of **3c** in cyclohexane at low conversion produces *tert*-butyl 3-benzazepine-3-carboxylate in low quantum efficiency. However, acetone-sensitized irradiation of **3c** results in rapid loss of **3c** and the

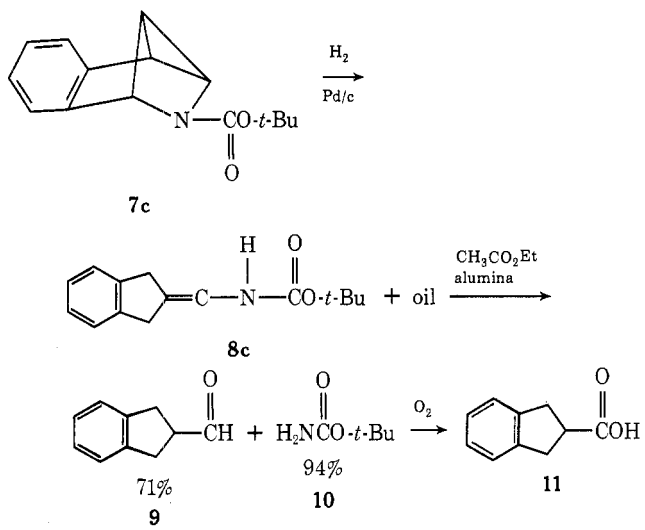


3c **6c**

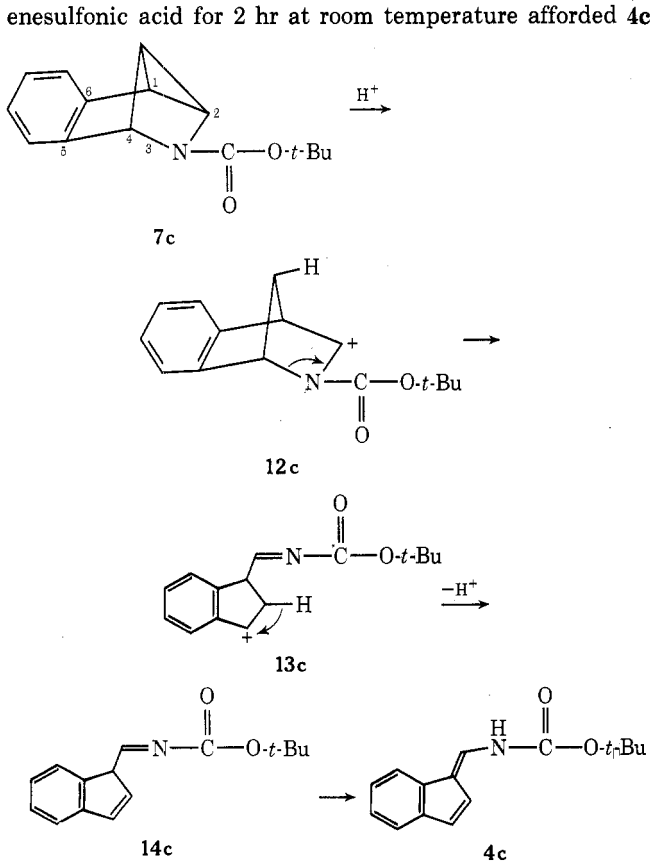
formation of an acid and thermally labile product. While initial attempts at isolation of this material were complicated by product decomposition during irradiation and attempted purification, by using base-washed apparatus and maintaining the temperature below 30° a colorless liquid could be isolated in 94% yield after chromatography on activity IV basic alumina. This material, which was isomeric with **3c**, showed a carbonyl absorption (5.85 μ) in the ir and exhibited four distinct one-proton signals in the nmr in addition to the aromatic and *tert*-butyl absorptions:[1d] τ 5.17 (1 H, d), 6.14 (1 H, distorted t), 6.60 (1 H, m), 7.43 (1 H, m). The absence of olefinic absorption in the adduct suggests a tetracyclic structure, for which **7c** seemed most reasonable. This structural assignment is further supported by its hydrogenation and acid-catalyzed rearrangement studies reported below.

Several attempts at clean partial hydrogenation of **7c** were made. The most successful of these employed atmospheric hydrogenation in ethyl acetate using 5% Pd/C as catalyst. The uptake of 1–1.5 equiv of hydrogen followed by work-up yielded 20–30% of an impure crystalline mate-

rial in addition to a yellow oil. The crystalline solid decomposed on attempted column chromatography on a variety of supports to *tert*-butyl carbamate and 2-formylindan; the latter compound underwent rapid air oxidation to 2-indancarboxylic acid. The structures of the *tert*-butyl carbamate and 2-indancarboxylic acid were rigorously established by comparison with synthesized authentic samples. Owing to the instability of this hydrogenation mixture, identification of the remaining products was not attempted. This sequence of reactions is outlined below.



In view of the acid sensitivity of the crude reaction mixture, the acid-catalyzed rearrangement of **7c** was also studied. Treatment of **7c** in ether with a trace of *p*-toluenesulfonic acid for 2 hr at room temperature afforded **4c**

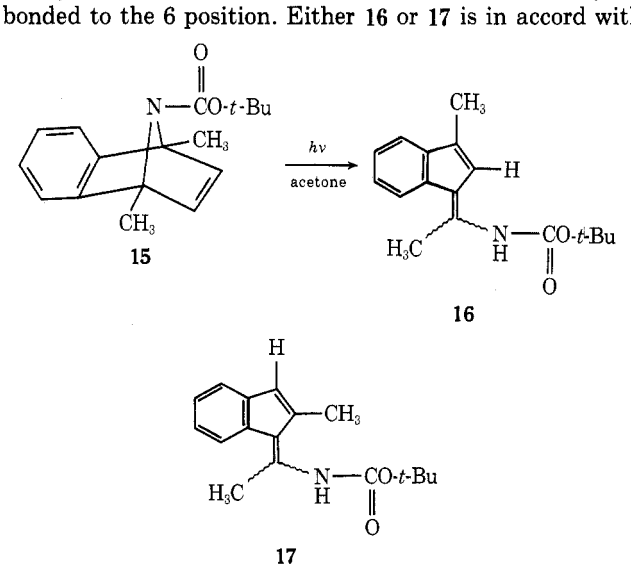


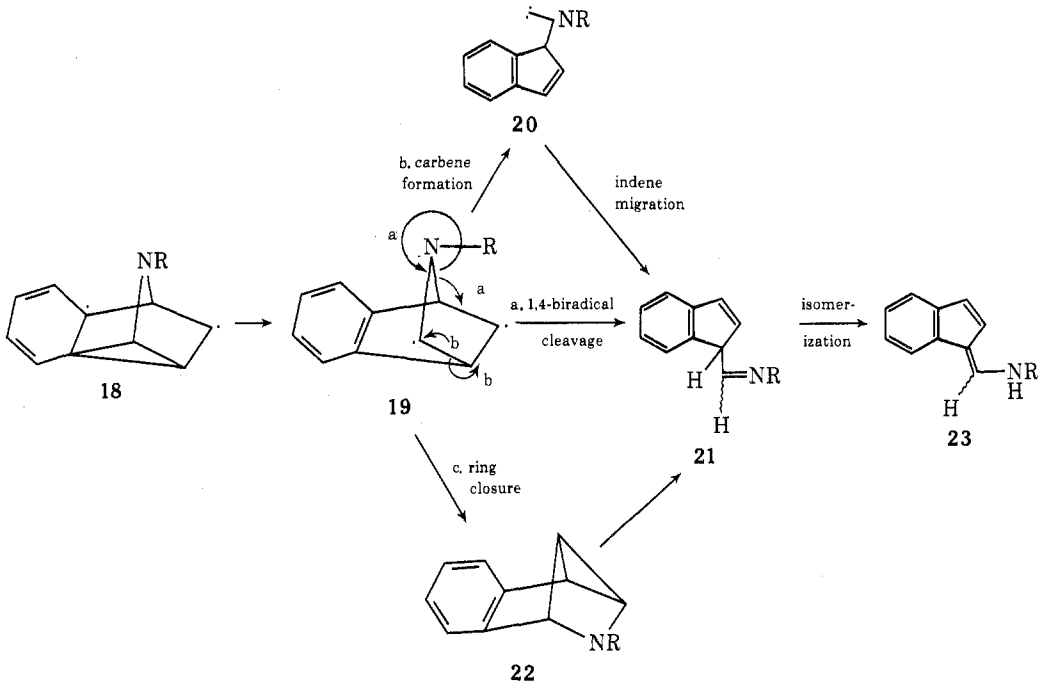
in 93% yield. The structural assignment for this product is supported by the similarity of its spectrscopic properties with those reported for the analogous heterocyclic systems.[3] Furthermore, it was established that **4c** was the major decomposition product in those irradiations in which precautions against temperature and fortuitous acid catalysis were not employed. The reaction course may be conveniently viewed as shown above.

Having established that the acetone-sensitized photolysis of **3c** proceeds in high yield to afford the product of di-π-methane rearrangement, it was of interest to measure the quantum efficiency of the **3c** → **7c** transformation for comparison with the parent hydrocarbon. Quantum-yield determinations at 3000 Å at ~20% conversion gave Φ = 0.93 ± 0.1. Thus, this nitrogen analog of the hydrocarbon rearranges with both high synthetic yield and high quantum efficiency.

Photosensitized Rearrangements of Other 7-Azabenzonorbornadienes. The marked contrast between the results noted here and the previous work of Prinzbach for **3a** and **3b** prompted us to reexamine the photosensitized chemistry of **3a**. Irradiation of 0.1% acetone solutions of **3a** under conditions analogous to those employed for **3c** was followed by nmr examination of the crude irradiation mixtures. No signals in the nmr spectrum attributable to the tetracyclic azetidine structure were observed; instead, the spectrum closely resembled those described for the respective benzofulvenes, **4a** and **5a**.

Surmising that the steric hindrance afforded by the *tert*-butoxycarbonyl group could be a necessary prerequisite for isolation of the tetracyclic azetidine structure, the photosensitized irradiation of readily available **15** was examined. This molecule not only would have afforded a second example of the rearrangement but also would have simplified the nmr spectrum of the azetidine, perhaps allowing specific assignment of the one-proton signals noted in **7c**. However, here too no tetracyclic azetidine could be isolated. In this case 12 different runs were made and analyzed by nmr. The crude nmr spectra of these irradiations were complex and not reproducible from run to run, suggesting the presence of unstable intermediate(s). However, the only compound which could be isolated pure was a yellow, crystalline solid (53%). The ir of this material showed NH absorption at 2.95 μ and carbonyl absorption at 5.85 μ, while the uv spectrum exhibited maxima at 230 nm (ϵ 9530), 280 (19,000), and 324 (13,600), characteristic of the 6-amino-2,3-benzofulvene moiety. The nmr showed the aromatic and NH absorption as a broad multiplet at τ 2.34–2.97, one vinyl proton as a multiplet centered at τ 3.50, one methyl group as a singlet at τ 7.43, a second methyl group as a broadened singlet at τ 7.82, and the *tert*-butyl group as a singlet at τ 8.46. The uv spectrum establishes the material as a 6-amino-2,3-benzofulvene, while the absence of olefin absorption below τ 4 and the methyl resonance at τ 7.43 indicate that one methyl is bonded to the 6 position. Either **16** or **17** is in accord with





this spectroscopic data. As **16** is most readily accommodated in the general mechanistic scheme of this reaction, the product from **15** is tentatively assigned as **16.**

Discussion

These studies demonstrate that photosensitized rearrangement of **3c** produces the strained tetracyclic azetidine, **7c,** in high yield and quantum efficiency. A remaining question is the mechanism of benzofulvene formation in structurally similar systems. Three different routes for benzofulvene formation, each deriving from a structural rearrangement of the hypothetical di-π-methane intermediate **19,** can be considered. For each mechanism an uncharacterized intermediate, **21,** is present which produces the benzofulvene by tautomerization.

Path a involves 1,4-biradical cleavage to afford **21,** a process well precedented in 1,4-biradical systems. Path b involves cleavage to form carbene **20** followed by indene migration yielding **21** and has some analogy from the recent work of Ipaktschi on the photochemistry of dibenzonorbornadienes.[4] Path c involves di-π-methane rearrangement of **18** to **22,** which undergoes thermal or acid-catalyzed rearrangement to **23.** This work has rigorously defined path c as of major importance for the **3c** → **4c** conversion, since the intermediate tetracyclic azetidine can be isolated and subjected to further rearrangement to afford **4c.**

Our unsuccessful efforts to characterize tetracyclic azetidines under mild conditions from **3a** and **15** are puzzling. Since we deem it unlikely that **3a** and **15** are undergoing excited-state processes fundamentally different from that of **3c,** the failure to isolate tetracyclic rearrangement products must be due to their instability. Whether the instability of these strained isomers is due to structural effects in the molecules or due to trace impurities which catalyzed decomposition is at present unknown.

Experimental Section

Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer. Uv spectra were determined with a Cary 14 recording spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer. Nmr spectra were measured at 60 MHz using TMS as internal standard. All elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All photolyses were carried out in an atmosphere of purified nitrogen.

7-*tert*-Butoxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (3c). This material was prepared by the procedure of Carpino and Barr, mp 74–75° (lit. mp 72–73°).[5]

Direct Irradiation of 7-*tert*-Butoxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (3c). The following is typical of several different irradiations performed (Table I). A stirred solution of 0.500 g (2.06 mmol) of **3c** in 70 ml of purified cyclohexane was irradiated for 90 min through quartz with a bank of 16 RPR-3000 Å lamps. After removal of the solvent from the yellow solution, the residue was chromatographed on silica gel (40 × 2.3 cm column slurry packed in 5% ether–hexane). Elution with 0.5 l. of 5% ether–hexane yielded 0.0257 g of a yellow, crystalline solid. Recrystallization of this material from methanol yielded *tert*-butyl 3-benzazepine-3-carboxylate (**6c**) as yellow needles: mp 95.5–97.0°; ir (KBr) 5.90 (s), 6.11 (w), 6.72 (w), 6.95 (w), 7.35 (m), 7.43 (s), 7.57 (s), 7.66 (m), 7.95 (s), 8.08 (m), 8.53 (m), 8.98 (m), 9.11 (w), 11.14 (s), 11.71 (w), 12.02 (w), 12.74 (s), 13.04 (m), and 13.30 μ (w); uv max (cyclohexane) 253 nm (ϵ 59,400) and 321 (1520); nmr (CCl_4) τ 3.29 (4 H, m), 3.94 (2 H, d, J = 10 Hz), 4.84, (2 H, d, J = 10 Hz), and 9.54 (s, 9 H).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.02; H, 7.01; N, 5.76. Found: C, 74.03; H, 7.25; N, 5.69.

Continued elution with 1.2 l. of 10% ether–hexane yielded 0.4616 g of recovered starting material as established by ir and nmr.

Triplet-Sensitized Irradiation of 7-*tert*-Butoxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (3c). A solution of 0.500 g (2.06 mmol) of **3c** in 150 ml of dried, purified acetone was irradiated for 0.5 hr with Corex-filtered light from a Hanovia 450-W medium-pressure source. In order to avoid acid-catalyzed rearrangement of the photoproduct, the photolysis cell and all glassware subsequently used in work-up were washed with dilute ammonium hydroxide and dried at *ca.* 70° for several hours. Removal of the solvent *in vacuo* below 30° yielded a light yellow oil, which was chromatographed on activity IV Woelm basic alumina (2.3 × 38 cm column, slurry packed in 2% ether–hexane). Elution proceeded as follows: 0.3 l., 2% ether–hexane, small amount of uncharacterized material; 1.3 l., 2% ether–hexane, 0.4669 g (1.93 mmol, 94%) of **7c** as a clear oil homogeneous by tlc [ir (CCl_4) 3.32 (w), 5.85 (s), 6.85 (w), 7.23 (w), 7.37 (s), 7.55 (s), 7.76 (m), 8.02 (w), 8.18 (w), 8.56 (m), 8.70 (w), 8.84 (s), 9.12 (w), 11.10 (w), 11.26 (w), 11.55 μ (w); nmr (calcium carbonate treated CCl_4) τ 2.60 (1 H, m), 2.88 (3 H, m), 5.17 (1 H, d), 6.14 (1 H, distorted t), 6.60 (1 H, m), 7.43 (1 H, distorted t), and 8.79 (9 H, s); mass spectrum *m/e* (rel intensity) 243 (parent, 7), 39 (33), 41 (90), 44 (60), 55 (15), 56 (37), 57 (100), 56 (16), 114 (15), 115 (80), 116 (88), 117 (19), 140 (11), 141 (18), 143 (80), 144 (14), 170 (12), 187 (35); exact mass measurement, theoretical, 243.1259; observed, 243.1244].

Hydrogenation of 5-*tert*-Butoxycarbonyl-5-azatetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (7c). In a 250-ml standard taper base-washed erlenmeyer flask with stopcocked side

Table I
Direct Irradiation of 3c in Cyclohexane

Starting material, g	Irradiation time, min	Recovered 4, g	5, g	Yield,[a] %
0.50[b,c]	90	0.477	0.011	47
0.50[b,d]	90	0.462	0.026	67
0.50[b,d]	180		0.028	

[a] Yield based on recovered starting material. [b] Irradiation was in 70 ml of cyclohexane with RPR-3000 Å source. [c] Pyrex vessel. [d] Quartz vessel.

arm inlet was placed 50 mg of 5% Pd/C, a magnetic stirring bar, and 50 ml of reagent-grade ethyl acetate. After equilibration of the catalyst with hydrogen, a solution of 0.50 g of **7c** in 50 ml of ethyl acetate was injected *via* syringe and hydrogen uptake followed. After 50 min, 1.1–1.5 equiv of hydrogen had been allowed to react and the uptake of hydrogen ceased. Filtration of the reaction mixture through Celite, followed by removal of the ethyl acetate *in vacuo*, gave a clear oil which was triturated with a few drops of cold hexane and filtered to give 0.116 g (0.473 mmol, 23%) of white solid 2-(*tert*-butylcarbamoyl)methyleneindan (**8c**). Purification of this material by recrystallization was difficult since the melting point of recrystallized material changed with time. A triply recrystallized sample from ethyl acetate–hexane gave plates with a melting point as high as 143.5–144.5°. This purest material, when allowed to stand, decreased in melting point with time. The compound hydrolyzed on all column supports (silica gel; neutral alumina, activities II and III; basic alimina, activities II–IV; PDEAS) to *tert*-butyl carbamate and 2-formylindan (*vide infra*) and, therefore, could not be purified by chromatography. The ir spectra of crude and recrystallized solid were identical; the nmr spectra differed only in minor extra absorption in the aromatic and τ 6.9–7.3 regions. The triply recrystallized material, mp 143.5–144.5°, showed ir (KBr, Perkin-Elmer 457) 2.87 (s) and 3.01 (m) (NH split by Fermi resonance), 3.38 (w), 5.88 (s, carbonyl), 6.56 (s, amide II band), 6.87 (w), 6.93 (w), 7.19 (w), 7.32 (m), 7.43 (m), 7.77 (w), 7.90 (m), 7.85 (m), 8.04 (m), 8.50 (m), 8.55 (m), 8.78 (w), 9.13 (w), 9.37 (w), 9.57 (w), 9.72 (w), 9.91 (s), 10.12 (w), 11.37 (w), 13.35 (m), and 14.33 μ (w); uv max (95% ethyl alcohol) 261 nm (ϵ 852), 267 (1270), and 273 (1360); mass spectrum *m/e* (rel intensity) 245 (P, <0.5), 39 (28), 41 (59), 43 (22), 44 (13), 51 (11), 56 (29), 59 (88), 62 (27), 63 (13), 65 (11), 91 (23), 115 (82), 116 (100), 117 (68), 127 (12), 128 (28), 129 (15), 131 (17), 145 (36), 146 (77). The compound was sublimed at 80° (1.5 mm) and exact mass measured: calculated, 245.1416; found, 245.1413.

The residual oil (0.394 g) from the hydrogenation showed ir and nmr spectra similar to those of **8c**. However, numerous attempts at purification of this material proved futile.

Hydrolysis of 2-(*tert*-Butylcarbamoyl)methyleneindan (8c). A 12.7-mg (0.052 mm) sample of recrystallized 2-(*tert*-butylcarbamoyl)methyleneindan was dissolved in 5 ml of ethyl acetate and stirred for 11 hr under nitrogen with a 0.50-g portion of Woelm alumina (neutral, activity III). An internal standard of 6.3 mg of acetophenone was added and the product mixture was analyzed quantitatively on a 15 ft × 0.125 in. column of 5% PDEAS on 60/80 mesh Chromosorb W at 90°. Results of this analysis showed the hydrolysis mixture to consist of 4.3 mg (0.037 mm, 71%) of *tert*-butyl carbamate and 7.3 mg (0.050 mmol, 96%) of 2-formylindan. Preparative gas-phase chromatography of the hydrolysis mixture on a 10 ft × 0.25 in. column of PDEAS on 60/80 Chromosorb W at 99° gave the highly volatile *tert*-butyl carbamate (38%), identical in melting point, vpc retention time, and ir with the authentic sample, and 59% of 2-formylindan: ir (neat) 3.27 (w), 3.40 (m), 3.49 (m), 3.66 (m, O=CH), 5.85 (s, C=O), 6.23 (w), 6.78 (m), 6.89 (m), 6.99 (m), 7.24 (w), 7.60 (w), 7.70 (w), 8.01 (w), 8.58 (w), 9.28 (w), 9.49 (w), 9.80 (w), 10.67 (w), 11.25 (w), 12.27 (w), 12.88 (w), and 13.40 μ (s). The 2-indanyl aldehyde rapidly air oxidized to crystalline 2-indancarboxylic acid, identical in melting point and ir with the authentic sample.

1-*tert*-Butoxycarbonylaminomethyleneindene (4c). A sample of **7c**, prepared from 0.500 g (2.06 mmol) of **3c** in the manner described above, was dissolved in 5 ml of anhydrous ether. After the addition of 2–3 mg of *p*-toluenesulfonic acid, the vessel was stoppered and the solution was stirred in the dark at ambient temperature for 2 hr. At this time the ether was evaporated and the yellow reaction residue was immediately impregnated on activity IV Woelm basic alumina (2.3 × 34 cm column, slurry packed in 2% ether–hexane). Elution proceeded as follows: 500 ml, small amount of unidentified oil; 125 ml, 30 mg of unidentified yellow solid; 125 ml, nil; 750 ml, 0.466 g (1.92 mm, 93%) of yellow solid 1-*tert*-butoxycarbonylaminomethyleneindene (**4c**) [mp (methanol, pale yellow needles) 152–153.5°; ir (KBr) 2.88 (w, NH), 3.21–3.37 (w), 5.76 (m, C=O), 6.07 (m), 6.73 (m), 6.98 (m), 7.24 (w), 7.36 (w), 7.81 (m), 8.17 (m), 8.76 (s), 9.04 (w), 9.30 (w), 9.48 (w), 10.06 (m), 10.90 (w), 11.07 (w), 11.53 (m), 11.68 (m), 12.74 (m), 13.05 (m), 13.19 (m), 13.52 (w), 13.78 (m), and 14.37 μ (w); uv max (CH_3CN) 233 nm (ϵ 5160), 272 (25,800), 279 (30,000), and 333 (20,500); nmr ($CDCl_3$) τ 2.17–2.53 (3 H, m), 2.57–2.94 (3 H, m), 3.13 (1 H, AB, J = 5.5 Hz), 3.27 (1 H, J = 5.5 Hz), and 8.48 (9 H, s); mass spectrum *m/e* (rel intensity) 243 (P, 29), 244 (P + 1, 4), 50 (3), 51 (2), 53 (1), 55 (12), 56 (21), 57 (100, B), 58 (4), 59 (42), 60 (1), 61 (1), 62 (4), 63 (6), 64 (2), 65 (1), 70 (4), 71 (2), 74 (2), 75 (2), 86 (2), 87 (3), 88 (4), 89 (2), 113 (5), 114 (32), 115 (29), 116 (28), 117 (1), 140 (9), 141 (12), 142 (3), 143 (53), 144 (5), 169 (74), 170 (9), 187 (68), and 188 (7)].

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.27; H, 7.22; N, 5.61.

Triplet-Sensitized Irradiation of 7-Methoxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (3a). The same procedure was employed as for the triplet-sensitized irradiation of **3c** except that 250-mg (1.25 mmol) samples of **3a** were irradiated in 150 ml of purified acetone in base-washed glassware from −10° to ambient temperatures. After removal of solvent *in vacuo* at approximately 0°, an ambient-temperature nmr of the photoproduct was taken in calcium carbonate treated carbon tetrachloride. In no case were the characteristic proton absorptions [τ 5.17 (1 H, d), 6.14 (1 H, distorted t), 6.60 (1 H, m), and 7.43 (1 H, distorted t)] of a polycyclic azetidine observed. Instead, complex nmr spectra with absorptions occurring in the regions reported for benzofulvenes were obtained.[3]

***tert*-Butyl 2,5-Dimethylpyrrole-1-carboxylate.** A procedure analogous to that used for the preparation of *tert*-butyl pyrrole-1-carboxylate[5] was employed with the following quantities of material: 23.8 g (0.25 mol) of 2,5-dimethylpyrrole, 7.8 g (0.201 mol) of potassium, and 28.8 g (0.201 mol) of *tert*-butyl azidoformate. After work-up, ether and tetrahydrofuran were removed by atmospheric distillation below 80° and 2,5-dimethylpyrrole was removed by short-path distillation between 66 and 82° (15 mm). The remaining dark liquid was chromatographed on 600 g of silica gel (5.8 × 50 cm colum, slurry packed in 1% ether–hexane). Elution proceeded as follows: 0.5 l., 1% ether–hexane, nil; 0.5 l., 1% ether–hexane, 0.630 mg of unidentified dark oil; 1.5 l., 1% ether–hexane, nil; and 4.5 l., 3% ether–hexane, 8.96 g (0.046 mol, 23%) of slightly yellow liquid *tert*-butyl 2,5-dimethylpyrrole-1-carboxylate (pure by nmr). Clear liquid *tert*-butyl 2,5-dimethylpyrrole-1-carboxylate can be obtained by distillation at 106–108° (15 mm) or 38–40° (1 mm): ir (NaCl plates) 3.37 (m), 5.76 (s, carbonyl), 7.25 (m), 7.37 (s), 7.56 (s), 7.68 (s), 8.04 (m), 8.57 (m), 8.97 (s), 11.77 (m), and 12.81 μ (m); nmr (CCl_4) τ 4.37 (2, H, s), 7.68 (6 H, s), and 8.47 (9 H, s).

Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.33; H, 8.72; N, 6.90.

7-*tert*-Butoxycarbonyl-2,3-benzo-1,4-dimethyl-7-azabicyclo-[2.2.1]hepta-2,5-diene (15). An analogous procedure was employed as for the preparation of **3c** using the following reagents: 8.61 g (44.2 mmol) of *tert*-butyl 2,5-dimethylpyrrole-1-carboxylate, 9.7 g (55.4 mmol) of *o*-fluorobromobenzene, and 1.5 g (62.5 mmol) of magnesium. After work-up and removal of tetrahydrofuran by atmospheric distillation, the remaining brownish liquid was distilled through a short-path apparatus, bp 88–90° (0.05 mm). This nearly pure (by nmr) orange distillate was impregnated on Woelm activity IV basic alumina (2.3 × 38 cm column, slurry packed in 2% ether–hexane) and eluted with 2% ether–hexane. Slightly orange 7-*tert*-butoxycarbonyl-2,3-benzo-1,4-dimethyl-7-azabicyclo[2.2.1]hepta-2,5-diene (**15**, 3.3 g, 12.2 mmol, 28%) was recovered: ir (NaCl plates) 5.86 (s, carbonyl), 6.91 (m), 7.28 (m), 7.35 (m), 7.59 (s), 7.92 (m), 8.03 (m), 8.59 (s), 9.40 (m), 12.86 (m), 13.40 (s), and 14.46 μ (m); nmr (CCl_4) τ 2.95 (4 H, symmetrical m), 3.42 (2 H, s), 7.94 (6 H, s), and 8.67 (9 H, s). Molecular distillation, bp 90° (0.05 mm), gave **15** as a colorless oil.

Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.40; H, 7.81; N, 5.37.

This compound turns orange on standing but still appears to be pure by nmr.

Triplet-Sensitized Irradiation of 7-*tert*-Butoxycarbonyl-2,3-benzo-1,4-dimethyl-7-azabicyclo[2.2.1]hepta-2,5-diene (15). The same procedure was employed as for the triplet-sensitized irradiation of **3c** except that 125–250-mg (0.55–1.10 mmol) samples of **15**

were irradiated in 150 ml of purified acetone in base-washed glassware from −10° to ambient temperatures. After removal of solvent *in vacuo* at approximately 0°, an ambient-temperature nmr of the photoproduct was taken in calcium carbonate treated carbon tetrachloride. Results were not reproducible but in no case were the characteristic proton absorptions [τ 5.17 (1 H, d), 6.14 (1 H, distorted t), 6.60 (1 H, m), and 7.43 (1 H, distorted t)] of a polycyclic azetidine **7c** observed. Some of the nmr spectra resembled those of fulvenes. One of the 250-mg (1.10 mmol) runs was chromatographed on Woelm activity IV basic alumina (2.3 × 33 cm column, slurry packed in 2% ether–hexane). Elution proceeded as follows: 1.0 l., 2% ether–hexane, small amount of unidentified yellow oil; 1.5 l., 5% ether–hexane, 0.134 g (0.59 mmol, 53%) of 1-*tert*-butoxycarbonylamino-1,4-dimethylmethyleneindene (16) [yellow plates, mp 97.5–98.5° (pentane–ether); ir (KBr) 2.95 (m, NH), 5.85 (s), 6.13 (s), 6.64 (s), 6.92 (m), 7.00 (m), 7.37 (m), 7.61 (m), 7.67 (m), 7.97 (m), 8.10 (s), 8.65 (s), 11.53 (m), 13.32 (s), and 13.56 μ (m); uv max (CH_3CN) 230 nm (ϵ 9530), 280 (19,100), and 324 (13,600); nmr (CCl_4) τ 2.34–2.97 (5 H, m), 3.50 (1 H, m), 7.43 (3 H, s), 7.82 (3 H, broad s), and 8.46 (9 H, s); mass spectrum *m/e* (rel intensity) 271 (18, P), 272 (4, P + 1), 51 (5), 55 (5), 56 (9), 57 (100, B), 59 (32), 77 (5), 115 (6), 127 (13), 128 (39), 129 (14), 130 (13), 153 (7), 154 (8), 155 (6), 156 (6), 170 (17), 171 (62), 172 (8), 182 (6), 197 (65), 198 (13), 215 (48), and 216 (6)].

Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.04; H, 7.76; N, 5.01.

Quantum Yield Measurements. These determinations were made in the previously described[6] two-compartment cell on magnetically stirred solutions under a nitrogen atmosphere using light from a Bausch and Lomb high-intensity grating monochrometer. The light intensity was measured immediately prior to and immediately following irradiation, and if these values differed by more than 10% the run was discarded.

Direct Irradiation of 3c. A solution of 0.50 g of carbamate in 65 ml of purified cyclohexane was irradiated at 300 nm and the analysis for formation of **5c** was made by uv analysis at 321 nm. The data below summarize the quantum yields measured at the indicated per cent conversion: Φ = 0.048 (0.26%), Φ = 0.065 (0.34%), Φ = 0.060 (0.60%), Φ = 0.057 (0.61%), Φ = 0.043 (0.85%), and Φ = 0.045 (0.91%).

Sensitized Irradiation of 3c. A solution of 0.243 g of **3c** in 65 ml of purified acetone was irradiated at 300 nm and 20.5 mg of benzalazine was added to the irradiated solution. After removal of solvent *in vacuo*, the residue was dissolved in sodium carbonate washed carbon tetrachloride for nmr analysis. The nmr spectra taken immediately after irradiation allowed calculation of the amount of **7c** formed by comparing the area of the benzalazine singlet (τ 1.48, 2 H) with the one-proton signals of the photoproduct at τ 5.17, 6.14, and 6.60. The results for two determinations were Φ = 0.95 and Φ = 0.91 at 16–17% conversion.

Registry No.—**3a**, 28035-70-3; **3c**, 5176-28-3; **4c**, 50585-27-8; **5c**, 50585-28-9; **6c**, 34813-08-6; **7c**, 34813-09-7; **8c**, 34813-10-0; **15**, 50585-34-7; **16**, 50585-35-8; 2-formylindan, 37414-44-1; *tert*-butyl 2,5-dimethylpyrrole-1-carboxylate, 50585-36-9; 2,5-dimethylpyrrole, 625-84-3; *tert*-butyl azidoformate, 1070-19-5; *o*-fluorobromobenzene, 1072-85-1.

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Stereochemical Course of Bromocyclizations of γ,δ-Unsaturated Alcohols. II.[1] Approaches to Various Oxaazabicyclooctane and -nonane Systems

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Received October 30, 1973

γ,δ-Unsaturated alcohols, *N*-methyl-2-hydroxymethyl-2-phenyl-4-pentenoic acid amide (**2**), 2-hydroxymethyl-2-phenyl-4-penten-1-ol (**6**), 3-hydroxymethyl-3-phenyl-5-hexen-1-ol (**10**), 3,3-diphenyl-1-methylamino-5-hexen-2-ol (**14d**), 1-chloro-3,3-diphenyl-5-hexen-2-ol (**14c**), and 3,3-diphenyl-1-methylamino-2-methyl-5-hexen-2-ol (**19**) were bromocyclized to the corresponding tetrahydrofurfuryl bromides (**3**, **7** and **8**, **11** and **12**, **15a**, **15c**, and **20** and **21**). The stereochemistry in each case was determined unambiguously by further intramolecular cyclization or lack of it to the corresponding oxaazabicyclooctanes (**4**, **5**, **16**, and **22**) and oxaazabicyclononane (**13**).

We have previously described the synthesis of several substituted tetrahydrofurfurylamines by bromocyclizations of corresponding γ,δ-unsaturated alcohols, followed by substitution of bromine with alkylamines.[1] The interesting pharmacological properties of some of these compounds coupled with simplicity of the synthetic approach have stimulated our additional investigation in this field with the aim to extend the synthesis to various bicyclic systems.

Results

The original attempt to synthesize 3-methyl-1-phenyl-6-oxa-3-azabicyclo[3.2.1]octane (**5**) was made *via* diethyl (allyl phenyl) malonate **1** (Chart I, R = OEt) which was selectively hydrolized to the monoacid **1a**. Sequential treatment of **1a** with thionyl chloride, methylamine, and $LiAlH_4$ afforded the amido alcohol **2** *via* acid chloride **1b** and amide **1c**, respectively.

Bromocyclization of **2** afforded stereoselectively *cis*-3-*N*-methylcarboxamido-3-phenyltetrahydrofurfuryl bromide (**3**).[2] Treatment of **3** with sodium hydride in DMF afforded 3-methyl-1-phenyl-6-oxa-3-azabicyclo[3.2.1]octan-2-one (**4**). The attempted reduction of **4** to **5** with $LiAlH_4$ was not successful, resulting in either unchanged starting material or the product of ring fission.

Another approach utilizing diol **6** was more fruitful. The bromocyclization of **6** was known to give a mixture[1] of two isomers which we have now separated by column chromatography. The ratio of cis isomer **8** to trans isomer **7** was found to be very close to 1:2. The stereochemistry was assigned on a basis of successful conversion of **8** *via* mesylate **8a** to the desired **5** upon treatment with methylamine.

In a similar approach, 4-methyl-1-phenyl-7-oxa-4-azabicyclo[4.2.1]nonane (**13**) was prepared (Chart I). Successive alkylation of ethyl phenylacetate by treatment with sodium hydride and chloroethyl vinyl ether, followed by sodi-