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THE DIRECT AND PHOTOSENSITIZED CHEMISTRY OF 7-t-BUTOXYCARBONYL-2,3-BENZO-7-BICYCLO[2.2.1]HEPTA-2,5-DIENE

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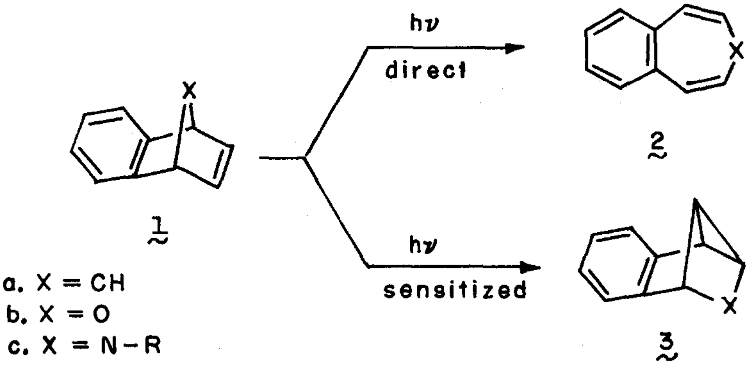
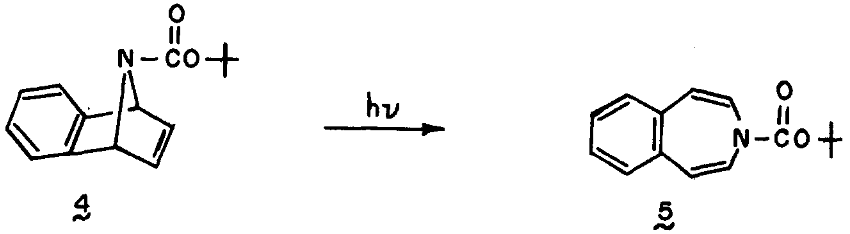
The photochemistry of the 2,3-benzobicyclo[2.2.1]hepta-5-ene ring system presents an interesting anomaly. While the parent hydrocarbon, 1a, showed an efficient triplet state reaction to yield the tetracyclic product, 3a, the singlet state reaction produces uncharacterized material.[2] In contrast, the 7-oxo analog, 1b, yielded benz[f]oxepin, 2b, under direct irradiation and formed dimers and polymeric material from sensitized reactions.[3] In spite of the negative results recorded in the sensitized reactions of 1b, we felt the potentially interesting chemistry associated with strained nitrogen bicyclics such as 3c warranted an examination of the 7-azabenzonorbornadiene system. We report here the singlet and triplet photochemistry of 7-t-butoxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene, 4.



The direct photolysis of 4 in cyclohexane with 300 nm light yielded after silica gel chromatography a yellow crystalline solid, mp 95.5-97.0°, which has been characterized as t-butyl-3-benzazepine-3-carboxylate, 5, on the basis of spectroscopic and analytical data.



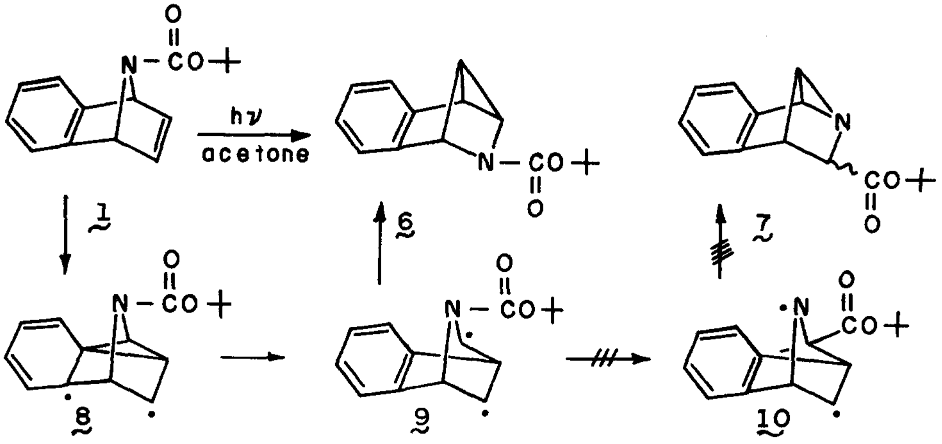
The most definitive evidence was afforded by the nmr (CCl_4) which showed the aromatic hydrogens as a multiplet centered at 3.29 τ, the vinyl hydrogens as an AB quartet centered at 4.38 τ (J = 10 Hz) and the t-butyl group as a sharp singlet at 8.54 τ. The results from several irradiations are listed in Table I.

Table I. Direct Irradiation of 4 in Cyclohexane

Starting Material	Irradiation Time (min.)	Recovered 4 (g)	5 (g)	Yield[a]
0.50 g[b,c]	90	0.477	0.011	47%
0.50 g[b,d]	90	0.462	0.026	67%
0.50 g[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.

In contrast to the direct irradiation, the acetone sensitized photolysis of 4 afforded after chromatography on activity IV basic alumina a 94% yield of clear oil homogeneous by



tlc. While the material was extremely heat and acid sensitive, it could be handled and stored conveniently below 30° in base-washed apparatus. The nmr spectrum in calcium carbonate treated carbon tetrachloride (Fig. 1) showed four one-proton multiplets in addition to aromatic and t-butyl absorptions. While the data was consistent with structure 6, the

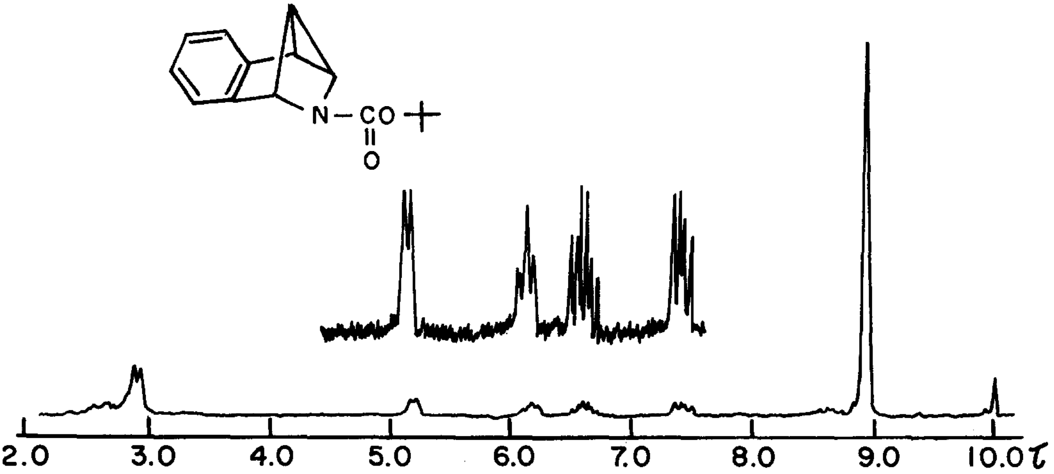
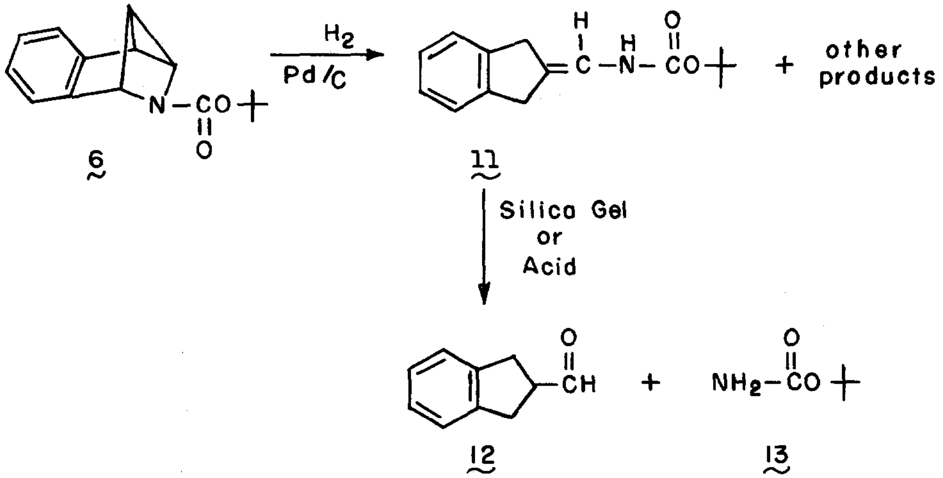


Figure 1.

spectroscopic properties did not exclude 7, a product arising from acyl migration in the proposed diradical intermediate, 9.[4] Thus, we sought experimental evidence for the carbamate structure, 6.

Hydrogenation of 6 in ethyl acetate using 5% Pd/C resulted in the uptake of 1-1.5 moles of hydrogen[5] and the formation of a white crystalline solid, mp 143.5-144.5°,[6] in addition to a mixture of unidentified oils. The crystalline isomer showed prominent ir absorptions (KBr) at 2.87, 3.01 (N-H split by Fermi resonance), 5.88 (carbonyl) and 6.56 μ (amide II band). The similarity of the UV spectrum of 11 with that of indane excluded any conjugated structures: [11 λ_{max} (95% EtOH) 261 (ϵ = 852), 267 (ϵ = 1270), and 273 (ϵ = 1360)]; indane 261 (ϵ = 850), 267 (ϵ = 1350), and 274 (ϵ = 1550). Further support for 11 came from its hydrolysis in 70%



yield on silica gel or alumina to 2-indanyl aldehyde and t-butylcarbamate.

Since the hydrogenation studies rule out acyl migration in the photolysis, the structure of the photoisomer was assigned as 6 on the basis of the analogous rearrangement of the benzonorbornadiene. In view of the accessibility of 4 and the high yield of its sensitized photolysis, 6 may prove a valuable intermediate in the synthesis of nitrogen bicyclics *via* cycloaddition processes. The rearrangement chemistry of 6 is under current study.

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References

1. (a) Ohio State University Fellow, 1969-70; (b) Ohio State University Undergraduate Research Scholar, 1968-69; (c) Alfred P. Sloan Fellow, 1971-1973.
2. (a) J. R. Edman, *J. Amer. Chem. Soc.*, **88**, 3454 (1966); (b) *ibid.*, **91**, 7103 (1969).
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4. For examples of facile ester migrations see: (a) D. M. Madigan and J. S. Swenton, *ibid.*, **92**, 7513 (1970); (b) M. J. Jorgenson and T. J. Clark, *ibid.*, **90**, 2188 (1968).
5. The amount of hydrogen uptake varied with the run and in each case the crystalline hydrogenation product was isolated in 20-30% yield.
6. The freshly crystallized (hexane-ethyl acetate) and sublimed material exhibited the sharp mp. Material which had been purified and allowed to stand decreased in mp with time.