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# DIRECT AND SENSITIZED PHOTOISOMERIZATIONS OF A DIAZABICYCLO[2.2.2]OCTENONE

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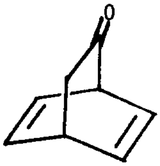
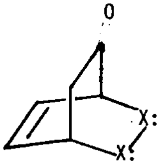
In recent papers we described the direct[2] and sensitized[3] irradiation of bicyclo[2.2.2]-octadienones of type 1. The predominant direct reaction (singlet state) was aromatization by elimination of a ketene. When the reaction was triplet sensitized, however, 1,2-acyl migration leading to a tricyclo[3.3.0.0$^{2,8}$]octenone (a semibullvalone[4]) was observed. It seemed worthwhile to study the effect on these reactions of replacing one of the C-C $\pi$-bonds in 1 by a $\sigma$-bond with non-bonding electrons on each atom, as in 2. In this paper we describe the photoisomerization of one such system.

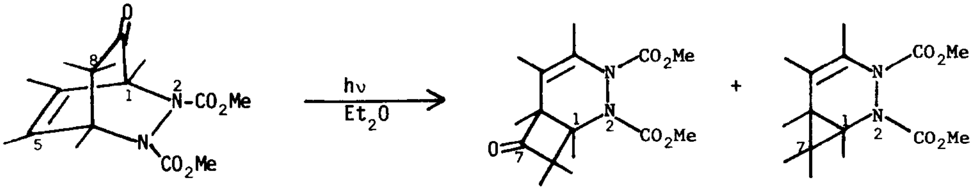


1



2

Direct irradiation[5] of a 1% ether solution of 3[6] ($\lambda_{max}^{95\%\ EtOH}$ 300 nm, $\epsilon$ 429; 210 nm, $\epsilon$ 6160) with a 450 watt Hanovia Type L mercury arc lamp through Pyrex or Corex gave only two products, whose relative yields depended on the irradiation time. The products were readily separated by preparative vpc (SE-30 column, 220°) and are assigned structures 4 (N, N'-dicarbomethoxy-1,4,5,6,8,8-hexamethyl-2,3-diazabicyclo[4.2.0]oct-4-en-7-one) and 5 (N, N'-dicarbomethoxy-1,4,5,6,7,7-hexamethyl-2,3-diazabicyclo[4.1.0]oct-4-ene). The ratio of 4/5 was initially high,

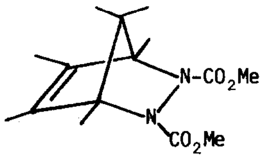


3 4 5

ranging from 4-13 depending on irradiation conditions. But the uv spectrum of 4 ($\lambda_{max}^{cyclohexane}$ 311 nm, ε 158; 210nm, ε 6425) showed that after appreciable amounts were formed from 3, it could effectively compete with 3 for the light. Prolonged irradiation of 3 or separate irradiation of 4 (1% ether solution, Pyrex) gave an essentially quantitative yield of 5; at no time during the latter photolysis could any 3 be detected in the reaction mixture.

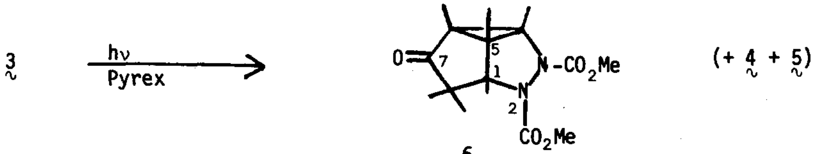
Structures 4 and 5 were assigned on the basis of spectroscopic and mechanistic criteria. Compound 4 was a white crystalline solid,[7] mp 122-125° (hexane) with carbonyl bands at 1772 (cyclobutanone[8]), 1739 and 1701 $cm^{-1}$. Its mass spectrum had a small parent peak at m/e 324.[9] The nmr spectra of molecules which contain the diurethane fragment $-N(CO_2Me)-N(CO_2Me)-$ can be quite complex due to the tendency for this moiety to lock in rigid conformations.[10] A detailed discussion of the nmr spectra of 4 and 5 is not possible here, but the gross features can be presented. When a range of chemical shifts is given, more than one peak is present in the spectrum, and the areas under the separate peaks are not necessarily equal. The nmr spectrum of 4 ($CDCl_3$) showed two adjacent allylic methyls (J=1.1 Hz) at τ 7.94 (C-4)[11] and 8.28 (C-5), four aliphatic methyls at τ 8.48-8.51 (C-1), 8.77-8.81 (6H) and 8.92 (3H), and two O-methyls at τ 6.18-6.22.

Compound 5 was an oil[7] with a parent peak at m/e 296 and only one carbonyl absorption, at 1724 $cm^{-1}$. The nmr spectrum ($CDCl_3$) had peaks for two adjacent allylic methyls (J=1.0 Hz) at τ 7.96 (C-4)[11] and 8.32 (C-5), aliphatic methyls at τ 8.52-8.57 (C-1), 9.00-9.07 (endo-C-7), 8.91-8.94 (6H) and two O-methyls at τ 6.20-6.26. This spectrum eliminates the alternative structure 5', which has a symmetry plane.[10] The uv spectrum (95% EtOH) of 5 had shoulders at 294 nm (ε 278) and 260 nm (ε 666) and a maximum at 218 nm (ε 9260).[12]



5'

Irradiation of 3 in acetone (1% solution) through Pyrex gave quite a different result. Although minor amounts of 4 and 5 were obtained, the major product (91%)[13] was a new crystalline compound,[7] mp 115.5-117°, assigned structure 6 (N,N'-dicarbomethoxy-1,4,5,6,8,8-hexamethyl-2,3-diazatricyclo[3.3.0.0$^{4,6}$]octan-7-one). Compound 6 had a parent peak at m/e 324 and one carbonyl absorption, at 1725 cm$^{-1}$. The uv spectrum (95% EtOH) showed only weak shoulders at 288 nm (ε 57), 248 nm (ε 649) and 230 nm (ε 1256) and a strong peak at 206 nm (ε 6240). The nmr spectrum ($CDCl_3$) had six singlets for aliphatic methyls, at τ 8.53, 8.41 (C-1 and C-4),[11] 8.88 (C-6), 8.77 (C-5) and 9.03, 9.12 (C-8) as well as a peak for two O-methyls at τ 6.32.



6

To determine whether 3 or 4 was the immediate precursor of 6, a 1% solution of 4 in acetone was irradiated through Pyrex. After 1 hour, 4 and 5 were present in nearly equal amounts, together with only a minor amount of 6 (and no 3). After 12.5 hours, only 5 (74%) and 6 (26%) were present.

Although our mechanistic conclusions can only be regarded as tentative pending a more quantitative study of these reactions, it seems highly probable that 3 is converted to 4 via the n,π* singlet state, and to 6 via the n,π* triplet state. The photoreactions of 4 are less clear; it readily loses carbon monoxide to form 5 (possibly via the triplet), and it probably is also converted to 3 (whence 6 may arise, on irradiation of 4 in acetone). The mechanistic details, as well as the potentially interesting ground state chemistry of 4 - 6, are being studied further.

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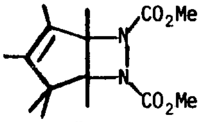
## REFERENCES

1. National Institutes of Health Predoctoral Fellow at Michigan State University, 1967-68.
2. R. K. Murray, Jr. and H. Hart, *Tetrahedron Letters*, 4995 (1968).
3. H. Hart and R. K. Murray, Jr., *Tetrahedron Letters*, 379 (1969).
4. A logical extention of the trivial name semibullvalene; for the initial proposal of this name, see H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966).
5. Controls for all irradiations described in this paper showed no dark reactions in 8-10 days.
6. For synthesis, see R. K. Murray, Jr. and H. Hart, preceding paper.
7. All compounds gave satisfactory C, H and N analyses.
8. See K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, Inc., San Francisco, 1962, p. 42.
9. The mass spectra of **3** - **6** contain many interesting features, which will be discussed elsewhere because of space limitations.
10. On an nmr time scale; see J. E. Anderson and J. M. Lehn, *Tetrahedron*, **24**, 123 (1968) and J. M. Lehn and J. Wagner, *ibid.*, **25**, 677 (1969).
11. Assignments are based on spectra of compounds obtained from **3** with deuterium label in the C-4 and C-6 methyl groups.
12. Structure **5"** cannot be rigorously excluded, for **5**, at this time. It could arise from a vinylcyclopropane → cyclopentene thermal rearrangement of **5**. This possibility is being investigated.



**5"**

13. The yield varies some with conditions. In general **4** is present only initially. Prolonged irradiations give only a mixture of **5** and **6**.