Thermal and Photochemical Rearrangements, and *X*-Ray Crystal Structure of a 2-Benzazocine Derivative

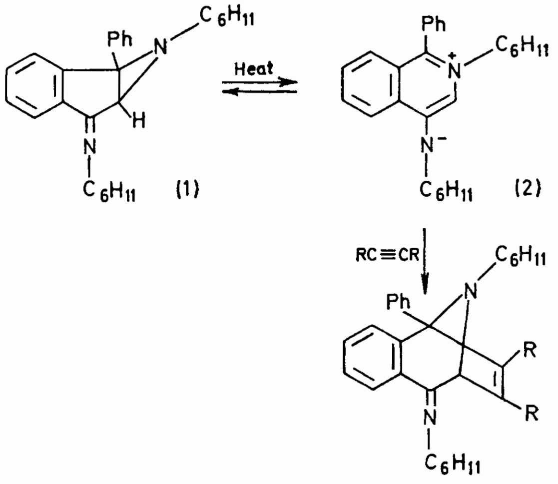
By Albert Padwa,* P. Sackman, Eli Shefter, and Eligio Vega
(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

Summary Dimethyl 8-oxo-1-phenyl-12-azatricyclo[7,2,1,$0^{2,7}$]dodeca-2(9),3,5,11-tetraene-10,11-dicarboxylate (**4**) at 115° in toluene undergoes a novel rearrangement to a benzazocine derivative (**5**) which undergoes further rearrangement on photolysis; the structure of (**5**) has been determined by *X*-ray crystallography.

The thermal and photochemical cleavage of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive C–C multiple bonds are well known.[1–5] Recently, Lown and Matsumoto reported on the thermal disallowed valence tautomerism of the aziridine (**1**) to the isoquinolinium imine (**2**) and subsequent trapping of the latter as an azomethine ylide in a series of 1,3-dipolar cycloadditions.[6] We have found that thermolysis of a mixture of (**1**) and dimethyl acetylenedicarboxylate followed by column chromatography (acid alumina) gave the related ketone (**4**).† This species, when heated in toluene, undergoes a novel rearrangement to the benzazocine (**5**), m.p. 189—191°, *m/e* 445 (M^+).‡

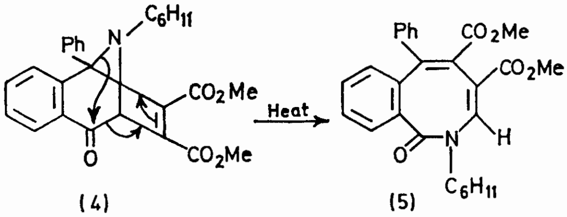
The structure of the rearranged product (**5**) was unequivocally proved by an *X*-ray single-crystal structure analysis. Three-dimensional intensity data were measured by the stationary-counter–stationary-crystal method, using Cu-K_α radiation and balanced filters (Ni *vs.* Co), on a GE XRD-6 diffractometer equipped with a single crystal orientator.

Crystal data: Monoclinic, $P2_1/c$. $a = 7{\cdot}855$, $b = 18{\cdot}816$, $c = 17{\cdot}629$ Å, $\beta = 115{\cdot}83°$. 1721 unique reflections ($2\theta = 0$—110°) out of a possible 2413 were considered observed. The structure was derived from Patterson and Fourier syntheses and refined by least squares to R 0·051 for all the data. The overall geometry of the molecule is shown in the Figure.



(1) (2) (3)

R = CO_2Me

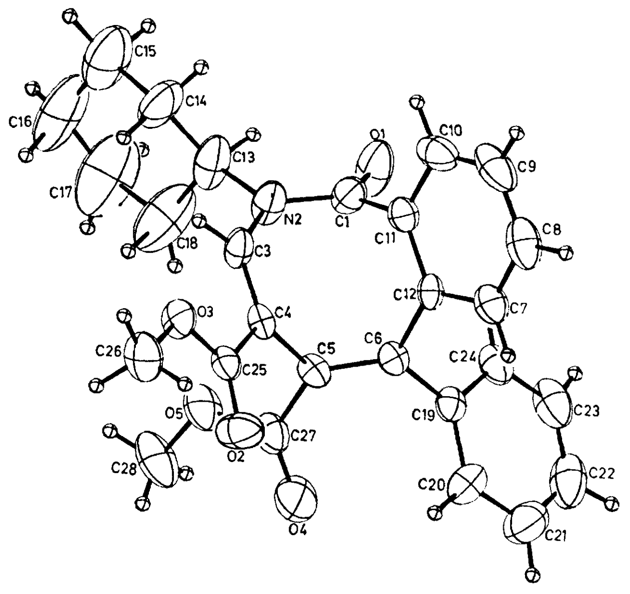


(4) (5)

---

† Ketone (**4**) could also be obtained by the mild acid hydrolysis of cycloadduct (**3**).

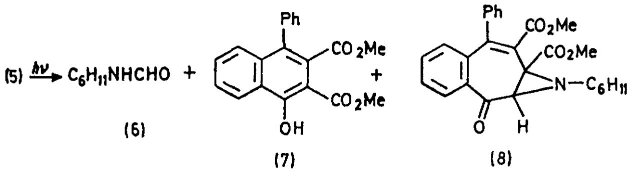
‡ All compounds had satisfactory elemental analyses. Complete spectroscopic and degradative details will be given later.

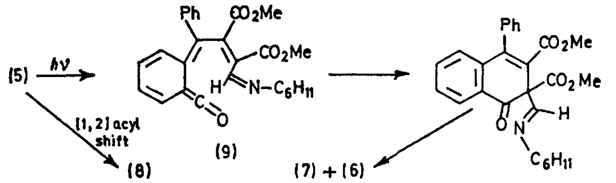


FIGURE

The rearranged adduct (**5**) also exhibits interesting photochemistry. Irradiation of a solution of (**5**) in benzene through a Corex filter for 4 h gave a mixture of (**6**) (14%), (**7**) (23%), and (**8**) (43%).

The structures of the photoproducts (**7**), m.p. 146—148° and (**8**), m.p. 154—156°) are based on their spectroscopic and analytical data.‡





The photochemistry of (**5**) may involve a photoinduced ring opening to ketene (**9**) followed by ring cyclization and hydrolysis (on workup) to (**6**) and (**7**). Aziridine (**8**) may be considered to be derived by a [1,2] shift of the acyl group. This latter process is reminiscent of the formation of substituted cyclopropanes from the irradiation of $\beta\gamma$-unsaturated ketones.[7]

We thank the National Institutes of Health and the Alfred P. Sloan Foundation for financial support.

(*Received, 5th April* 1972; *Com.* 548.)

---

[1] H. W. Heine and R. Peavy, *Tetrahedron Letters*, 1965, 3123; *J. Org. Chem.*, 1966, **31**, 3924; H. W. Heine, A. B. Smith, and J. D. Bower, *ibid.*, 1968, **33**, 1097; H. W. Heine and R. Henzel, *ibid.*, 1969, **34**, 171.

[2] A. Padwa and L. Hamilton, *Tetrahedron Letters*, 1965, 4364; *J. Heterocyclic Chem.*, 1967, **4**, 118; A. Padwa and W. Eisenhardt, *Chem. Comm.*, 1968, 380.

[3] R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, 1967, **89**, 1753; R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Letters*, 1966, 397; R. Huisgen, W. Scheer, and H. Mader, *Angew. Chem. Internat. Edn.*, 1969, **8**, 602; 1963, **2**, 633, 644; R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, 1967, **100**, 1802; J. H. Hall and R. Huisgen, *Chem. Comm.*, 1971, 1187, 1188.

[4] J. W. Lown, G. Dallas and T. W. Maloney, *Canad. J. Chem.*, 1969, **47**, 3557, 4335; *Chem. Comm.*, 1968, 1543; 1971, 247.

[5] P. B. Woller and N. H. Cromwell, *J. Heterocyclic Chem.*, 1968, **5**, 579; *J. Org. Chem.*, 1970, **35**, 888.

[6] J. W. Lown and K. Matsumoto, *Chem. Comm.*, 1970, 692; *J. Org. Chem.*, 1971, **36**, 1405.

[7] For leading references see D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, 1971, **93**, 4304.