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PROPELLANES—LXXV

A [2 + 2] PHOTOCYCLOADDITION OF AN N=N BOND TO A C=C BOND†

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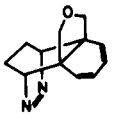
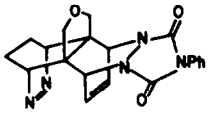
Abstract—Irradiation of an azo-propellane derivative in which an olefinic bond is proximate to the azo group forms a cage compound containing a 1,2-diazacyclobutane ring.

To the single case[1] in which an N=N double bond and a C=C double bond interact, forming a 1,2-diazacyclobutane ring by [2 + 2] photocycloaddition, were added several more of the same type.[2]

We have reported the preparation of the azo-propellane **1**.[3] We have now prepared it somewhat more efficiently at the urazole hydrolysis step. Treatment of **1** with 4-phenyl-1,2,4-triazoline-3,5-dione gave **2** in which the two double bonds are apparently even more proximate than in the cases cited above where a crystal structure shows a distance of 2.91 Å between the corresponding double bonds.[2] Irradiation of **2** at 350 nm indeed afforded the cage structure **3**, thus affording an example of such a photochemical cycloaddition in the propellane series.[4]



1



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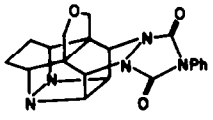

3

EXPERIMENTAL

Preparation of **1**. A modification of the published procedure[3] was used, from the same starting material (60 mg) and KOH (20 mg) in isopropanol (8 ml) heated under reflux in an N_2 atmosphere for 2.5 hr. After cooling, the solvent was removed at the water pump and the residue was diluted with water (10 ml). The whole was extracted with CH_2Cl_2 (5 × 15 ml). After drying ($MgSO_4$) and removal of solvent the residue was treated with cupric chloride (1.5 g) in water (10 ml). A brick red solid was immediately formed. The whole was stirred magnetically overnight and the solid was removed and washed with small amounts of water and ether. The cuprous chloride complex (49 mg; 94%) in CH_2Cl_2 (10 ml) was decomposed by adding cold conc ammonium hydroxide. The organic layer was separated and the blue aq solution was extracted with CH_2Cl_2 (3 × 15 ml). After drying ($MgSO_4$) of the combined organic extracts and removal of solvent at the water pump the diazo compound **1** (28.5 mg; 82%) was obtained.

Diels–Alder reaction of **1**. To a soln of **1** (20 mg) in CH_2Cl_2 (3 ml) was added a soln of PTAD (18 mg) in acetone (3 ml). The red color disappeared at once. After removal of the solvent the residue **2** (26 mg; 70%) had m.p. 225° (dec, acetone), from 262° N_2 evolves. Found: N, 18.62. $C_{20}H_{19}N_5O_3$ requires N, 18.56%.) UV($CHCl_3$): 380 nm(sh). IR($CHCl_3$): 765, 1705. NMR($CDCl_3$): δ 7.26 (s, 5 arom H); 6.16 (t', J' = 5 Hz, 2 vinylic); 5.06 (m, 2 allylic H); 4.63 (t', J' = 4 Hz, 2 methine); 4.33, 3.43 (ABq, J = 10 Hz, 4 CH_2O); 2.14–1.68 (m, 4 CH_2).

Irradiation. A soln of **2** (10 mg) in acetonitrile (80 ml) was irradiated for 6 hr (Rayonette; > 350 nm). After removal of solvent the cage **3** was obtained (quant) m.p. > 320° (dec begins at 227°). (Found: N, 18.54%. $C_{20}H_{19}N_5O_3$ requires 18.54%.) IR(KBr): 3010, 2995, 1770, 1715. NMR ($CDCl_3$): 7.45 (s, arom H); 4.62 (m, 4 CHN); 4.08 (m, 4 CHO); 3.05–2.84 (2 CH); 1.90 (m, 4 CH_2).

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[2]B. Albert, W. Berning, C. Burschka, S. Hünig, H.-D. Martin, and F. Prokschy, *Chem. Ber.* **114**, 423 (1981).
[3]M. Korat and D. Ginsburg, *Tetrahedron* **29**, 2373 (1973).
[4]We have been informed by Professor H. Prinzbach (Freiburg) that he was about to submit a manuscript for publication including similar work on the MTAD analog of **2**.

†Part LXXIV. P. Ashkenazi and D. Ginsburg, *Tetrahedron* **40**, 3329 (1984).