CHEMISTRY LETTERS, pp. 779-780, 1975. Published by the Chemical Society of Japan

WOLFF REARRANGEMENT OF 2-DIAZO-3,4-BIS(DIPHENYLMETHYLENE)CYCLOBUTANONE INTO 1,2-BIS(DIPHENYLMETHYLENE)CYCLOPROPANES

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Irradiation of 2-diazo-3,4-bis(diphenylmethylene)cyclobutanone (2) in the presence of alcohol and amine afforded 1-alkoxycarbonyl- and 1-carbamoyl-2,3-bis(diphenylmethylene)cyclopropane respectively.

Although the Wolff rearrangement of six- and five-membered cyclic diazoketones has been studied,[1] no such rearrangement of four-membered cyclic diazoketone has yet been reported. We now report the rearrangement of the title compound (2) into three-membered ketene (5) via ketocarbene (4).

The action of basic Al_2O_3 in $CHCl_3$ at 0°C on 1, which was prepared from 3,4-bis(diphenylmethylene)cyclobutanedione[2] and tosylhydrazine, afforded 2. When a solution of 2 in benzene containing MeOH, iso-PrOH, and aniline was irradiated at room temperature with a 100W high pressure Hg-lamp, 1-methoxycarbonyl-, 1-isopropoxycarbonyl-, and 1-phenylcarbamoyl-2,3-bis(diphenylmethylene)-cyclopropane (3a, 3b, and 3c) were obtained respectively. The structures of 1, 2, and 3 were elucidated on the basis of the spectral data (Table 1). The reaction presumably proceeds by a Wolff rearrangement of the initially produced ketocarbene (4) into 5.

However, Cu-catalyzed decomposition of 2 in MeOH afforded 2,3-bis(diphenylmethylene)4-methoxy-cyclobutan-1-one (6)[2] in 40% yield. This reaction can be interpreted by assuming a Cu-complex of 4 (i.e., ketocarbenoid) as an intermediate, because it is well established that ketocarbenoid undergoes a Wolff rearrangement with difficulty.[3]

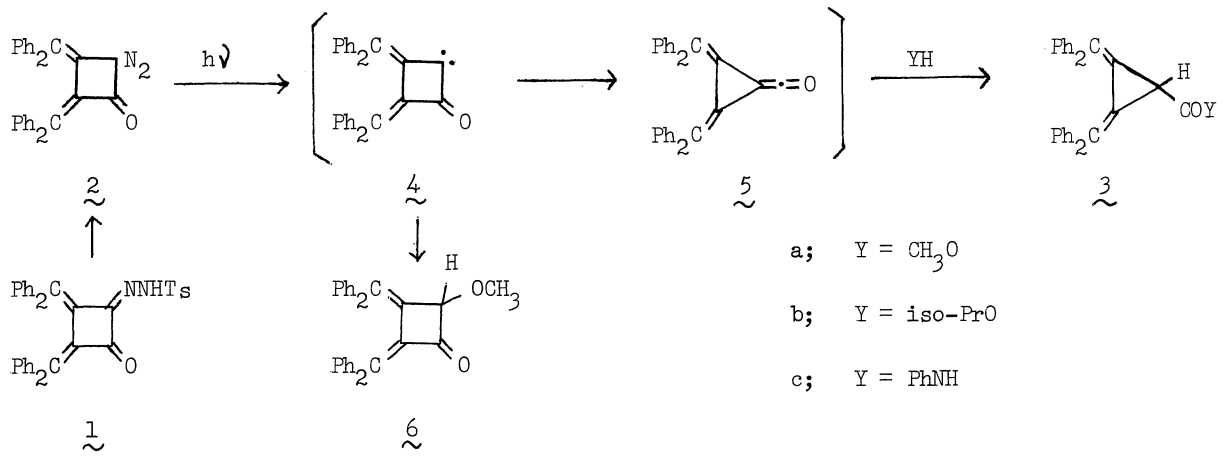

TABLE 1. Yields, Melting Points, and Spectral Data[4)]

Compound	Yield (%)	mp (°C)	$\nu^{Nujol}_{C=O}$ (cm^{-1})	$\lambda^{CHCl_3}_{max}$ nm ($\varepsilon \times 10^{-2}$)	τ_{CDCl_3}
1	quant.	145-146	1745	440 sh (84) 515 (101)	2.3-2.85 (m, 14), 2.9-3.4 (m, 10H) 7.63 (s, 3H)
2	87	123-124	1745	338 (61) 420 (51)	2.5-2.85 (m, 10H) 2.95-3.45 (m, 10H)
3a	75	158-159	1725	262 (282) 373 (360)	2.4-2.85 (m, 10H), 2.9-3.3 (m, 10H) 6.38 (s, 3H), 6.72 (s, 1H)
3b	58	161-162	1710	260 (297) 370 (361)	2.3-2.85 (m, 10H), 2.9-3.3 (m, 10H) 4.95 (Sep, 1H), 6.75 (s, 1H), 8.92 (d, 6H)
3c	45	171-172	1645	254 (332) 373 (339)	2.3-2.85 (m, 15H), 2.9-3.3 (m, 10H) 6.63 (s, 1H)

References

1) W. Kirmse, Carbene Chemistry, Academic Press, N. Y., 1971, P. 475.

2) F. Toda and K. Akagi, Tetrahedron, 27, 2801 (1971).

3) P. T. Lansburg and J. G. Calson, Chem. & Ind., (London), 1962, 821; M. Takebayashi, T. Ibata, H. Kohara and Bu. H. Kim, Bull. Chem. Soc., Japan, 40, 2392 (1967); M. Takabayashi, T. Ibata and K. Ueda, ibid., 43, 1500 (1970).

4) Satisfactory results of elemental analyses were obtained for all new compounds.

(Received June 6, 1975)