CHEMISTRY LETTERS, pp. 861-864, 1977. Published by the Chemical Society of Japan

CYCLOADDITION REACTION OF 8-ARYL-8-AZAHEPTAFULVENE TO ACETYLENEDICARBOXYLATE[1)]

Ken-ichi SANECHIKA, Shoji KAJIGAESHI, and Shuji KANEMASA*
Department of Industrial Chemistry, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube 755

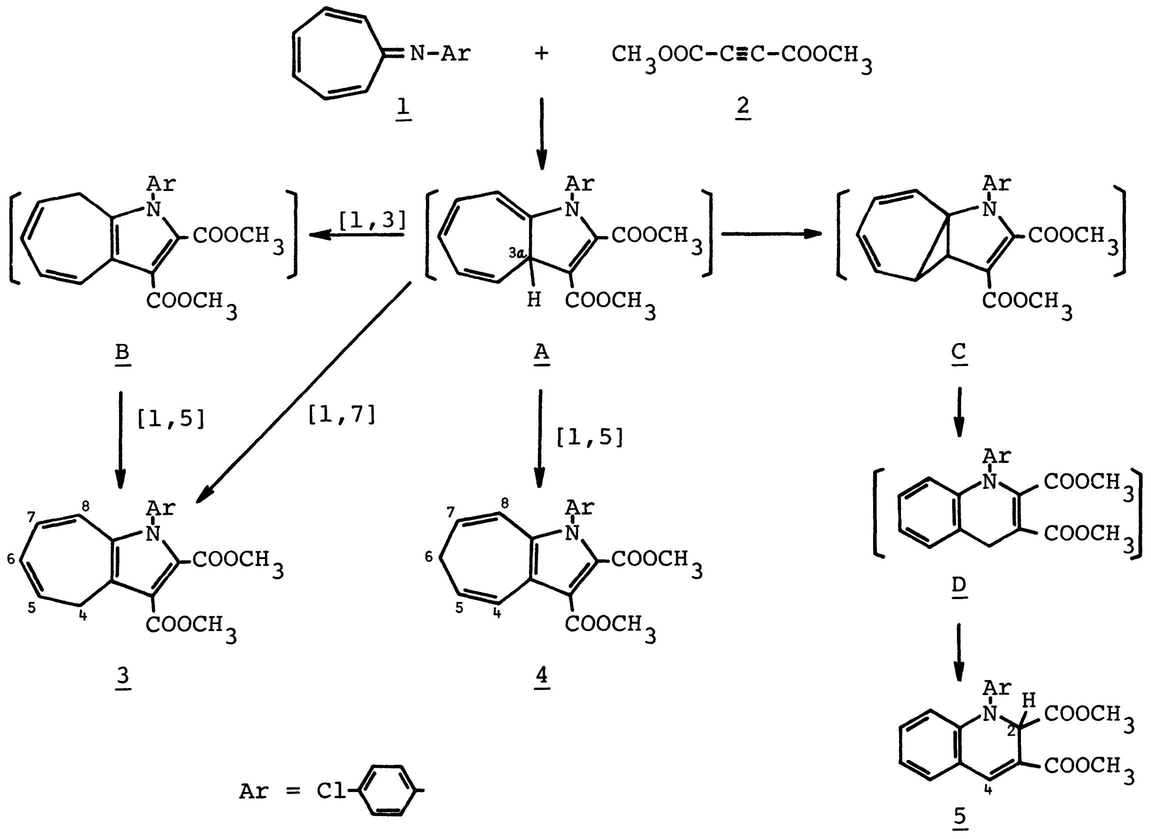
The [8+2] cycloaddition reaction of 8-aryl-8-azaheptafulvene to acetylenedicarboxylate, followed by hydrogen shifts or a rearrangement via intramolecular cyclic reaction, yielded 1,4-dihydro-1-azaazulene, 1,6-dihydro-1-azaazulene and 1,2-dihydroquinoline derivative. This reaction was extremely affected by the polarity of solvent.

The cross-conjugated system of 8-azaheptafulvene has been found to behave as an 8 pi electron addend in its cycloaddition reactions. Thus, 8-azaheptafulvene reacted with such heterocumulenes as isocyanate,2) isothiocyanate,2) ketene,3) and sulfene4) to give the corresponding [8+2] or [8+4] cycloadducts. The reactivity of 8-azaheptafulvene is incomparable to that of tropone which almost always gives the Diels-Alder cycloadducts with various types of addends.5) Rare examples of [8+2] cycloaddition reactions have been reported in some cases: the reactions of tropone with ketenes6) and of troponthione with maleic anhydride.7) Recently, Machiguchi et al.7) have reported that with dimethyl acetylenedicarboxylate troponthione affords thiachromene derivative which would be formed via norcaradiene intermediate from the original [8+2] cycloadduct.

The authors would like to cpmmunicate the reaction of 8-aryl-8-azaheptafulvene with acetylenedicarboxylate.

When a solution of 8-p-chlorophenyl-8-azaheptafulvene 1 and an equivalent amount of dimethyl acetylenedicarboxylate 2 in chloroform was heated at 40-50°C for 0.5 hr and then the reaction mixture was filtered through a short column packed with alumina using benzene as eluent, the mixture of three kinds of 1:1 adducts 3, 4, and 5 was obtained in a 55 : 20 : 25 ratio (73% yield), each of which was isolated by recrystallization.

The structures of 3 and 4 were determined to be 1,4-dihydro- and 1,6-dihydro-1-azaazulene derivative, respectively, on the basis of the following spectral data: 3: colorless prisms from MeOH, mp 119-121°C; IR (cm^{-1}) 1720 and 1705 (ester); PMR ($CDCl_3$, δ ppm) 3.24 (d, 2H, J_{4-5}= 6.0 Hz, 4-CH_2), 3.68, 3.91 (each s, 6H, OCH_3), 5.68 (dt, 1H, J_{5-6}= 10.0 Hz, 5-H), 6.02 (m, 1H, 6-H), and 6.20 (m, 2H, 7- and 8-H) as well as aromatic protons; Mass (m/e) 357 and 359 (M^+), and 4: colorless prisms from $CH_3COOC_2H_5$, mp 144-146°C; IR (cm^{-1}) 1735 and 1710 (ester); PMR ($CDCl_3$, δ ppm) 2.48 (t, 2H, J_{6-5}= J_{6-7}= 6.7 Hz, 6-CH_2), 3.70, 3.87 (each s, 6H, OCH_3), 5.36-5.65 (m, 2H, 5- and 7-H), 6.03 (d, 1H, J_{8-7}= 10.0 Hz, 8-H), and 6.97 (d, 1H, J_{4-5}= 10.0 Hz, 4-H) besides aromatic protons; Mass (m/e) 357 and 359 (M^+). The PMR spectrum measured just after 1 was treated with 2 in deuteriochloroform at - 10°C indicated that these two products were derived by a hydrogen shift from the initial [8+2] cycloadduct A of 1 to 2. The characteristic signals of A, which had appeared at 3.46 (m, 3a-H), 5.10 (dd, 4-H), and 5.50 (br. d, 8-H), gradually disappeared with the elapse of time and after 1 day at room temperature only the signals for 3, 4, and 5 were observed.



The third product 5, mp 121-122°C, whose solution in benzene showed a strong fluorecence, was assigned to be 1,2-dihydroquinoline derivative on the basis of the following spectral properties: pale yellow prisms from $CH_3COOC_2H_5$; IR (cm^{-1}) 1730 and 1710 (ester); PMR ($CDCl_3$, δ ppm) 3.73, 3.90 (each s, 6H, OCH_3), 5.56 (s, 1H, 2-H), 6.80-7.40 (m, 8H, aromatic protons), and 7.65 (s, 1H, 4-H); Mass (m/e) 357 and 359 (M^+). This compound 5 would be produced from the initial [8+2] cycloadduct A via the sequence of reactions which contained the intramolecular cyclic reaction of A to C, the subsequent ring enlargement to D, and the hydrogen shift to the final product 5. This type of rearrangement has been reported in the case of the reaction of troponthione with dimethyl acetylenedicarboxylate.[7)]

No [8+2] cycloadducts of 1 to heterocumulenes have undergone such a hydrogen shift and a ring rearrangement as mentioned above. The migration of hydrogen at 3a-position of the initial [8+2] cycloadduct A seemed to be driven by aromatization of its five-membered ring into pyrrole ring. The isomerization into 5 probably occured by the similar reason.

It was found that in the reaction of 1 with 2 the yields of products extremely depended upon the nature of the solvent as shown in Table 1. More polar solvents such as methanol and nitromethane gave 3 as major product, 4 as minor one, and no 5. On the other hand, the reaction in benzene afforded not 3 but 5 as major product and 4 as minor one.

Table 1. The Reaction of 1 with 2

Solvents	Reaction Conditions	Yields (%) of Products			
		Total	3	4	5
Methanol[a)]	40-50°C, 0.5 hr	80	75	25	+
Nitromethane[a)]	40-50°C, 0.5 hr	70	71	29	+
Chloroform[a)]	40-50°C, 0.5 hr	73	55	20	25
Chloroform	Room temp., 1 day	-	61	22	17
Benzene	Room temp., 4 days	76	0	31	69
Benzene	Reflux, 2 hrs	-	0	29	71

a) The [8+2] cycloadduct A isolated from the reaction of 1 with 2 at - 10°C was heated in the corresponding solvent.

The formation of 4 is rationalized by a thermally allowed [1,5] hydrogen shift, while the hydrogen migration into 3 would proceed through the mechanism via a more polar transition state. Two mechanisms are possible for the formation of 3: a [1,3] hydrogen migration of A to B followed by a [1,5] hydrogen shift, and a [1,7] hydrogen migration of A to 3. No detection of the intermediate B indicates that the major product 3 on the reaction in polar solvent would be formed by a [1,7] hydrogen migration of A. This kind of [1,7] hydrogen migration has been reported in the case of the [8+2] cycloadduct of heptafulvene to dimethyl acetylenedicarboxylate.8) Furthermore the ratio between 3 and 4 remained unchanged when the mixture of 3 and 4 was heated in benzene or chloroform for a long time. This result shows that 3 and 4 are inconvertible each other, and that 5 is unable to be derived from 3 and 4. The major product 5 on the reaction in nonpolar solvent was probably yielded through the mechanism via a nonpolar transition state.

REFERENCES

1. Part 9 of this series, "Azafulvenes". For Part 8, see reference 4.
2. K. Yamamoto, S. Kajigaeshi, and S. Kanemasa, Chem. Lett., 1977, 85.
3. K. Yamamoto, S. Kajigaeshi, and S. Kanemasa, Chem. Lett., 1977, 91.
4. T. Iwasaki, S. Kajigaeshi, and S. Kanemasa, Bull. Chem. Soc. Jpn., submitted.
5. Y. Kitahara, I. Murata, and T. Nitta, Tetrahedron Lett., 1967, 3303; S. Ito, H. Takeshita, Y. Shoji, Y. Toyooka, and T. Nozoe, Tetrahedron Lett., 1968, 3215; S. Ito, H. Takeshita, and Y. Shoji, Tetrahedron Lett., 1968, 1815; T. H. Kinstle and P. D. Carpenter, Tetrahedron Lett., 1968, 3943.
6. J. Ciabattoni and H. W. Anderson, Tetrahedron Lett., 1967, 3377; R. Gompper, A. Studeneer, and W. Elser, Tetrahedron Lett., 1968, 1019.
7. T. Machiguchi, M. Hoshino, S. Ebine, and Y. Kitahara, Chem. Commun., 1973, 196.
8. W. von E. Doering and D. W. Wiley, Tetrahedron, 11, 183(1960).

(Received June 2, 1977)