STUDIES OF POLYAZAPENTALENES. V.[1] THE CYCLOADDITION REACTION OF 8-METHYLDIBENZO[b,e]-1,3a,6a-TRIAZAPENTALENE WITH ASYMMETRICAL ACETYLENES

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Triazapentalene (I) reacted with asymmetrical acetylenes (II) to give the corresponding [3+2] cycloadducts as major products. It has been found that phenyl- and *p*-chlorophenylacetylene added to I in different directions, and that methyl phenylpropiolate gave two [3+2] cycloadducts.

Recently, we have found that dibenzo[b,e]-1,3a,6a-triazapentalenes[2,3] behave as azomethine imines in the cycloaddition to symmetrical acetylenes, and give the corresponding [3+2] cycloadducts as major products.[1] This is the first example of an azomethine imine extending over two rings. Consequently, we planned to investigate the scope of this new cycloaddition reaction and to study orientation phenomena of the cycloaddition. This paper deals with the cycloaddition reaction of 8-methyldibenzo[b,e]-1,3a,6a-triazapentalene (I) with asymmetrical acetylenes.

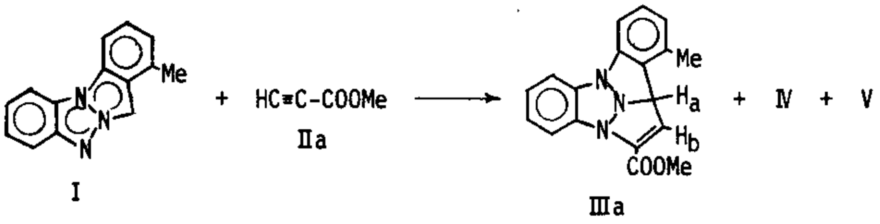
The reaction of I with methyl propiolate (IIa) afforded a 1:1 adduct (IIIa) (mp 159-160°C, yellow prisms) as a major product, together with another 1:1 adduct (IV) (mp 225-225.5°C, red plates) and/or 1:2 adduct (V) (mp 197-198°C, colorless prisms), depending on the nature of solvents (Table 1).[4]

Table 1. Reaction of I with IIa at 80°C for 24 h

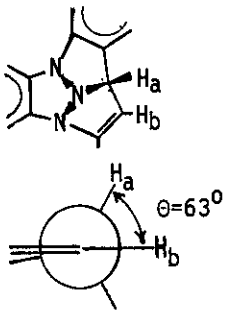
Solvent	Product, %		
	IIIa	IV	V
Benzene	53	0	1.5
EtOH	25	10	3
MeCN	27	13	0

By comparing its ir and uv spectra with those of the [3+2] cycloadduct[1] of I to dimethyl acetylenedicarboxylate, IIIa may be assigned as an expected [3+2] cycloadduct. The nmr spectrum of IIIa showed two doublets (each 1H, J=3 Hz) at δ 5.67 (H_a) and 6.28 (H_b), besides signals of two methyls and aromatic protons. The doublet at δ 6.28 did not appear and a singlet (1H) was observed at δ 5.67 in the spectrum of IIIa-d_1, prepared from I and methyl monodeuteriopropiolate (IIa-d_1). Thus, it is evident that the nitrogen atom of the azomethine imine moiety of I combines with α-carbon atom of IIa.

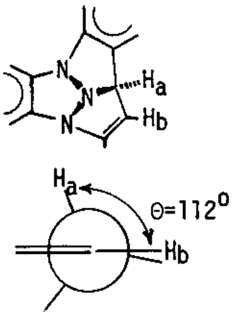
If a configurational inversion of the central nitrogen atom in IIIa does not occur, two configurations A and B are possible for the structure of IIIa: H_a in A is situated outside, while that in B is situated inside of the tricyclic ring

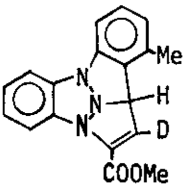


A



B

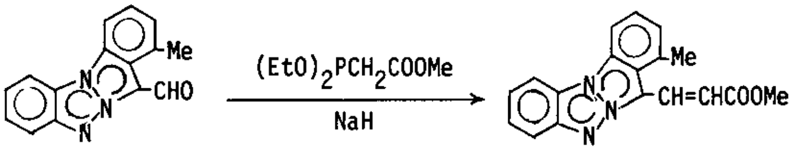




IIIa-d_1

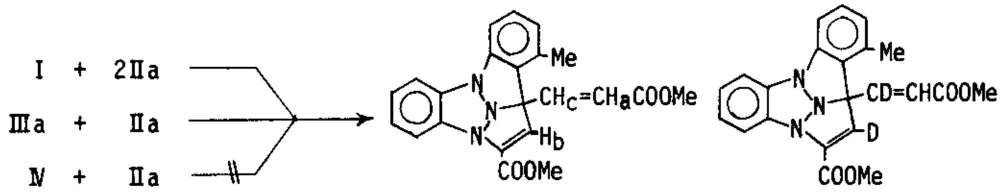
plane. An inspection of the Dreiding models indicates that the dihedral angle θ between H_a and H_b, is about 63° in A, while it is 112° in B. The calculated J_{ab} values are 3.6 and 9.1 Hz when θs are 63° and 112°, respectively.[5] The observed J_{ab} value (3 Hz) is compatible with the calculated value (3.6 Hz) when θ is 63°. Therefore, it may be concluded that configuration A is more reasonable than B for the structure of IIIa.

On the other hand, another 1:1 adduct (IV) has been determined to be a Michael-type adduct of IIa to the 7-position of I. It is identical with an authentic sample prepared from 7-formyltriazapentalene (VI)[6] and diethyl methoxycarbonylmethylphosphonate.



VI

IV



V

V-d_2

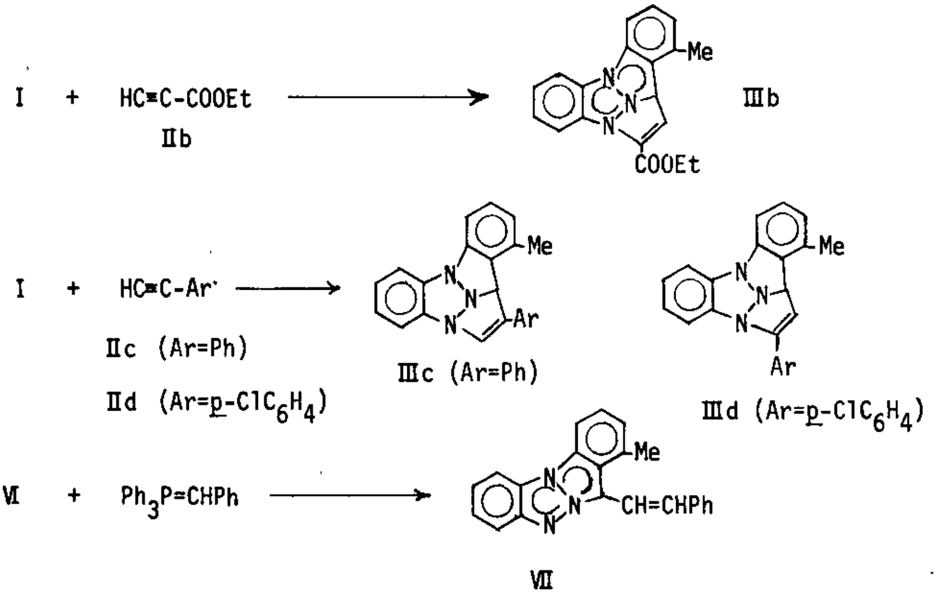
The reaction of I with two equivalents of IIa afforded a 1:2 adduct (V) quantitatively. The adduct V was also obtained by the reaction of IIIa with IIa, but not from IV and IIa. On the basis of these observations and of its spectral data, V was viewed as a Michael-type adduct of IIa to IIIa. The ir spectrum of V showed carbonyl bands at 1740 and 1710 cm^{-1}. The nmr spectrum exhibited three signals at δ 5.0 (H_a, d, J=15 Hz), 7.2 (H_b, s), and 7.67 (H_c, d, J=15 Hz), together with those of three methyls and aromatic protons. When irradiated at δ 5.0, the doublet (H_c) changes to a singlet. Furthermore, in the spectrum of V-d_2 prepared from I and two equivalents of IIa-d_1, the signals ascribable to H_b and

H_c did not appear, and only a singlet is exhibited at δ 5.0. The two ethylenic hydrogens H_a and H_c must be situated in <u>trans</u>-configuration on the basis of J_{ac} value of 15 Hz.

Similarly, I reacted with ethyl propiolate (IIb) to give a 70% yield of the expected [3+2] cycloadduct (IIIb) (mp 142-143°C, yellow prisms). Phenyl- (IIc) and p-chlorophenylacetylene (IId) added to I, affording the corresponding 1:1 adducts, IIIc (mp 273-275°C, yellow prisms) and IIId (mp 196-197°C, yellow prisms), in 30 and 45% yields, respectively.

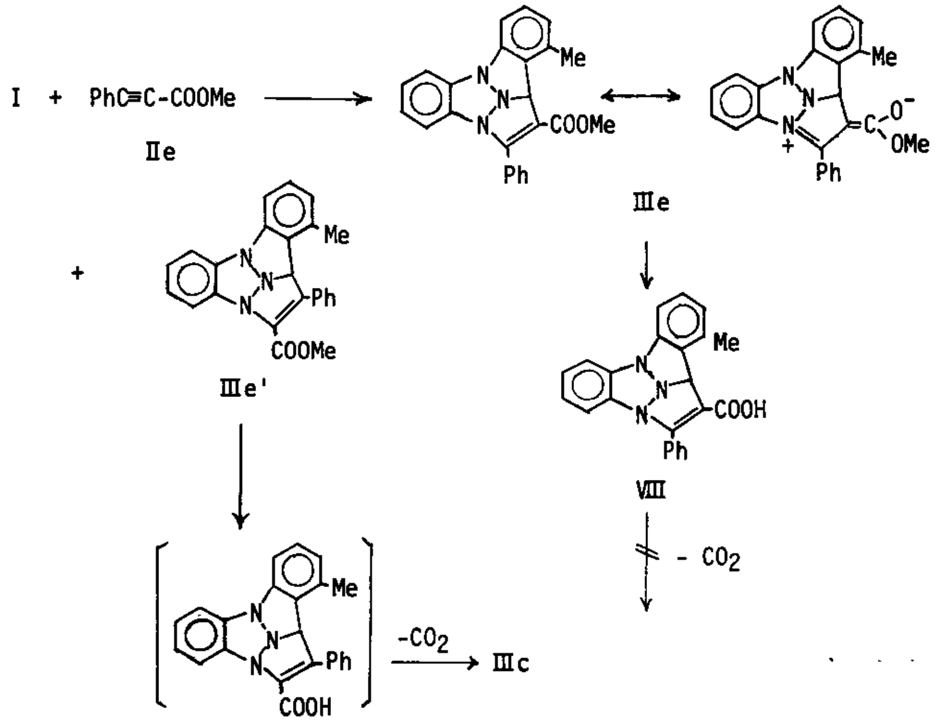
The ir spectrum of IIIc is quite similar to that of IIId. Comparison of the potential Michael-type adduct (VII) (mp 163-164°C, orange yellow needles), prepared by the Wittig reaction, showed it to be different from IIIc, thus indicating that IIIc and IIId are [3+2] cycloadducts. However, it is quite interesting to note that IIc and IId added to I in different directions: the β-carbon atom of IIc combines with the nitrogen atom of azomethine imine moiety of I, while in the case of IId, the reverse is true.

A singlet ascribable to one olefinic proton appeared at δ 5.65 in the nmr



spectrum of IIIc, together with multiplets of methine (1H) and aromatic protons (12H) at δ 6.9-8.3. On the other hand, the spectrum of IIId showed two doublets at δ 5.4 and 5.76 (each 1H, J=3 Hz), besides signals of aromatic protons, thus providing strong support for the assigned structures.

In the reaction of I with methyl phenylpropiolate (IIe), two cycloadducts, IIIe (mp 267-268°C, yellow needles) and IIIe' (mp 178-178.5°C, yellow prisms), were isolated in 21 and 16% yields, respectively. However, the relative amount of IIIe to IIIe' was determined to be 1:3 by nmr analysis of the reaction mixture. The ir spectra of both adducts are similar each other, but the νCO (1700 cm^{-1}) of IIIe appeared at a lower frequency than that (1740 cm^{-1}) of IIIe'. This can be rationalized by a significant contribution of the mesomeric form in IIIe as shown below.



When treated with an ethanolic potassium hydroxide solution under reflux, IIIe gave the corresponding carboxylic acid (VIII) (mp 179-180°C, νCO 1639 cm^{-1}) in 80%

yield, while under same conditions, IIIe' did not afford the carboxylic acid. Instead, IIIc which is the [3+2] cycloadduct of I to IIc, was obtained in 75% yield, evidently by hydrolysis and elimination of carbon dioxide from IIIe'. This fact clearly supports the assigned structure for IIIe'.

On the other hand, carboxylic acid (VIII) resisted all attempts of decarboxylation even when thermally treated with copper powder in quinoline. This would be due to similar resonance stabilization to IIIe.

Also, the nmr and mass spectra supported the assigned structures for IIIe and IIIe'. It has been found that the steric repulsion between methyl and phenyl groups in IIIe' is larger than that between methyl and methoxycarbonyl groups in IIIe from the study of nuclear Overhauser effect. This suggests that IIIe' is more puckered than IIIe.

REFERENCES

1 Presented in part at the 4th ICHC, Utah, July, 1973. Part IV of this series: O. Tsuge and H. Samura, Tetrahedron Letters, 1973, 597.

2 O. Tsuge and H. Samura, J. Heterocyclic Chem., 1971, **8**, 707.

3 O. Tsuge and H. Samura, Org. Prep. & Proced. Int., 1972, **4**, 273.

4 All compounds gave satisfactory analytical values, and the nmr spectra were measured in $CDCl_3$ by using TMS as an internal reference.

5 The calculated values of J_{ab} were obtained by the Carbish's equations: $J=6.6\cos^2\theta + 2.6\sin^2\theta$ ($0^o \leq \theta \leq 90^o$), $J=11.6\cos^2\theta + 2.6\sin^2\theta$ ($90^o \leq \theta \leq 180^o$) (E. W. Carbish, J. Amer. Chem. Soc., 1964, **86**, 5561).

6 O. Tsuge and H. Samura, Chem. Letters, 1973, 175.

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