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DIBENZO-1,3a,6a-TRIAZAPENTALENES AS NEW CYCLIC AZOMETHINE IMINES*

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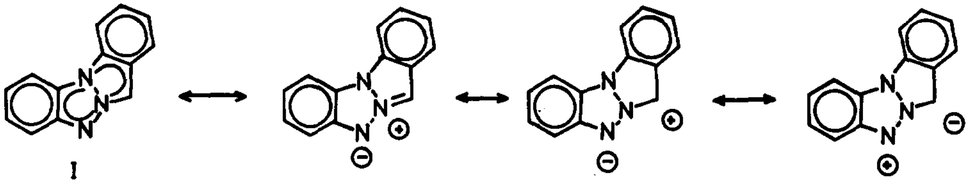
In previous papers we have reported on the preparation[1,2] and electrophilic substitution reactions[3] of a new aromatic azapentalene ring system, dibenzo-1,3a,6a-triazapentalenes. Dibenzo-1,3a,6a-triazapentalene (I) can be represented in terms of the following mesomeric forms which include azomethine imine structures.



I

According to HMO-calculations,[3] the signs at all positions in HOMO (highest occupaied molecular orbital) of I are as shown in Fig. 1, and indicate that I has apparently an azomethine imine moiety. Consequently, it was of interest to investigate the cycloaddition reaction of I in order to determine whether or not it would indeed behave as an azomethine imine. Since I is rather unstable and is only obtainable in poor yield,[1] we investigated the reaction of methyl derivatives of I. This paper deals with the reaction of 8-methyl- (IIa) and 7-methyldibenzo-1,3a,6a-triazapentalene (IIb)[2] with dimethyl (IIIa) and diethyl acetylenedicarboxylate (IIIb), and tolane (IIIc).[4]

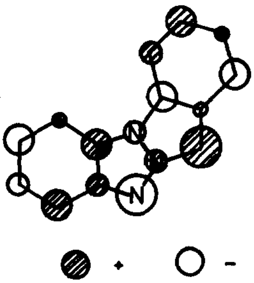


Fig. 1

The reaction of IIa with one equivalent of IIIa in CH_2Cl_2 at 30° for 24 hr afforded two isomeric 1:1 adducts, IVa and Va, in 32 and 1% yields, together with tarry materials. When a solution of IIa and IIIa in EtOH was refluxed in the presence of catalytic amounts of sulfuric acid for 24 hr, IVa and Va were obtained in 60 and 32% yields respectively. In the reaction of IIb with IIIa under similar acid catalytic conditions, however, a 1:1 adduct IVb was obtained in 90% yield and no product of type of Va was formed.

The structures of main products IVa (mp 197-199°, yellow prisms) and IVb (mp 149-150°, yellow prisms) were shown to be the corresponding (3+2) cycloadducts by their spectral data.

IVa. ν_{max}^{KBr} cm^{-1}: 1750, 1730 (sh). λ_{max}^{EtOH} nm (log ε): 237 (4.34), 269 (4.29), 300 (3.86), 395 (3.58). $\delta_{ppm}^{CDCl_3}$: 2.66 (3H, s, CH_3), 3.57, 3.99 (each 3H, s, OCH_3), 6.8 -7.7 (7H, m, aromatic protons), 8.7 (1H, s, >CH). Mass m/e: 363 (M^+).

IVb. ν_{max}^{KBr} cm^{-1}: 1755, 1710. λ_{max}^{EtOH} nm (log ε): 240 (3.80), 299 (3.50), 365 (3.47). $\delta_{ppm}^{CDCl_3}$: 1.96 (3H, s, CH_3), 3.75, 3.86 (each 3H, s, OCH_3), 6.7-7.8 (8H, m, aromatic protons). Mass m/e: 363 (M^+).

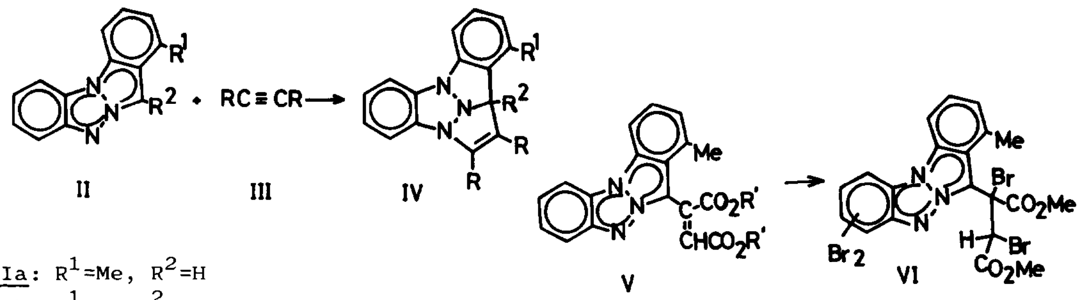
On the other hand, the minor product Va (mp 232-233°, dark violet needles) was assumed to be a Michael-adduct on the basis of the following spectral data. ν_{max}^{KBr} cm^{-1}: 1730 (sh), 1720. λ_{max}^{EtOH} nm (log ε): 241 (4.48), 260 (4.14), 350 (4.04), 365 (4.25), 382 (4.44), 500 (3.63). $\delta_{ppm}^{CDCl_3}$: 2.50 (3H, s, CH_3), 3.63, 3.83 (each, 3H, s, OCH_3), 7.1-8.0 (8H, m, olefinic and aromatic protons). Mass m/e: 363 (M^+).

The structure of Va was also supported by the fact that no product of type Va was formed in the reaction of IIb as mentioned above, and by the result of the bromination of Va. Bromination of Va in CH_2Cl_2 at 20° afforded tetrabromide VI (mp 225-226° dec, red needles) in 58% yield.

VI. ν_{max}^{KBr} cm^{-1}: 1735, 1723. $\lambda_{max}^{CH_2Cl_2}$ nm (log ε): 253 (4.19), 399 (4.12), 412 (4.01), 434 (3.59). $\delta_{ppm}^{CDCl_3}$: 2.05 (1H, s, >CH),(5) 2.60 (3H, s, CH_3), 3.80, 4.00 (each 3H, s, OCH_3), 7.3-8.0 (5H, m, aromatic protons). Mass m/e: 677, 679, 681, 683, 685 (M^+).

The above spectral data indicate clearly that two bromine molecules reacted with the olefinic bond and phenyl ring of Va. However, the positions of bromine substitution on phenyl ring(s) are not clear at the present stage.

Similarly, IIa reacted with IIIb (in benzene, 60°, 24 hr) to give the corresponding (3+2) cycloadduct IVc (mp 108-109°, yellow prisms) and Michael-adduct Vb (mp 165-166°, dark violet needles) in 23 and 2% yields, respectively.(6)



IIa: R^1=Me, R^2=H
IIb: R^1=H, R^2=Me

IIIa: R=CO_2Me
IIIb: R=CO_2Et
IIIc: R=Ph

IVa: R^1=Me, R^2=H, R=CO_2Me
IVb: R^1=H, R^2=Me, R=CO_2Me
IVc: R^1=Me, R^2=H, R=CO_2Et
IVd: R^1=Me, R^2=H, R=Ph

Va: R'=Me
Vb: R'=Et

The (3+2) cycloadduct IVd (mp 225-226°, yellow prisms, 18% yield) was the sole product of the reaction of IIa with IIIc in refluxing xylene.

IVc. ν_{max}^{KBr} cm^{-1}: 1760, 1740 (sh). λ_{max}^{EtOH} nm (log ε): 237.5 (4.36), 271 (4.28), 300 (3.95), 399 (3.59). $\delta_{ppm}^{CDCl_3}$: 0.98, 1.41 (each 3H, t, $-CH_2-C\underline{H}_3$), 2.56 (3H, s, $C\underline{H}_3$), 4.02, 4.48 (each 2H, q, $-C\underline{H}_2-CH_3$), 6.8-7.7 (7H, m, aromatic protons), 8.7 (1H, s, $\geq C\underline{H}$). Mass m/e: 391 (M^+).

IVd. λ_{max}^{EtOH} nm (log ε): 241 (4.45), 258 (4.39), 280 (4.26), 377 (3.58). $\delta_{ppm}^{CDCl_3}$: 2.41 (3H, s, $C\underline{H}_3$), 6.7-7.95 (17H, m, aromatic protons), 8.65 (1H, s, $\geq C\underline{H}$). Mass m/e: 399 (M^+).

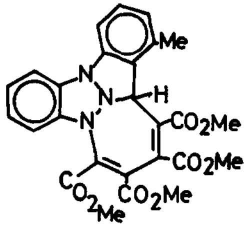
Vb. ν_{max}^{KBr} cm^{-1}: 1720, 1700 (sh). λ_{max}^{EtOH} nm (log ε): 241 (4.48), 262 (4.14), 350 (4.04), 365 (4.25), 384 (4.45), 508 (3.65). $\delta_{ppm}^{CDCl_3}$: 1.02, 1.22 (each 3H, t, $-CH_2-C\underline{H}_3$), 4.05, 4.30 (each 2H, q, $-C\underline{H}_2-CH_3$), 7.1-8.0 (8H, m, olefinic and aromatic protons). Mass m/e: 391 (M^+).

When a solution of IIa and two equivalents of IIIa in CH_2Cl_2 was refluxed for 12 hr, a 1:2 adduct VII (mp 179-180°, yellow prisms) was obtained in 60% yield. On the basis of the spectral data, VII was tentatively assigned as the diazepine derivative which corresponds to a formal (3+2+2) cycloadduct.

VII. ν_{max}^{KBr} cm^{-1}: 1760, 1730. λ_{max}^{EtOH} nm (log ε): 264 (3.82), 327 (3.25), 400 (2.95). $\delta_{ppm}^{CDCl_3}$: 2.35 (3H, s, $C\underline{H}_3$), 3.70, 3.88 (each 3H, s, $OC\underline{H}_3$), 3.77 (6H, s, $OC\underline{H}_3$), 6.11 (1H, s, $\geq C\underline{H}$), 6.5-7.8 (7H, m, aromatic protons). Mass m/e: 505 (M^+).

Thus, we found that dibenzo-1,3a,6a-triazapentalenes behave as a cyclic azo-

IIa + 2 IIIa ⟶

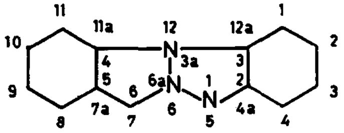


VII

methine imine. We are now investigating the reaction of II with other dipolarophiles and the results will be published in the near future.

References

* Studies of Polyazapentalenes. IV. Part III of this series: O. Tsuge and H. Samura, Chem. Lett., 1973, in press. Dibenzo-1,3a,6a-triazapentalene may be named as 5,7-dehydro-5H,7H-indazolo[1,2-a]benzotriazole or 5,7-dehydro-5H,7H-dibenzo[b,e]-1,3a,6a-triazapentalene. In this paper the triazapentalene nomenclature is employed and abbreviated as dibenzo-1,3a,6a-triazapentalene. The following numbering system has been adopted in this paper.



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1) O. Tsuge and H. Samura, J. Heterocyclic Chem., 8, 707 (1971).
2) O. Tsuge and H. Samura, Org. Prep. Procd. Int., 5 (1973), in press.
3) O. Tsuge and H. Samura, Chem. Lett., 1973, in press.
4) We have also tried the reaction of I with III and indeed obtained the expected adducts. However, they were extremely difficult to purify.
5) An inspection of the Dreiding models indicated that there is a steric interaction between 8-methyl group and the methoxycarbonyl group (or bromine atom) in VI, and that the methine hydrogen is suffered a significant shielding effect by the dibenzotriazapentalene ring in a favored configuration of VI.
6) An unidentified 1:1 adduct (mp 148°) was obtained in trace amounts. All new compounds in this paper gave satisfactory analyses.