CHEMISTRY LETTERS, pp. 621-622, 1980.

PHOTOCHEMICAL SYNTHESIS OF TRICYCLIC 1H-1,2-DIAZEPINES

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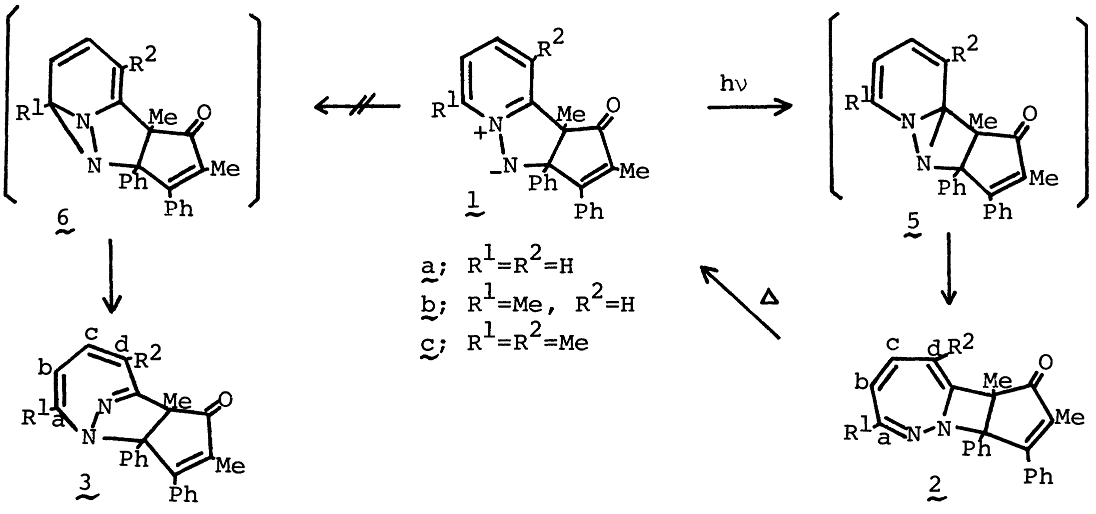
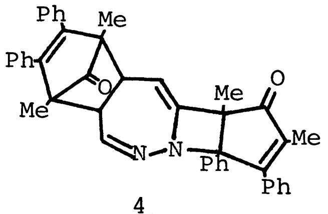
The photochemical reaction of tricyclic N-iminopyridinium ylides afforded 1H-1,2-diazepines containing novel structures by the selective electrocyclic ring closure followed by ring opening.

The photochemical reaction of N-iminopyridinium ylides to give 1H-1,2-diazepines has been extensively studied.[1] This reaction is sensitive to the substituent effects and the successful examples are limited to the ylides possessing an electron-withdrawning chromophore at the imino position[1,2] except for N-iminoquinolinium dimers.[3] Recently we reported the first example of the stable tricyclic N-iminopyridinium ylides possessing a non-conjugated substituent at the imino position.[4] As a part of detailed investigation of these novel ylides, we have examined their photochemical behaviors.

When a methanol solution of **1a** was irradiated with a 400W-high pressure mercury lamp under nitrogen atmosphere, tricyclic diazepine **2a** (mp 103-107°C, 62%) was obtained as the only isolable product.[5] The structure of **2a** was deduced on the basis of the spectroscopic data along with chemical evidence. **2a**; λmax (EtOH) 293 nm (logε=4.04), νmax (KBr) 1700 cm^{-1}, δppm ($CDCl_3$) 0.88 (s, 3H), 2.19 (s, 3H), 5.03 (dd, Hd, J=6.0, 1.5 Hz), 5.40 (ddd, Hb, J=11.0, 4.0, 1.5), 5.81 (dd, Hc, J=11.0, 6.0), 6.15 (d, Ha, J=4.0), 6.9-7.5 (m, 10H). The fact that the coupling constant J_{bc} is distinctly larger than J_{ab} and J_{cd} is inconsistent with the structure **3a**,



but can be reasonably accomodated by the structure 2a. Reaction of 2a with 2,5-dimethyl-3,4-diphenylcyclopentadienone in refluxing toluene produced a 1:1 adduct 4 (mp 193-194°C, 40%).[6] On the other hand, heating of 2a in chloroform at 120°C in a sealed tube for 1 h afforded the starting ylide 1a in 80% yield. Irradiation of 1b and 1c under the same conditions as that of 1a also afforded the diazepines 2b (mp 201-205°C, 18%) and 2c (oil, ca 10%), respectively, although the reactions are slower and the yields are worse than that of 1a.[7] The formation of the diazepines 2 can be explained by ring opening from the assumed primary photoproducts 5 formed by the selective electrocyclic ring closure of the pyridinium ylides. The selectivity observed here is different from the reported examples in which the ring closure on the less hindered α-carbon is favored.[1] This may be attributed to the fused five-membered ring which causes the difference of the bond length of the diaziridine ring formed in the electrocyclic ring closure and may also affect the ring opening.



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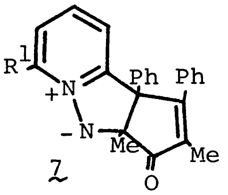
2. V. Snieckus and G. Kan, Chem. Commun.. 172 (1970).
3. T. Tsuchiya, J. Kurita, H. Igeta, and V. Snieckus, ibid., 640 (1974).
4. Y. Yamashita and M. Masumura, Tetrahedron Lett., 1979, 1765 . The possibility of the ylide 7, the corresponding regioisomers of the ylide 1, instead of 1 could be denied by the inspection of the mass fragmentation pattern in addition to the reported reason, because the fragments due to loss of benzonitrile were observed as follows.

   1a; m/e 352 (50%, M^+), 208 (100%),
   105 (51%, 8a-PhCN), 104 (44%).
   1b; m/e 366 (48%, M^+), 222 (100%),
   119 (27%, 8b-PhCN), 118 (34%).



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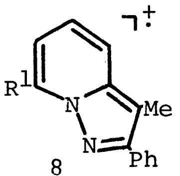

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8a; R^1=H m/e=208
8b; R^1=Me m/e=222

5. Satisfactory elemental analyses were obtained for all new compounds reported in this paper.
6. 4; νmax (KBr) 1705, 1780 cm^{-1}, δppm ($CDCl_3$) 1.10 (s, 3H), 1.28 (s, 3H), 1.49 (s, 3H), 1.75 (s, 3H), 3.04 (brs, 2H), 5.10 (brs, 1H), 6.4-7.3 (m, 19H), 7.5-7.7 (m, 2H). A 1H-1,2-diazepine is known to react with 2,5-dimethyl-3,4-diphenylcyclopentadienone; T. Mukai, Y. Yamashita, H. Sukawa, and T. Tezuka, Chem. Lett., 1975, 423 .
7. The yields of the diazepines 2 were obtained when the ylides disappeared, and no other products except the diazepines could be isolated.

(Received February 20, 1980)