Photochemical Isomerisation of Dimethyl 1,2-dihydropyridazine-1,2-dicarboxylate

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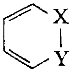
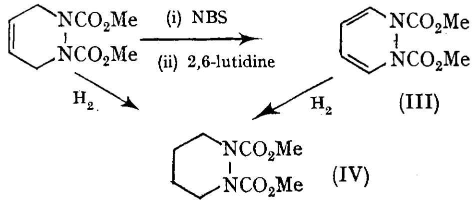
PHOTOCHEMICAL valence isomerisations of cyclohexa-1,3-dienes are of interest as a pathway to hexa-1,3,5-trienes and bicyclo[2,2,0]hexenes.[1] We are investigating the photochemistry of 1,2-heterosubstituted cyclohexadienes (I) in order to determine the effect of the heteroatoms on the product distribution. This system is of special interest because one of the expected products, the bicyclo[2,2,0]hexene (II) might provide an approach to free cyclobutadiene.



(I)

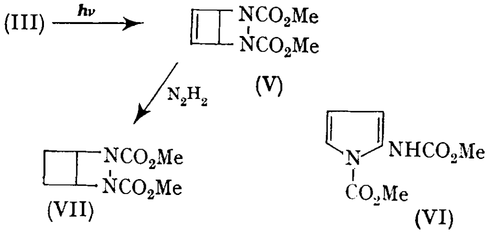
(II)

We report here our observations on the photochemical transformations of dimethyl 1,2-dihydropyridazine-1,2-dicarboxylate (III)[2] which was obtained from dimethyl 1,2,3,6-tetrahydropyridazine-1,2-dicarboxylate[3] in 81% yield *via* allylic bromination followed by dehydrobromination.[4]



The proof of structure (III)† follows from its spectral properties‡: n.m.r. 6H (CO_2CH_3) singlet 3·81 δ, 4H vinyl AA′XX′ multiplet, $\nu_A = 5{\cdot}71\ \delta$, $\nu_X = 6{\cdot}73\ \delta$, $|J_{AX} + J_{AX'}|$ 7·7 c./sec.; λ_{max} (EtOH) 296 (ϵ 2900) and its quantitative hydrogenation to (IV) [2·05 moles H_2 uptake/mole (III)], identical to an authentic sample[3] (t.l.c.; i.r.).

Upon irradiation in ether (high-pressure mercury arc, $\lambda > 285$ mμ), (III) was transformed into two photoisomers,§ which were isolated by preparative t.l.c. in 61 and 14% yield, and a small amount of polymeric material.



The major photoisomer was assigned structure (V)‡ on the basis of its spectral properties: n.m.r. 6H (CO_2CH_3) singlet at 3·81 δ, 4H AA′XX′ multiplet, $\nu_A = 5{\cdot}51\ \delta$, $\nu_X = 6{\cdot}74\ \delta$, $|J_{AX} + J_{AX'}|$ 3·6 c./sec.; only end absorption in the u.v. spectrum, ϵ_{210} (EtOH) 4×10^3; and its conversion by

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† If the methoxycarbonyl groups are situated in a *trans*-diaxial arrangement, an examination of the orbital geometry shows that this molecule may be considered a Möbius 4*n* aromatic system (E. Heilbronner, *Tetrahedron Letters*, 1964, 1923).

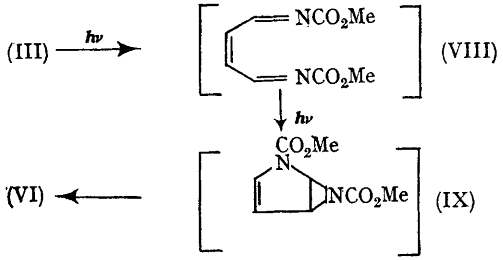
‡ Satisfactory microanalytical data were obtained for all new compounds. N.m.r. spectra were determined in $CDCl_3$ and δ values are in p.p.m. downfield from Me_4Si.

§ Mass spectra gave parent ions at *m/e* 198.

di-imide reduction into (VII) [n.m.r. 6H(CO_2CH_3) singlet at 3·81 δ, 2H multiplet at 4·80 δ, and a 4H multiplet at 4·23 δ].

The spectral properties of the minor photoisomer are consistent with structure (VI)‡: n.m.r. two 3H (CO_2CH_3) singlets at 3·77 and 3·95 δ and an ABMX pattern, ν_A = 6·38 δ ν_B = 6·148, ν_M = 6·86 δ, ν_X = 9·05 δ, J_{AB} 3·7, J_{AM} 2·2, J_{AX} 0·4, J_{BM} 3·2, J 0·5 c./sec.; λ_{max} (C_6H_{12}) 275 mμ (ε 5700); i.r. (CCl_4) NH absorption at 3380 cm.$^{-1}$ and CO_2CH_3 absorptions at 1735 and 1745 cm.$^{-1}$. The formation of (VI) is envisaged as a further photoreaction of (VIII) to give (IX) followed by a rearrangement to (VI).

N.m.r. spectral analysis demonstrated that (VI) was present in the crude photolysis product. Attempts at detecting (VIII) have thus far proved unsuccessful.



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[1] H. Prinzbach and I. H. Hartenstein, *Angew. Chem. Internat. Edn.*, 1963, **2**, 477; E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, 1963, **85**, 3297; G. M. Sanders and E. Havinga, *Rec. Trav. chim.*, 1964, **83**, 665; K. Dimroth, *Ber.*, 1937, **70**, 1631; E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, 1964, **86**, 950.

[2] J. Rigaudy and J. C. Brelière, *Bull. Soc. chim. France*, 1968, 455, report that the sole photoisomer of diethyl 3,6-diphenyl-1,2-dihydropyridazine-1,2-dicarboxylate is the hexatriene.

[3] K. Alder and H. Niklas, *Annalen*, 1954, **585**, 81.

[4] We were unable to repeat the observations of M. Rink, S. Mehta, and K. Grabowski, *Arch. Pharm.*, 1959, **292**, 225, in their preparation of diethyl 1,2-dihydropyridazine-1,2-dicarboxylate.