Dimethyl Δ^3-1,2-Diazetine-1,2-dicarboxylate: A New Four-membered 6π-Ring System

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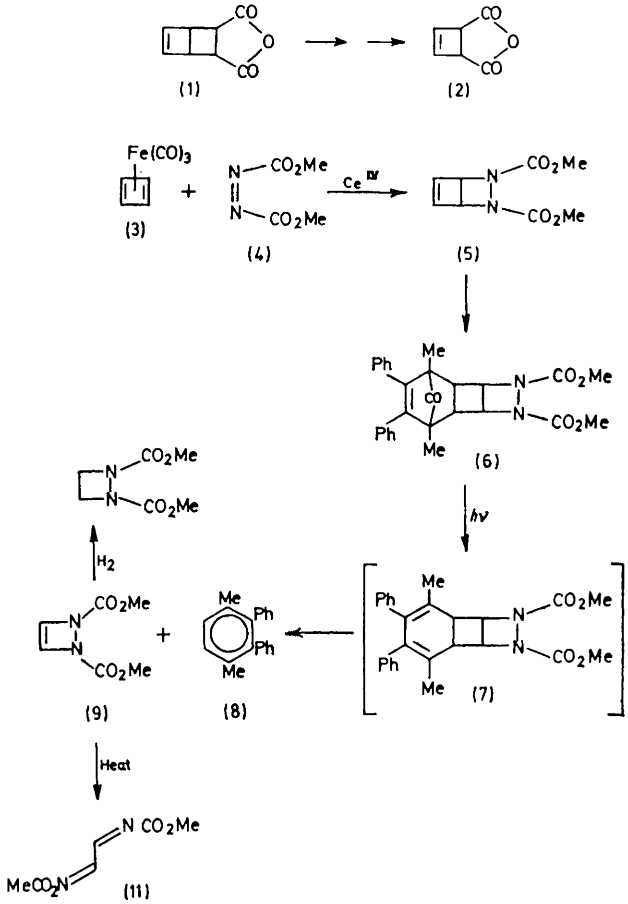
Summary Dimethyl Δ^3-1,2-diazetine-1,2-dicarboxylate has been prepared by photolysis of the 1:1 adduct of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone and 2,3-dimethoxycarbonyl-2,3-diazabicyclo[2,2,0]hex-5-ene; this new ring system formally satisfies the Hückel ($4n + 2$) rule, but no pronounced stability was observed, and the absence of a ring current suggests that it is not aromatic by this criterion.



Δ^3-1,2-Diazetine (and derivatives thereof) is the π-excessive heterocyclic analogue isoelectronic with cyclobutadiene dianion† and formally satisfies the simple Hückel classification of aromaticity. Conflicting reports on its predicted aromaticity have appeared.[3] Derivatives of 1,2-dithiete, the sulphur analogue of this potential 6π-system have been prepared,[4] but their properties may be atypical owing to the contribution from the sulphur *d*-orbitals.

We were initially interested in the synthesis of the Δ^3-1,2-diazetine system in view of the successful conversion of the bicyclo[2,2,0]hexene (**1**) into the cyclobutene (**2**),[5] *via* our 1,2-photoaromatisation reaction.[6] Similarly, the diaza-analogue (**5**) has been converted into the diazetine (**9**) as follows: Reaction of cyclobutadiene [formed by oxidation of its iron tricarbonyl complex (**3**) with ceric ammonium nitrate] with (**4**) at 0° formed the diazabicyclohexene (**5**) (31%; identical with the product from u.v. irradiation of 1,2-dimethoxycarbonyl-1,2-diazacyclohexa-3,5-diene[7]). Cycloaddition of (**5**) with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone formed a 1 : 1 adduct (**6**), m.p. 177·5—178° (^{1}H n.m.r. spectrum consistent with formulation). Irradiation‡ of (**6**) in CDCl$_3$ at 0° caused elimination of carbon monoxide to form (**7**) (undetected) which yielded, in the 1,2-photoaromatisation step, the aromatic hydrocarbon (**8**), together with a relatively unstable substance which was isolated by t.l.c. (95% purity). The ^{1}H n.m.r. spectrum [δ 6·57 (2H, s, vinylic-H) and 3·88, (6H, OMe) p.p.m.] and mass spectrum [*m/e* 172 ($C_6H_8N_2O_4$)] were entirely consistent with the Δ^3-1,2-diazetine structure (**9**). Further, hydrogenation (Pd–C) yielded the dihydro-derivative (**10**)§ [^{1}H n.m.r. δ 4·34 (4H, s, cyclobutyl-H) and 3·87 (6H, s, OMe) p.p.m.; *m/e* 174].

The Δ^3-1,2-diazetine was thermally unstable [$t_{\frac{1}{2}}$ (20°) 6·9 h; $t_{\frac{1}{2}}$(34°) 1·8 h] even at ambient temperatures and isomerised to the ring-opened product (**11**) [^{1}H n.m.r. δ 8·36 (2H, s, imino-aldehydic-H) and 3·98 (6H, s, OMe) p.p.m.]. Rapid polymerisation on attempted isolation frustrated further characterisation of this product.

The question of aromaticity is always a difficult one. Certainly HMO calculations show only a small stabilisation energy for (**9**), and suggest that it is not aromatic to a significant extent. This is further supported by the ^{1}H n.m.r. spectrum of (**9**) (*vide supra*) which indicates no diamagnetic ring current [*cf.* α-vinylic proton resonance in *N*-ethoxycarbonylpyrrole (heteroaromatic, δ 7·36 p.p.m.); *N*-ethoxycarbonylazonine (nonaromatic, [9b] δ 6·4 p.p.m.)]. Thus while the evidence suggests that compound (**9**) is nonaromatic, we defer a more general comment on this ring system until other members of the series have been prepared.¶

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† In the 4-membered alicycles, the 2π-system (cyclobutadiene dication) has been formed at −75° and characterised by ^{1}H n.m.r. spectroscopy,[1] but attempts to form the 6π-equivalent (cyclobutadiene dianion) have been unsuccessful.[2a] Pettit and his co-workers have now obtained evidence for its intermediacy.[2b]

‡ American Hanovia (450 W) medium-pressure Hg lamp, 0°, Vycor filter, N$_2$ atmosphere, 137 mg/0·5 mg in CDCl$_3$.

§ Contrary to that reported,[8] we could find no evidence (mass-spectral) for the formation of any 1 : 1 adduct on attempted thermal cycloaddition of dimethyl azodicarboxylate on ethylene. Indeed ^{1}H n.m.r. studies on the crude product showed no resonances corresponding to (**10**).

¶ Anastassiou and his co-workers[9a] have recently reported that the aromatic properties of the azonine ring system are particularly sensitive to the *N*-substituent.

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