Identification of 1:2 Molar Adducts from 2-Methylquinolines as Cyclobuta[4,5]pyrrolo[1,2-*a*]quinolines by *X*-Ray Diffraction and ^{13}C Nuclear Magnetic Resonance Studies

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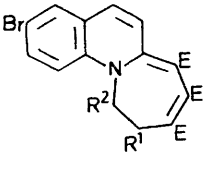
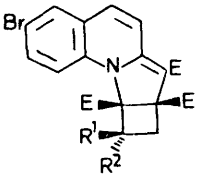
Summary One of the products from 6-bromo-2-methylquinoline and dimethyl acetylenedicarboxylate has been identified as tetramethyl 3-bromo-7a,8,9,9a-tetrahydrocyclobuta[4,5]pyrrolo[1,2-*a*]quinoline-7,*r*-7a,*t*-9,*c*-9a-tetracarboxylate by an *X*-ray diffraction study, and its *c*-9 isomer has been identified by a comparison of the ^{13}C n.m.r. and other spectra.

THE reaction between dimethyl acetylenedicarboxylate and 2-methylquinoline was first investigated by Diels and his co-workers,[1] and their provisional structure for their 'red adduct' was revised later.[2] 6-Bromo-2-methylquinoline gives two analogous isomeric 2:1 molar adducts, previously thought to have the structures (**1a**) and (**1b**).[2] A ^{13}C tracer study has shown that the carbon originally present in the methyl group of the quinoline remains bound to two hydrogen atoms in both products.[3] Although a plausible scheme was put forward to explain the formation of structure (**1b**), the only route which could be devised to account for the formation of (**1a**) involved the very unattractive postulate of a non-stabilised primary carbanion.



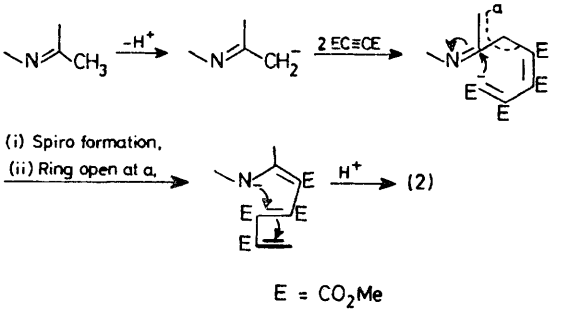
(1a) R^1=H, R^2=E
(1b) R^1=E, R^2=H



(2a) R^1=H, R^2=E
(2b) R^1=E, R^2=H

E = CO_2Me

Partly because of this, an *X*-ray crystal structure determination of the compound previously given the structure (**1a**) was undertaken. This compound proved to possess structure (**2a**); the *R* factor is at present 5·13%. All the spectral data[2] are consistent with this structure; in particular the ^{13}C n.m.r. spectrum shows quaternary carbon resonances at δ 59·29 and 73·56 p.p.m., assigned to C-7a and C-9a respectively, and resonances identified by off-resonance decoupling experiments due to C-8 and C-9 respectively at δ 30·80 and 42·80 p.p.m. The ^1H n.m.r. spectrum shows an ABX system for the protons of the cyclobutane ring, but of particular interest are the very high field 1-H (τ 3·68) and 9-CO_2Me (τ 6·68) resonances. 1-H is clearly in the shielding region of the 9-CO_2Me, which the *X*-ray structure shows is folded over the cyclic system, and the ester-methyl group is in the shielding region of the aromatic ring. The u.v. spectrum for (**2a**) shows a maximum at 498 nm, which is at a surprisingly long wavelength for such a short conjugated system.



SCHEME

The isomer previously given structure (**1b**), and which has almost identical u.v. and mass spectra to compound (**2a**), must now be allocated structure (**2b**). No other orientations of the ester groups are possible since those at positions

7a and 9a must be *cis* to each other because of the nature of the fused 5:4 system. There are no high-field aromatic protons or ester methyl groups in the ^{1}H n.m.r. spectrum, which has been fully analysed, supporting the above stereochemical assignment. The ^{13}C spectrum of (**2b**) shows resonances corresponding to C-7a,-8, -9, and -9a at δ 57·60, 30·36, 44·10, and 78·20 p.p.m.

These observations necessitate a reappraisal of the structures of all adducts previously assigned structures by analogy with those of (**1a**) and (**1b**)[4] and the ^{13}C n.m.r. spectra for most of the available compounds are consistent with structures similar to (**2**) and will be reported shortly. The Scheme, showing partial structures, accounts for the formation of compounds like (**2**); other mechanisms may be written, but at present we have no experimental evidence which would distinguish between them.

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[1] O. Diels and H. Kech, *Annalen*, 1934, **519**, 87 and earlier papers.
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[3] R. M. Acheson and R. F. Flowerday, *J.C.S. Perkin I*, 1975, 394.
[4] R. M. Acheson and M. S. Verlander, *J.C.S. Perkin I*, 1974, **430**. and earlier papers; J. B. Taylor, D. R. Harrison, and F. Fried, *J. Heterocyclic Chem.*, 1972, **9**, 1227.