

NOVEL C₁₀ CARBOCYCLIC SYSTEMS VIA SCHMIDT FRAGMENTATION OF
 PENTACYCLO[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]UNDECANE-8,11-DIONE

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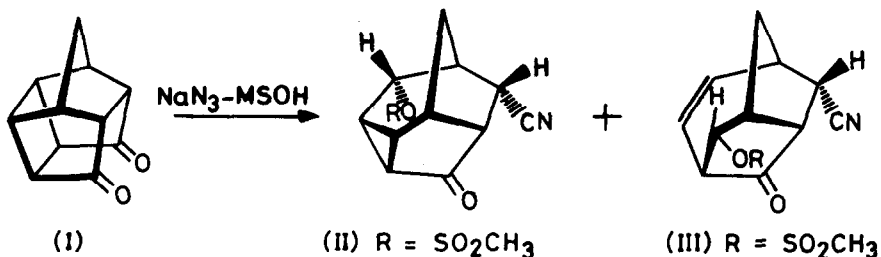
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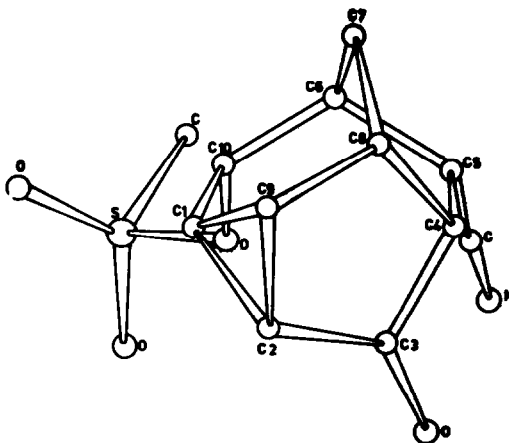
The pentacyclic dione (I), readily available from the UV irradiation of the cyclopentadiene-p-benzoquinone Diels-Alder adduct, has proved to be a versatile precursor for the synthesis of new polycyclic systems of current interest.¹ In this note, we wish to delineate a novel, unanticipated rearrangement pathway from pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (I) to new C₁₀ carbocyclic systems (II)² and (III)² under Schmidt reaction conditions.



Treatment of pentacyclic dione (I) with sodium azide (1 equivalent) in methanesulphonic acid (2 hr, 0-5°) afforded a mixture of products from which two crystalline compounds A and B were separated by chromatography on silica gel in 15 and 10% yield, respectively. The spectral data for compound A [mp 179°; C₁₂H₁₃NO₄S; m/e 267; ir (KBr): ν_{max} 2260 (cyano), 1725 (carbonyl), 1345, 1180 cm⁻¹ (sulphonate ester); pmr (60 MHz, DMSO-d₆): δ 5.6 (1H, t, J = 6 Hz, H-C-OMS), 3.19 (3H, s, CH₃-S-C(=O)-O), 1.4-3.1 (9H, en, ring CH) was indicative of a new tetracyclic structure. However, the spectral data could not

reveal the exact nature of the carbocyclic framework.

The chemical structure and stereochemistry (II) for compound A was therefore determined by a direct single crystal X-ray analysis. The monoclinic crystals of (II) conform to the space group $p2_1/a$ with $a = 10.013$, $b = 9.620$, $c = 12.532$ Å, $\beta = 95.87^\circ$ and $Z = 4$. A total of 1529 reflections having net amplitudes above their standard deviations, were determined with $\text{MoK}\alpha$ radiation using the moving crystal, moving counter technique on a CAD-4 diffractometer. The structure was solved by direct methods with the aid of programme MULTAN.⁴ Seventeen out of the eighteen non-hydrogen atoms were located on an E-map calculated with phase-set having the lowest R_{Karle} value. The missing atom was located from a difference fourier map. Block-diagonal least squares refinement of positional and isotropic temperature factors of the non-hydrogen atoms converged at $R = 0.135$. At this stage, positions of all the hydrogen atoms were obtained from a difference fourier map. Further refinement of the positional and anisotropic temperature factors of the non-hydrogen atoms and the positional and isotropic temperature factors of hydrogen atoms has brought down the R index to 0.038. A perspective view of the molecule is shown in Fig. 1.



THE MOLECULAR STRUCTURE OF TETRACYCLO [4.3.1.0^{3,6}.0^{4,7}]
DECAN-3-ONE DERIVATIVE

FIG. 1

The structure (III) for compound B was deduced from its spectral data, mp: 171° ; $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$; ir (KBr): ν_{max} 2280 (cyano), 1750 (carbonyl), 1360, 1170

(sulphonate ester), 710 cm^{-1} (cis-disubstituted olefin); pmr (270 MHz, DMSO- d_6): δ 6.30 (1H, t, $J = 10.5\text{ Hz}$), 5.94 (1H, t, $J = 10.5\text{ Hz}$), 4.94 (1H, s, $\underline{\text{H}}\text{-C-OMs}$), 3.52 (1H, q, $J_1 = 11\text{ Hz}$, $J_2 = 8\text{ Hz}$, $\underline{\text{H}}\text{-C-CN}$), 3.26 (3H, s, $\underline{\text{CH}}_3\text{-SO}_2$), 3.25 (1H, m, ring CH), 3.2 (1H, ring CH), 3.11 (1H, d, $J = 10.5\text{ Hz}$), 3.02 (1H, m, ring CH), 2.09 (1H, m, $\underline{\text{H}}\text{-C-H}$), 1.96 (1H, d, $J = 13\text{ Hz}$, $\text{H-C-}\underline{\text{H}}$). Although the gross spectral features were compatible with either structure (III) or 2-protoadamantenone formulation (IV), the spin decoupling experiments⁵ at 270 MHz summarised in Fig. 2 and the magnitude of coupling constants (based on vicinal dihedral angles) were in better agreement with (III). Further support for structure (III) was derived from the fact that it was quantitatively formed from (II) on solvolysis in methanesulphonic acid. Also (III) underwent a facile oxa-di- π -methane rearrangement to (V), mp 194° ; $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$; ir (KBr): ν_{max} 2270 (cyano), 1705 cm^{-1} (carbonyl); pmr (60 MHz, DMSO- d_6): δ 5.25 (1H, m, $\underline{\text{H}}\text{-C-OMs}$), 3.15 (3H, s, $\underline{\text{CH}}_3\text{-SO}_2$), 1.5-3.5 (complex en, ring CH); cmr (22.63 MHz, DMSO- d_6): δ 205.23 (s, $\underline{\text{C}}=\text{O}$), 119.71 (s, $-\text{C}\equiv\text{N}$), 80.39 (d, $\text{H-C-}\underline{\text{O}}\text{Ms}$), 37.9 (q, $\underline{\text{CH}}_3\text{-SO}_2$) and 49.19, 42.04, 40.38, 36.39, 35.09, 30.08, 29.44 (unassigned 8 C's).

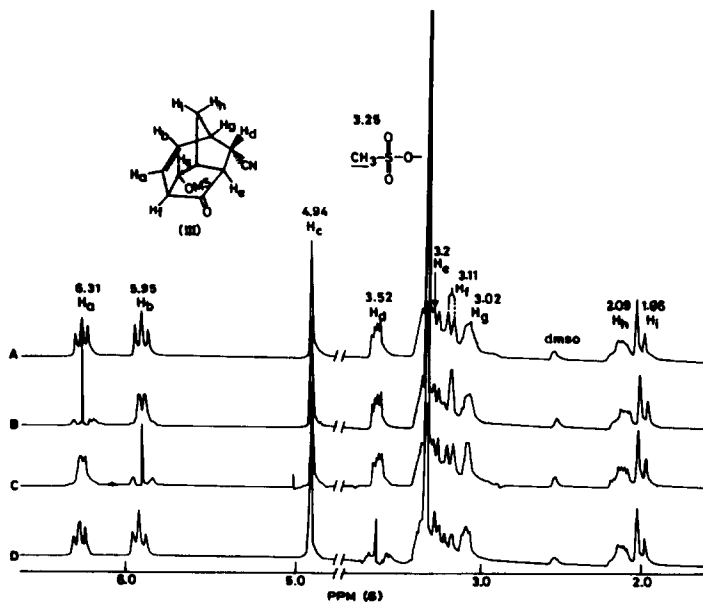
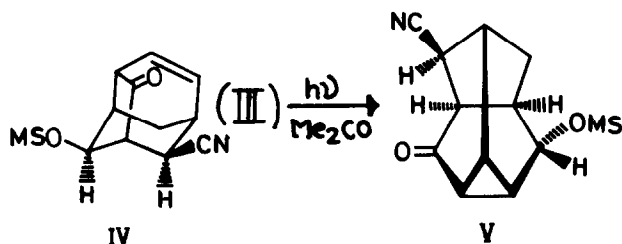


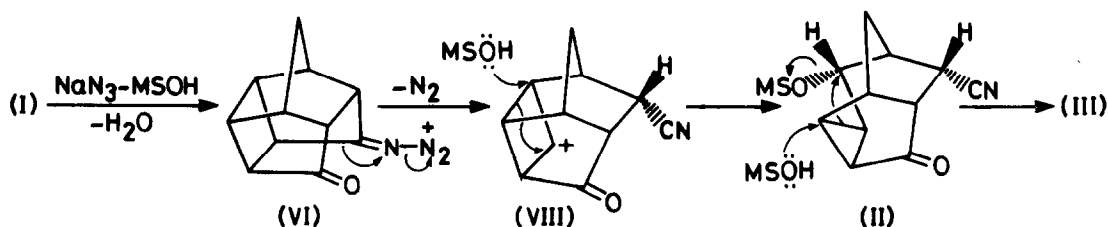
FIG. 2

270 MHz PMR spectra of (III) in DMSO- d_6 : A, standard spectrum; B, spectrum decoupled from H_b ; C, spectrum decoupled from H_b ; D, spectrum decoupled from H_d .



A reasonable mechanism for the formation of (II) and (III) from (I) is depicted in Scheme 1. Regiospecific fragmentation of 7-8 bond in (VI) to cyclobutyl carbonium ion (VII) and a stereospecific rearrangement to cyclopropyl-carbinyl system furnishes (II). A cyclopropylcarbinyl \rightarrow homoallylic rearrangement accounts for the formation of (III). Our more recent studies⁶ with (I) and related pentacyclic systems have demonstrated the generality and preparative utility of the I \rightarrow II + III type rearrangement.

Scheme 1



REFERENCES AND NOTES

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2. To the best of our knowledge, the carbon skeletons of (II) and (III) have not been reported in literature. However, the tricyclodecane graph³ mentions 3,7-ethano-tricyclo 3.3.0.0^{3,7} octane ring system (III) as a possible precursor of adamantane.
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4. G. Germain, P. Main and M.M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).
5. The 270 MHz pmr spectral data was obtained through the kind courtesy of Professor W. Herz. We wish to record our gratitude to him for this help.
6. G. Mehta and V.K. Singh, unpublished results.