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NEW REARRANGEMENTS OF CAGED SYSTEMS: INTERESTING MECHANISTIC DEVIATIONS THROUGH ANNULATION

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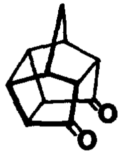
Recently, rearrangements of the caged pentacyclic dione 1 to novel carbocyclic systems 2 and 3 *via* Schmidt fragmentation and ceric ion oxidation have been reported from this laboratory[1]. Further interest in the chemistry of these caged systems have led us to explore the rearrangements of hexacyclo-$(7.4.2.0^{1,9}.0^{3,7}.0^{4,14}.0^{6,15})$ pentadeca-10, 12-diene-2, 8-dione[2] 4, an annulated derivative of 1, as a potential source of new and not readily accessible polycyclic systems. In this communication, we describe the deep seated rearrangement[3] of the hexacyclic dione 4 to benzo-annulated tricyclo $(5.2.1.0^{3,8})$ decane, tricyclo $(4.4.0.0^{3,7})$ decane and tricyclo $(4.2.1.0^{2,5})$ nonane ring systems during Schmidt fragmentation and ceric ion oxidation.

Brief exposure of the hexacyclic dione 4 to sodium azide in methanesulphonic acid (99%, 0-5°, 45 min) and column chromatography (SiO_2gel) of the resultant product mixture furnished two crystalline products 5 and 6 in 15 and 20% isolated yield, respectively. The structure of 5, mp 211°, was indicated from its analytical and spectral data: $C_{16}H_{15}NO_4S$, uv(MeOH): λ_{max} 256 and 208 nm; ir(KBr): 2250(cyano), 1690(carbonyl), 1180, 1360cm^{-1}(sulphonate ester) and characteristic aromatic bands; pmr(270 MHz, DMSO-d_6): δ 7.92(d, J_{ab}=8Hz, Ar-H_a), 7.68(t, J_{bc}=J_{cd}= 8Hz, Ar-H_c), 7.51(d, J_{cd}=8Hz, Ar-H_d), 7.45(t, J_{ab}=J_{bc}=8Hz, Ar-Hb), 4.56(s, *endo*-H_2), 3.89(dd, $J_{1,10}$=4.5Hz, J_{7-10}=12Hz, *exo*-H_{10}), 3.38(br with st, H_3), 3.28(s, CH_3-SO_2-O), 3.18(brt, H_8), 3.13(d with st, $J_{7,10}$=12Hz, H_7), 3.00(d, $J_{1,10}$=4.5Hz, H_1),



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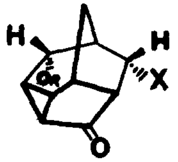

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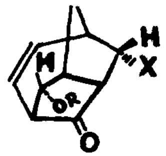

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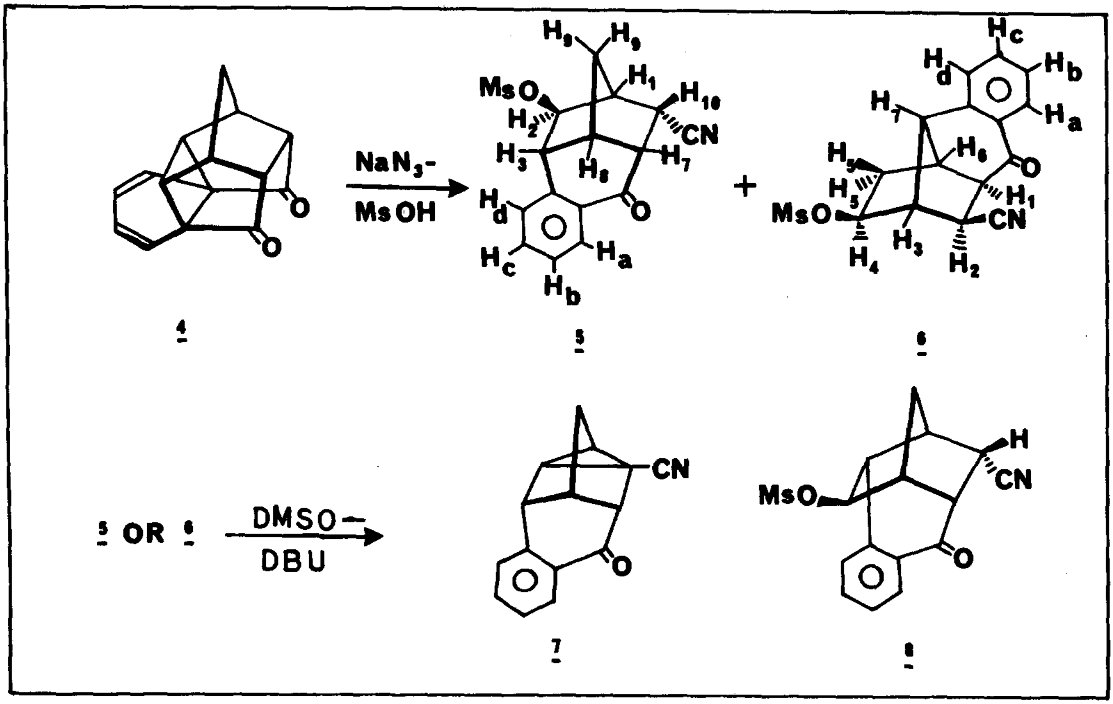
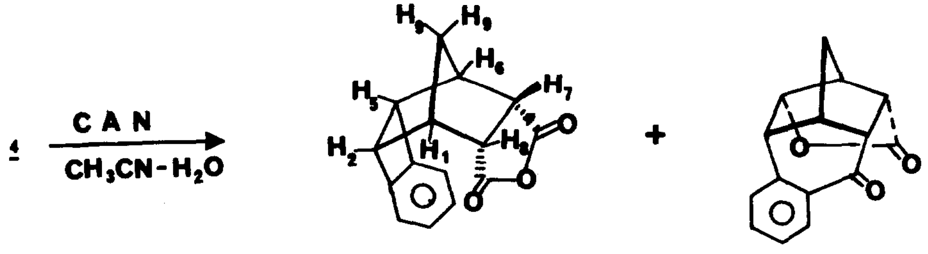


1.87(ABq, J_{gem}=12Hz, H_9). Similarly, 6, mp 207°, in conformity with its formulation, exhibited the following spectral characteristics: $C_{16}H_{15}NO_4S$, uv(MeOH): λ_{max} 250 and 210 nm; ir(KBr): 2260(cyano), 1692(carbonyl), 1180, 1365cm^{-1}(sulphonate ester) and characteristic aromatic bands; pmr(270 MHz, DMSO-d_6): δ 7.83(d, $J_{a,b}$=8Hz, Ar-H_a), 7.66(t, J_{bc}=J_{cd}=8Hz, Ar-H_c), 7.55(d, J_{cd}=8Hz, Ar-H_d), 7.47(t, J_{ab}=J_{bc}=8Hz, Ar-H_6), 5.02(d, $J_{4,5endo}$=6Hz, H_4), 3.47(S, H_7), 3.44(d, $J_{1,2}$=8Hz, H_2), 3.31(s, CH_3-SO_2-O), 3.03(d, $J_{1,2}$=8Hz, H_1), 2.96(S, H_3), 2.95(d, $J_{exo5,6}$= 4.5Hz, H_6), 2.01(dd, J_{gem}=14Hz, $J_{4,5endo}$=6Hz, endo H_9), 1.95(dd, J_{gem}14Hz, $J_{exo5,6}$=4.5Hz, exo H_9). Several of the proton assignments for compounds 5 and 6 were deduced through appropriate spin decoupling experiments at 270 MHz. When either 5 or 6 was treated with 1,5-diazabicyclo(5.4.0) undec-5-ene(DBU) in refluxing DMSO, a single crystalline compound 7,(mp 151°, $C_{15}H_{11}NO$; uv(MeOH):

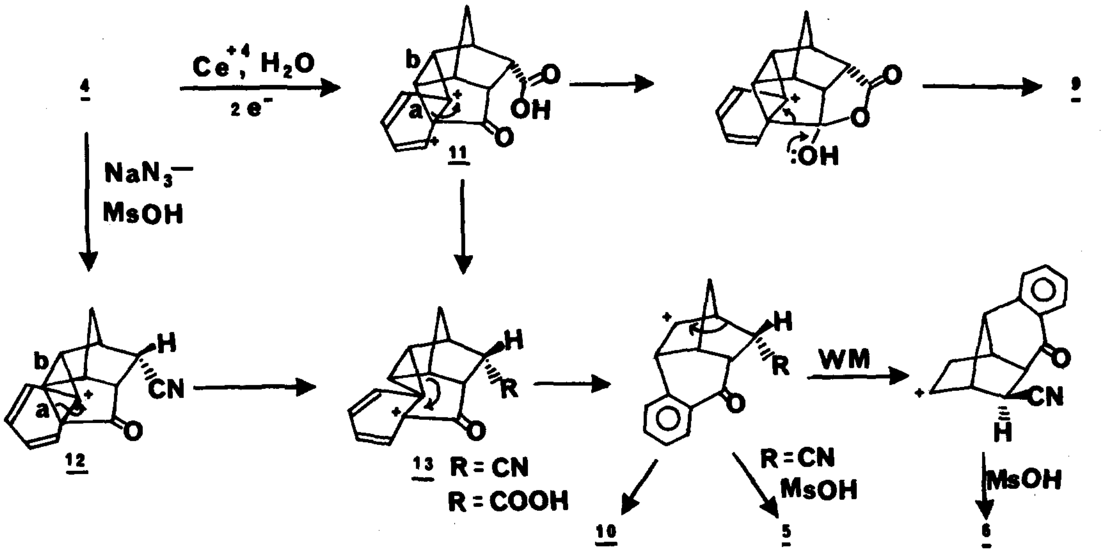


9 10

λ_{max} 251 and 217 nm; ir(KBr): 2240(cyano), 1685cm^{-1}(carbonyl); pmr(90 MHz, $CDCl_3$): δ7.2-8.3(m, 4H, Ar), 3.1(br with St, 1H), 3.05(narrow d, 1H), 2.65(br, 1H), 2.45 (s, 2H), 1.85(s, 2H); ^{13}cmr(22.63 MHz, $CDCl_3$)[4]: δ 135.4(d), 129.2(d), 129.1(d), 128.9(d), 57.4(d), 47.8(d), 44.5(d), 36.1(t), 34.3(d), 31.4(d)) was obtained in quantitative yield. This facile base catalysed 1,3-elimination of methanesulphonic acid from 5 and 6 to form 7 reveals the mutual structural relationship between 5 and 6 and rules out alternate formulations like 8 for either of these compounds.

Reaction of 4 with ceric ammonium nitrate(CAN) in aq.CH_3CN(0°, 1hr) yielded a mixture of products that were readily separated by column chromatography (SiO_2gel). The fast moving product(30%), mp 194-96°, exhibited uv spectrum (λ_{max}^{MeOH} 273 , 267 and 263 nm diagnostic of a benzocyclobutene chromophore[5] and is formulated as 9. The presence of the anhydride functionality and the symmetrical nature of 9 follows from its ir(KBr): 1795 and 1860cm^{-1}(anhydride); pmr (90MHz, $CDCl_3$):δ7.00-7.3(m, 4H, Ar), 3.85(m, 2H, H_2 and H_5), 3.3(t, J=3Hz, H_7 and H_8), 3.1(m, 2H, H_1 and H_6), 2.06(q, J=12Hz, 2H, H_9) and ^{13}cmr(22.63Hz, $CDCl_3$):δ 171.6(s, 2C), 145.1(s, 2C), 128.3(d, 2C), 126.8(d, 2C), 49.8(d, 2C), 49.8(t, 1C), 48.8(d, 2C), 41.9(d, 2C); spectral data. The slow moving product(40%) of CAN oxidation is assigned structure 10, mp 196°, on the basis of following spectral data: uv(MeOH): λ_{max}253 and 210 nm; ir(KBr): 1760(lactone), 1685cm^{-1}(carbonyl); pmr(90MHz, $CDCl_3$): δ7.15-8.1(m, 4H, Ar), 4.92(q, J_1=5Hz, J_2=8.5Hz, 1H, $-O-\overset{|}{C}-\underline{H}$), 3.47(m, 1H), 3-3.4(m, 4H), 1.93(q, J=10Hz, 2H); ^{13}cmr(22.63 MHz, $CDCl_3$): δ 195.9 (s, Ar-$\underline{C}$=O), 176.7(s, O-$\underline{C}$=O), 140.4(s, Ar), 134.5(d, Ar), 131.0(s, Ar), 129.2(d, Ar), 128.4(d, Ar), 127.6(d, Ar), 81.0(d, O-$\underline{C}$-H), 50.9(d), 50.6(d), 45.4(d), 44.8(d), 43.9(d), 35.7(t).

SCHEME—I



Probable mechanistic pathway for the formation of various rearrangement products is depicted in scheme I. It is interesting to note that the initiall formed carbonium ion intermediates 11 and 12 rearrange to an unusual, common, α-keto-carbonium ion 13, which is stabilised through π-delocalisation and cyclopropyl conjugation. It is perhaps this stabilisation, among other things, which directs the migration of bond 'a' in ions 11 and 12 as against the migration of bond 'b' in the earlier observed[1] rearrangements of pentacyclic dione

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References and Notes:

1(a) G. Mehta, P. Ghosh, B. Choudhury, V.K. Singh, R. Usha, K.I. Varughese and K. Venkatesan, Tetrahedron Letts., 4109 (1977); (b) G. Mehta, V.K. Singh and H. Duddeck, ibid., 1223 (1978).

2. A.S. Kushner, Tetrahedron Letts, 3275 (1971); N. Fillipescu and J.M. Mente J. Chem. Soc., B, 616 (1969).

3. We have investigated several aspects of the chemistry of readily available 4 and these findings will be reported shortly.

4. Quaternary carbons were not recorded in this case.

5. M.P. Cava and M.J. Mitchell, J. Amer. Chem. Soc., 81, 5409 (1959); C.D. Nenitzescu, M. Avram and D. Dinu, Chem. Ber. 90, 2541 (1957) and references cited therein.

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