superoxide produces singlet oxygen $(^1\Delta g)$.[18,19] Exciplex structures involving less complete charge transfer could also be used to rationalize the behavior.

Singlet oxygen has been hypothesized to oxidize Fe^{2+} in 0.8 N H$_2$SO$_4$[20] as well as pH 5 HClO$_4$.[21] In the latter case, oxidation efficiency was found to increase with pH in contrast to the results here. The extent of involvement of singlet oxygen in our system, if any, must await more precise data correlating **3** formation with measured yields of Fe^{3+}. Similarly, more detailed investigation might reveal that oxidants other than singlet oxygen were involved in the earlier studies since the proposed mechanisms were based on reasonable inference rather than rigorous proof.

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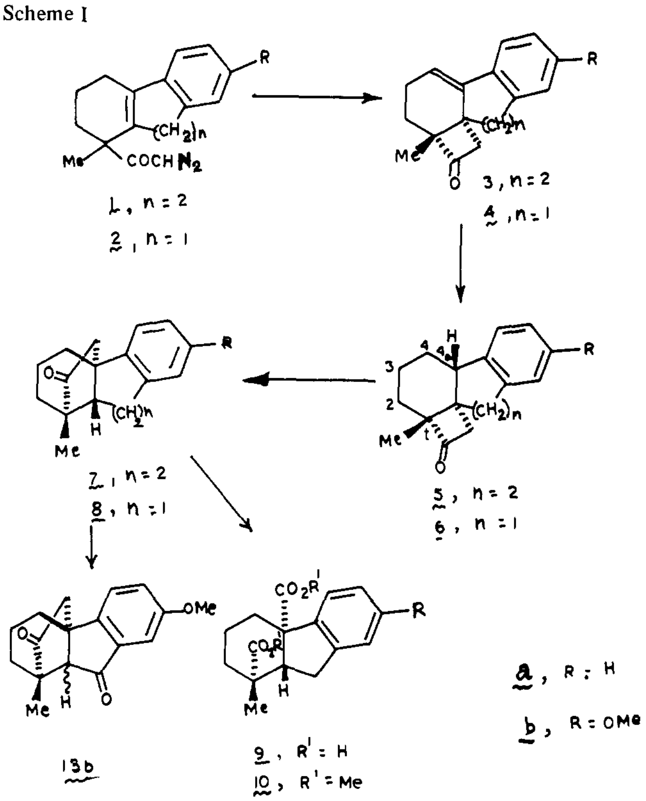
A Novel Rearrangement of Angularly Fused Cyclobutanone. Stereospecific Syntheses of Intermediates to the Diterpene Alkaloids and the C$_{20}$ Gibberellins[1]

Sir:

Recently we have developed[2] a simple efficient synthetic route to a few angularly fused polycyclic cyclobutanones **3a,b** and **4a,b** through intramolecular C-alkylations of the easily accessible β,γ-unsaturated diazomethyl ketones **1a,b** and **2a,b** and their stereocontrolled hydrogenation to the saturated cyclobutanones **5a,b** and **6a,b**. We now report a remarkable stereospecific rearrangement of these saturated cyclobutanones to the respective bridged ketones **7a,b** and **8a,b**. The importance of **7b** relating to the synthesis of *Garrya* and *Atisine* groups of the diterpene alkaloids and the C$_{20}$-gibberellins has already been established.[3] We also report here the transformations of the tetracyclic ketones **8a** and **8b** to some key hydrofluorene synthons **9a** and **9b** towards the C$_{20}$-gibberellins.[4]

Scheme I

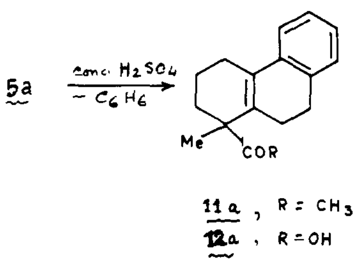


Thus, treatment of the strained[5] cyclobutanone **5a** with an excess (20–25 mole equiv) of triethyloxonium fluoborate[6] in anhydrous methylene chloride under dry nitrogen for 12–16 h afforded the known[3] bridged-tetracyclic ketone **7a** in 90–95% isolated yield. The corresponding methoxy analogue **5b** under the same sequence produced **7b**[3] in 90% yield. The intramolecular nature of this rearrangement has been established from the results of the reaction of **5a**-*4,4a*-d_2[7] with triethyloxonium fluoborate, which showed a pronounced isotope effect and required ca. 6 days at room temperature for complete conversion of the cyclobutanone to the cyclopentanone (monitored by ir). The rearranged ketone **7a**,[8] isolated in 85% yield, showed >99% of d_2 in the mass spectrum.

It may be mentioned that the reaction of the cyclobutanone **5a** with concentrated H$_2$SO$_4$ in benzene at ice-salt bath temperature (ca. −10 to −5°) produced the unsaturated methyl ketone **11a**[9] in excellent yield, as has been reported[11] in a similar case.

The triethyloxonium fluoborate catalyzed rearrangement of the major isomer[2] **6a** from the catalytic hydrogenation of the unsaturated hydrofluorene ketone **4a**[12] required somewhat longer reaction time (24 h) and afforded the liquid five-membered bridged ketone **8a**[13], bp 135–140° (0.3 mm) (bath temp) (*m/e* 226; $\nu_{\max}$ 1730 cm^{-1}; δ (CCl$_4$) 0.70 (3 H, s), 1.2–3.5 (11 H, complex mm), 7.06 (4 H, s)) in 90–95% yield; semicarbazone mp 235–238° dec. The corresponding methoxy analogue **6b**,[14] under identical conditions gave the respective rearranged ketone **8b**, bp 120–125° (0.1 mm) (bath temp)

Scheme II



(m/e 256; ν_{max} 1730 cm^{-1}; δ (CCl_4) 0.75 (3 H, s), 1.25–3.3 (11 H complex mm), 3.71 (3 H, s) and 6.57–7.03 (3 H, m)) in 93% yield; semicarbazone mp 216–217° dec. Benzylic oxidation[15] of the ketone **8b** with CrO_3–HOAc gave the 9-oxo derivative **13b**, mp 83–84° (m/e 270; λ_{max}^{EtOH} 222 nm (ϵ 18 900), 252 (ϵ 5670) and 325 nm (ϵ 1586); ν_{max} 1740 (s), 1715 (s), and 1615 (m)) which confirmed its assigned structure. Stereochemistry of the saturated cyclobutanones **6a** and **6b** and the respective rearranged ketones **8a** and **8b** has been assigned from their modes of formation in analogy to the respective hydrophenanthrene derivatives of established stereochemistry.[3]

To exemplify the synthetic usefulness of this rearrangement process for the introduction of an angular carboxyl group, we briefly record here transformations[3] of **8a** and **8b** to the dicarboxylic acids **9a**, mp 206–207° dec, and **9b** mp 212–213° dec, and dimethyl esters **10a**, bp 123–127° (0.05 mm) (bath temp) (ν_{max} 1725 cm^{-1}; δ (CCl_4) 0.90 (3 H, s), 1.38 (1 H, m), 1.95 (5 h, br s), 2.95 and 3.28 (2 H, partially resolved quartet, ABX system, J_{AB} = 13 Hz, J_{AX} = 3 Hz) and signal for 1 H masked under these, 3.55 (3 H, s), 3.60 (3 H, s), and 7.08 (4 H, s)), and **10b**, mp 83° (m/e 332; ν_{max} 1720 (s) and 1605 (w); δ (CCl_4) 0.90 (3 H, s), 1.31 (1 H, d, J = 7 Hz), 1.88 (5 H, br s), 2.84 and 3.25 (2 H, partially resolved quartet, ABX system, J_{AB} = 13 Hz, J_{AX} = 2 Hz) and signal for 1 H masked under these, 3.5 and 3.56 (6 H, 2s), 3.68 (3 H, s), and 6.46–7.0 (3 H, m)) in 60–65% yields through the corresponding hydroxymethylene (NaH, HCO_2Et) derivatives, followed by oxidation with alkaline hydrogen peroxide.

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(8) Mp and mmp 118° with the ketone-d_0; identity was further confirmed by mixed TLC. The comparison ir spectra (in $CHCl_3$) of this product and unlabeled ketone showed identical bands excepting the strong C–D stretch at 2160 cm^{-1} in the former. The mass spectral analysis showed the molecular ion as the base peak at m/e 242 corresponding to >99% d_2. ^{1}H NMR spectrum (in $CDCl_3$ at 60 MHz) of the deuterated ketone was identical with the ketone-d_0 except that the partly masked broad unresolved triplet at δ 1.96 (assigned to the C-10a proton) was absent. Moreover, the splitting pattern of the multiplets between δ 1.16 and 2.04 accounting for nine protons in the unlabeled ketone was changed and integrated to seven protons in the deuterated ketone along with a clear separation of the inner lines of the gem-$COCH_2$ protons at ca. δ 2.38 (ref 3).

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(13) Compounds described here are all racemates. New compounds gave satisfactory analytical and spectral data. NMR spectra were measured at 60 MHz in a Varian T60A model. The ir spectra were taken on a PE-21 model in $CHCl_3$ solution.

(14) The diazoketone **2b**, prepared from the corresponding acid, mp 156–157° (R. Dasgupta, *unpublished results*), on cyclization with 48% aqueous HBF_4 in $CHCl_3$ at 5–10° gave the unsaturated cyclobutanone **4b**, mp 94–95° (ν_{max} 1765 cm^{-1}, λ_{max}^{EtOH} 262 nm (log ϵ 4.26) and 300 nm (log ϵ 3.75); δ ($CDCl_3$) 1.28 (3 H, s), 3.78 (3 H, s), 6.11 (1 H, br t, J = 5 Hz), and 6.6–7.1 (3 H, m)) in 82% yield which on catalytic hydrogenation (EtOH, Pd-C) produced a single diastereomer **6b**, mp 75° (ν_{max} 1765 cm^{-1}, δ ($CDCl_3$) 1.25 (3 H, s), 3.75 (3 H, s), 1.36–3.5 (11 H, complex m), and 6.4–7.06 (3H, m)) in ca. 95% yield.

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Laser Flash Spectroscopy of Tris(2,2′-bipyridine)ruthenium(II) in Solution

Sir:

The properties of the excited states of transition metal complexes are of great interest since these compounds often absorb strongly in the visible and might be used in solar energy conversion.[1-4] The lowest excited state of $Ru(bpy)_3^{2+}$, which is commonly considered as a triplet charge transfer excited state, $(^3CT)Ru(bpy)_3^{2+}$,[5] exhibits very peculiar properties[7] and it has been extensively used in the last few years for both energy[7,8] and electron[2,7,9-16] transfer processes. We report here a study of this excited state by laser flash spectroscopy.

The experiments were performed at room temperature with an apparatus previously described.[17,18] The neodymium laser CILAS used for excitation emits in 60-ns pulses of approximately 1 J at 530 nm and 50 mJ at 353 or 265 nm after doubling, tripling, or quadrupling its normal frequency. For excitation at 530 nm the energy of the pulse was filtered to avoid dielectric breakdown and multiphoton effects. Transient optical densities were normalized to correct for variation in excitation intensity. The detection system, which uses an automatic back off already described,[19] is able to measure absorbance values as small as 5 × 10^{-4}. The samples were deaerated by bubbling with Ar. For each laser excitation a fresh sample of the solution was used.

The absorption spectrum obtained immediately after the end of the exciting flash was practically identical for water or acetonitrile solutions and for 265, 353, or 530 nm excitation. A typical spectrum for a solution 4.7 × 10^{-5} in water (λ_{exc} 265 nm) is shown in Figure 1. The same exponential kinetics was observed for (i) the recovery of the bleaching at the maximum of the ground state absorption (453 nm), (ii) the decay of the transient absorption (360 nm), and (iii) the decay of the transient emission (610 nm). For each one of these phenomena the first-order rate constant was (1.50 ± 0.05) × 10^6 s^{-1} in water and (0.95 ± 0.05) × 10^6 s^{-1} in acetonitrile. The first-order law was unchanged by varying the $Ru(bpy)_3^{2+}$ concentration in the range 0.15 × 10^{-4} to 6.0 × 10^{-4} M. In aqueous solution the rate constant was 2.3 × 10^6 s^{-1} in the presence of air and 4.8 × 10^6 s^{-1} in the presence of 1.0 × 10^{-3} M oxygen, which gives a value of 3.3 × 10^9 M^{-1} s^{-1} for the bimolecular rate constant of the reaction of the transient with oxygen. Excitation of $Ru(bpy)_3^{2+}$ solutions in acetonitrile containing 1.0 × 10^{-3} M retinol by a 530-nm pulse (which is exclusively absorbed by the ruthenium complex) caused the appearance of the characteristic absorption at 405 of the retinol triplet.[18] The formation of retinol triplet matched the recovery of $Ru(bpy)_3^{2+}$ absorption at 453 nm. The pseudo-first-order rate constant was 4.0 × 10^6 s^{-1}, which gives a value of 2.5 × 10^9 M^{-1} s^{-1} for the bimolecular rate constant of the reaction between the transient and retinol.

The results obtained indicate that the transient absorption and emission observed are due to the same excited state of $Ru(bpy)_3^{2+}$. The emission at 610 nm of excited $Ru(bpy)_3^{2+}$ had already been studied and assigned to the so-called triplet charge transfer excited state, $(^3CT)Ru(bpy)_3^{2+}$ [5,6,20] The