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Intramolecular Photochemical Oxetane Formation in Two β,γ-γ',δ'-Diunsaturated Ketones

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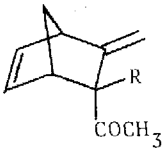
Although the photochemistry of β,γ-unsaturated ketones has been widely explored and numerous reaction pathways elucidated,[1] oxetane formation has been described only recently.[2,3] These examples have all involved intramolecular addition of the carbonyl group to the β,γ-olefinic bond. To our knowledge no β,γ-unsaturated ketone has been explored which yields competitive intramolecular oxetane formation at a more remote olefinic site. In this regard we wish to report here the photochemical reactions of β,γ-γ',δ'-diunsaturated ketones (1a) and (1b), both of which lead selectively to intramolecular oxetane formation at the γ',δ' olefin.

Irradiation of (1a)[4] and (1b)[4] in benzene or cyclohexane (0.02M) through pyrex ($\lambda \geq 2800$Å) leads exclusively to (2a)[5] and (2b)[5] in 68 and 61% yield,[5] respectively. The structure of (2a) and (2b) were deduced from their spectroscopic properties: (2a) showed ν_{max} 3075 (m), 3000 (m), 2945 (m), 1690 (m), 1390 (m), 1294 (m), 1264 (m), 1245 (m), 973 (s), 898 (m), 880 (s) cm^{-1};



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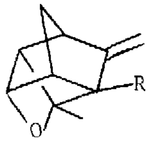

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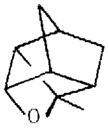

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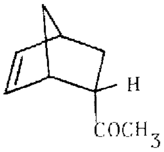

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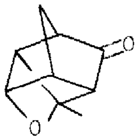

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a) R = H

b) R = CH_3

δ (60 MHz) 1.30 (s, 3H), 1.62-1.80 (m, 2H), 2.10-2.32 (m, 1H), 2.32-2.59 (m, 1H), 2.68-3.00 (m, 2H), 4.47-4.68 (m, 3H); (2b) showed ν_{max} 3080 (w), 2990 (s), 1680 (w), 1385 (m), 963 (s), 872 (s) cm^{-1}; δ (60 MHz) 1.11 (bs, 6H), 1.61-1.78 (m, 2H), 2.13-2.38 (m, 2H), 2.80-3.09 (m, 1H), 4.45-4.78 (m, 3H). Confirmation of structure (2a) was obtained by its conversion to the known oxetane (3) prepared photochemically from (4) according to the method of Sauers.[6] To this end oxidation of (2a) with ruthenium tetroxide/sodium periodate yielded ketone (5)[5] which displayed a carbonyl stretching band at 1773 cm^{-1}. When (5) was then subjected to a sealed tube[7] Wolff-Kishner reduction, (3) identical in all respects with an authentic sample was obtained. Interestingly, irradiation of the exo isomer of (1a) gave no volatile material.

The quantum yield for production of oxetane (2a), employing the conversion of (4) to (3) [Φ = 0.14][6] as actinometer, was 0.011. This thirteen-fold reduction in efficiency of oxetane formation compared to (4) results from the availability of additional energy wasting processes in (1a). A likely candidate for such energy dissipation is the unobservable isomerization or free rotor effect[8] of the β,γ double bond.

We next turned our attention towards defining the multiplicity of the excited state responsible for oxetane formation. Irradiation of (1a) (0.035M) in the presence of either *cis*-1,3-pentadiene (E_T = 56.9 Kcals/mole)[9] or 1,3-cyclohexadiene (E_T = 53 Kcals/mole)[10] over the concentration range of 0.1-1.0 M had no effect on the production of oxetane (2a), nor were either *trans*-1,3-pentadiene or the dimers of 1,3-cyclohexadiene observed. In addition, when a mixture of (1a) and propiophenone (E_T = 74.6 Kcals/mole)[11] was irradiated under conditions where the propiophenone absorbed greater than 90% of the light, no oxetane was obtained. Although it is tempting to conclude from the above results that (2a) arises from the singlet excited state as recently established for intramolecular oxetane formation in both β,γ and γ,δ-unsaturated aliphatic ketones,[3,6] the possibility exists that oxetane formation could proceed from an extremely short-lived non-quenchable triplet.

It thus appears that we have uncovered an intramolecular photochemical process in (1a) and (1b) which competes efficiently with the more commonly observed reaction pathways of β,γ-unsaturated ketones. This result is almost certainly due to the geometric constraints placed on the carbonyl group. Studies to examine less constrained β,γ-γ',δ'-diunsaturated ketones,[12] as well as to distinguish between the excited state multiplicity leading to oxetane formation are under active investigation in our laboratory.

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4. Ketone (1a)[5] and its exo isomer[5] were available in a ratio of 4:1 respectively by the Diels-Alder addition (0°-20°C) of cyclopentadiene to acetylallene [M. Bertrand and J. Le Gras, C. R. Acad. Sci., Paris, 259, 404 (1964)] prepared by a modification of the method of M. Bertrand and J. Le Gras, Bull. Soc. Chim. Fr., 2136 (1962). Ketone (1b) was prepared from the above Diels-Alder mixture by alkylation with methyl iodide. A variety of vpc conditions which included a polar and non-polar 500' capillary column failed to resolve (1b) from its epimer which by nmr analysis was present to the extent of 16%.

5. All new compounds described had satisfactory microanalysis and spectroscopic properties. Yields were determined by glc calibration.

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9. R. E. Kellogg and W. T. Simpson, J. Amer. Chem. Soc., 87, 4230 (1965).

10. D. F. Evans, J. Chem. Soc., 1735 (1960).

11. W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, J. Amer. Chem. Soc., 86, 4537 (1964).

12. Conia has explored the direct irradiation of two acyclic β,γ-γ',δ'-diunsaturated ketones (i.e., 3-isopropenyl-3-methyl-5-hexen-2-one and 3,4-dimethyl-4,7-octadiene-2-one) which yield products derived from γ-hydrogen atom abstraction and 1,3-acyl shift, respectively: J. M. Conia et M. Bortolussi, Bull. Soc. Chim. Fr., 3402 (1972).