Notes

Photochemistry of β,γ-Unsaturated Ketones. 10,11-Dimethyltricyclo[4.3.2.0]undec-10-en-2-one[1]

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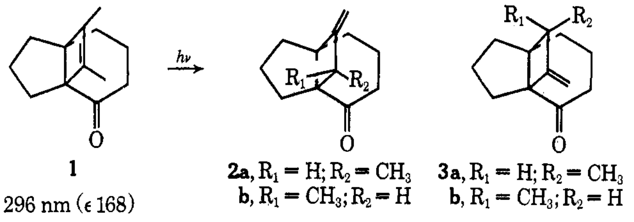
The photochemical 1,3-acyl migration[2] is a rearrangement common to β,γ-unsaturated ketones in which efficient mixing of carbonyl and olefinic orbitals occurs.[3] However, when this orbital mixing is inefficient (ϵ_{max} <150), olefin triplet reactions are usually observed.[3] Atom abstraction from solvent (photoreduction[3,4] being a special case), dimerization (or cycloaddition), and intramolecular atom abstraction reactions are viable olefin triplet reactions[5] of rigid olefins as well as β,γ-unsaturated ketones (ϵ_{max} <150) in which the olefinic group is rigid (*i.e.*, enones in which the olefinic group is in a five-membered or smaller ring). We have recently encountered an example of photochemically induced intramolecular hydrogen transfer (a process which is well documented for rigid olefins[6]) in β,γ-unsaturated ketone **1**[7] (ϵ_{max} 168).[8]



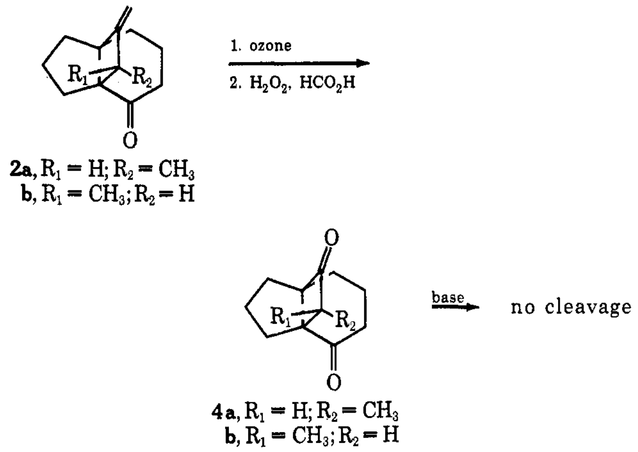
1
296 nm (ε 168)

2a, $R_1 = H; R_2 = CH_3$
b, $R_1 = CH_3; R_2 = H$

3a, $R_1 = H; R_2 = CH_3$
b, $R_1 = CH_3; R_2 = H$

Irradiation of 10,11-dimethyltricyclo[4.3.2.0]undec-10-en-2-one (**1**)[7] in hexane (Corex) produced a mixture of four new ketones in which 10-methyl-11-methylenetricyclo[4.3.2.0]undecan-2-one (**2a**) predominated (70%).[9]

Spectral information allowed us to initially determine the structure of the major photorearranged isomer as either **2** (**a** or **b**) or **3** (**a** or **b**). Oxidative cleavage of this major product produced diketone **4** (**a** or **b**), whose partial structure was verified by its resistance to base cleavage.[10]



2a, $R_1 = H; R_2 = CH_3$
b, $R_1 = CH_3; R_2 = H$

4a, $R_1 = H; R_2 = CH_3$
b, $R_1 = CH_3; R_2 = H$

The stereochemistry at the 10 position (methyl-bearing carbon) of **2** was then determined by comparing the effect of added shift reagent [Eu(DPM)$_3$] on the nmr chemical shift of the methyl group in **2** (**a** or **b**) with those of the methyl groups in model compounds **5** and **6**.[11] Plots of methyl group chemical shift against [Eu(DMP)$_3$]/[ketone] for the five methyl groups in these three ketones are shown in Figure 1. This graph clearly shows that the methyl group of the photorearrangement product is the same distance from the carbonyl group as is the 10-position methyl group in **5**;[12] thus its structure can be assigned as **2a**. In addition, the structure of the diketone obtained from ozonolysis of **2a** can be assigned as **4a**.

The hydrogen shift which produces **2** may be viewed as an orbital symmetry allowed [1,3] *suprafacial* sigmatropic reaction. The selectivity observed (70% of the reaction being migration of that hydrogen which is farthest from the carbonyl group and on the face of the π system away from the carbonyl) is a clear indication of some interaction between the carbonyl group and the olefinic group in the reacting species. The nature of this interaction remains to be ascertained.

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[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

[2] G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

[3] R. L. Cargill, T. Y. King, and A. B. Sears, *J. Org. Chem.*, **36**, 1423 (1971), and references cited therein.

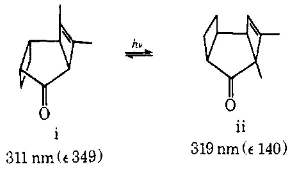
[4] (a) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); (b) P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, 5181 (1969); (c) R. L. Cargill and A. B. Sears, *ibid.*, 3555 (1972).

[5] H.-D. Scharf, *Fortschr. Chem. Forsch.*, **11**, 219 (1969).

[6] P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967).

[7] R. L. Cargill and J. W. Crawford, *J. Org. Chem.*, **35**, 356 (1970).

[8] Although ε 168 does not quite fit into the ε <150 category, the latter coefficient is only meant to roughly separate two categories of β,γ-unsaturated ketones. Another exception to this generalization is compound ii (ε <150), which does undergo photochemical 1,3-acyl migration.[3]



i
311 nm (ε 349)

ii
319 nm (ε 140)

[9] Irradiation of the unmethylated enone, λ_{max}^{EtOH} 296 nm (ε 85), in methylene chloride gave only the saturated ketone as expected. See Experimental Section.

[10] Had **4** (**a** or **b**) instead been a β diketone produced from oxidation of β,γ-unsaturated ketone **3** (**a** or **b**), treatment with base would have produced a keto acid.

[11] N. P. Peet, R. L. Cargill, and D. F. Bushey, *J. Org. Chem.*, **38**, 1218 (1973).

[12] M. R. Willcott, R. E. Lenkinkski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972).

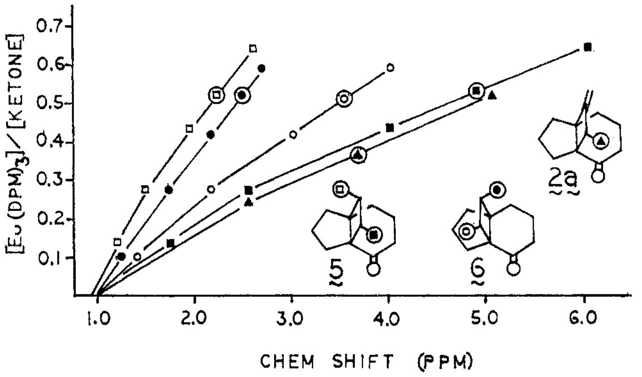


Figure 1.—Effect of nmr shift reagent on methyl groups at varying distances from binding site.

Experimental Section

10-Methyl-11-methylenetricyclo[4.3.2.0]undecan-2-one (2a).—A solution of 2.10 g (11.0 mmol) of 10,11-dimethyltricyclo-[4.3.2.0]undec-10-en-2-one (1)[7] in hexane (450 ml) was irradiated (Corex filter) for 5 hr. Progress of the reaction was monitored by the disappearance of 1 with glpc (3% DEGS, 8 ft × 0.125 in., 110°, 30 cc/min of He). The solvent was removed by distillation and the residue was short path distilled (68°, 0.20 mm) to afford 0.579 g of a four-component mixture. The major product **2a** (*ca.* 70% of mixture) was collected from glpc (20% Carbowax 1000M, 5.5 ft × 0.25 in., 150°, 85 cc/min of He): uv max (95% EtOH) 295 nm (ϵ 62); ir (CCl$_4$) 1690 cm^{-1}; nmr (CCl$_4$) δ 4.88 (m, 2, exo methylene), 2.3–1.1 (m, 13, all ring protons), 0.99 (d, J = 7.2 Hz, 3, methyl); mass spectrum (70 eV) m/e 190 (molecular ion).

Anal. Calcd for C$_{13}$H$_{18}$O: C, 82.06; H, 9.54. Found: C, 81.89; H, 9.63.

Infrared spectra (CCl$_4$) of the three minor components, each of which comprised *ca.* 10% of the isolated product mixture, were very similar to that of **2a**. An nmr spectrum of the crude reaction mixture indicated that **2a** was the major component before glpc analysis.[4c]

10-Methyltricyclo[4.3.2.0]undecane-2,11-dione (4a).—A 0.630-g (3.27 mmol) quantity of ketone **2** in methylene chloride (100 ml) was cooled (−78°) and ozone was passed through the solution until ozone was detected in the effluent gas. The reaction solution was concentrated, and the resulting yellow oil in formic acid (10 ml) and 30% hydrogen peroxide (5 ml) was heated at reflux for 30 min. Concentration of the reaction solution left 0.590 g (94%) of diketone **4a**: mp 108–109°; ir (CCl$_4$) 1770 (cyclobutanone C=O) and 1705 cm^{-1} (cyclohexanone C=O); nmr (CCl$_4$) δ 2.5–1.1 (m, 13, all protons except CH$_3$), 0.93 (d, J = 6 Hz, 3, CH$_3$).

Anal. Calcd for C$_{12}$H$_{16}$O$_2$: C, 74.97; H, 8.39. Found: C, 75.02; H, 8.46.

Attempted Base Cleavage of Diketone 4a.—A 0.590-g (3.07 mmol) quantity of **4a** and 10% Na$_2$CO$_3$ solution (200 ml) were heated at reflux for 2 hr. The cool reaction mixture was extracted with ether (2 × 40 ml) and the combined extracts were washed with saturated NaCl solution (20 ml), dried (MgSO$_4$), concentrated, and sublimed (80°, 0.2 mm) to yield 0.380 g (64%) of recovered **4a**. Acidification of the aqueous phase followed by work-up as above separated an additional 0.050 g (8%) of **4a**.

Irradiation of Tricyclo[4.3.2.0]undec-10-en-2-one.—A solution of 211 mg of tricyclo[4.3.2.0]undec-10-en-2-one[7] in 55 ml of methylene chloride was irradiated (Corex filter) for 30 min. The solvent was removed by distillation and the residual oil was purified by glpc (20% DEGS, 10 ft × 0.25 in., 200°, 50 ml/min He) to give 1,1,2,2-tetrachloroethane and 154 mg (72%) of tricyclo[4.3.2.0]undecan-2-one as the only volatile products: uv max (95% EtOH) 293 nm (ϵ 26); ir (CCl$_4$) 1700 cm^{-1}; the nmr spectrum (CCl$_4$) is a complex absorption centered at *ca.* δ 1.9. This ketone is identical with a sample prepared by catalytic hydrogenation.

The p-toluenesulfonylhydrazone was recrystallized from methanol-water, mp 140–140.5°.

Anal. Calcd for C$_{18}$H$_{24}$N$_2$O$_2$S: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.08; H, 7.25; N, 8.53.

Registry No.—**1**, 22241-70-9; **2a**, 38229-64-0; **4a**, 38229-65-1; tricyclo[4.3.2.0]undec-10-en-2-one, 22241-68-5; tricyclo[4.3.2.0]undecan-2-one, 38229-67-3; tricyclo[4.3.2.0]undecan-2-one p-toluenesulfonylhydrazone, 38229-68-4.

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[13] All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach uber Engelskirchen, West Germany. Infrared spectra were recorded using a Perkin-Elmer Model 257 grating spectrophotometer. All nmr spectra were determined using tetramethylsilane as an internal standard, with a Varian A-60 nmr spectrometer. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. Analytical gas-liquid partition chromatograms were determined using a Varian Aerograph 1200 flame ionization chromatograph, and preparative glpc separations were conducted using a Varian Aerograph 90-P-3 chromatograph. Irradiations were carried out using a Hanovia high-pressure mercury arc (450 W), internal probe, type L, with the filter specified.

O-Alkyl Cleavage of Methyl Esters by 1,5-Diazabicyclo[5.4.0]undecene-5

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In connection with the synthesis of diterpenoid intermediates an improved yield of lactone **2** from bromo ketone **1** was required. The transformation of bromo ketone **1** to a mixture of lactone **2** (47% yield) and ester **3** (40% yield) by refluxing in collidine has been previously reported[2,3] along with the observation that treatment of bromo ketone **1** with sodium methoxide yields only elimination product **3**. The suggestion was offered that a major factor in the contrasting behavior of sodium methoxide and collidine might be the steric requirements of the bases for proton abstraction. Thus we initiated an investigation into the improvement of the yield of lactone **2** by utilizing a variety of bases that have greater steric requirements than collidine. As a result of this study, we now wish to report that the base 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) is useful for the *O*-alkyl cleavage of methyl esters.

Reaction of bromo ketone **1** with 2 equiv of DBU in 10 equiv of *o*-xylene at 165° for 5 hr gave product **5** in 92% yield in the form of a white, crystalline solid, mp 122.5–123.5°. The infrared spectrum showed absorptions at 1650 and 1600 cm^{-1} for the α,β-unsaturated ketone system. The nmr spectrum exhibited resonance signals for a doublet (J = 6 Hz) at δ 1.41 for the C-4 methyl group, a singlet at 1.73 for the C-10 tertiary methyl group, a singlet at 4.33 for the methoxy group, a doublet (J = 1.8 Hz) at 6.91 for the vinylic proton, a multiplet at 7.39 for the C-13 and C-14 protons, and a doublet (J = 9 Hz) at 8.98 for the C-11 proton. Neither lactone **2** nor elimination product **3** were found in the reaction mixture.

Additional evidence for structure **5** was the observation that elimination product **3** could be isolated in 90.5% yield if bromo ketone **1** was allowed to react for only 15 min. Since DBU is known to be a facile de-

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[1] National Defense Education Act Graduate Fellow, 1971–1973.

[2] E. Wenkert, *et al.*, *J. Org. Chem.*, **30**, 713 (1965).

[3] E. Wenkert, *et al.*, *Can. J. Chem.*, **41**, 1924 (1963).