pounds such as Os carbonyl complexes (${}^{1}J({}^{187}\mathrm{Os},{}^{13}\mathrm{CO})$ is around 100 Hz[13]). Moreover, the indirect determination of T_1 via sequence 2 is the method of choice for low-γ spin $^{1}/_{2}$ nuclei in natural abundance samples where there is an observable scalar coupling to a sensitive nucleus like ^{1}H, ^{19}F, or ^{31}P.

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Registry No. 1a, 79151-48-7; **1b**, 122967-30-0; **1c**, 78251-04-4; **2a**, 34742-23-9; **2b**, 122967-31-1; **2c**, 82675-76-1; **3a**, 80822-03-3; **3b**, 122967-32-2; **3c**, 122967-35-5; **4a**, 122967-29-7; **4b**, 122967-33-3; **4c**, 122967-36-6; **5a**, 80822-04-4; **5b**, 122967-34-4; **5c**, 122967-37-7; **6**, 100603-30-3; ^{187}Os, 15766-52-6.

Supplementary Material Available: Indirect 2D (^{1}H,^{187}Os) and (^{31}P,^{187}Os) correlation diagrams of **5a** and **4a**, respectively (2 pages). Ordering information is given on any current masthead page.

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Acid Catalysis of the Photochemical Deconjugation Reaction of 3-Alkyl-2-cyclohexenones[1]

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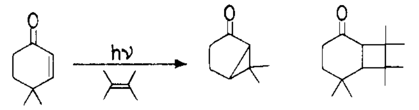
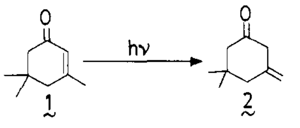
The most common photochemical reactions of simple 2-cyclohexenones are cycloadditions to alkenes[2] and lumiketone rearrangement[3] (eq 1); in addition, if a methyl group is present



(1)

in the 3-position, then photochemical rearrangement to the exocyclic deconjugated isomer can occur[4] (e.g., **1** → **2** in eq 2). The



(2)

deconjugation reaction is also seen for cyclohexenones which are part of fused ring systems.[4c,5] Despite extensive examination, many aspects of the mechanisms of these photochemical reactions remain controversial. In particular, the details of the mechanism of the deconjugation reaction are confused. For example, it has been reported that photochemical deconjugation unaccountably fails for the corresponding 3-ethyl- and 3-isopropyl-2-cyclohexenones,[4b] and there are conflicting results which suggest that the reaction is[5d,f] or is not[5m] second order in enone. The reaction is also oddly solvent sensitive and, depending upon the cyclohexenone structure, usually[4c,d,5d,g,h,j,l] but not always[5a–c,e] fails in alcohols, usually[4c,5g,i,j] but not always[5i] proceeds in alkane solvents, is relatively efficient in benzene[4c,5c–e,h,j,l] and ethyl acetate,[4d,5l] and proceeds in acetonitrile[4c] but not ether.[5i]

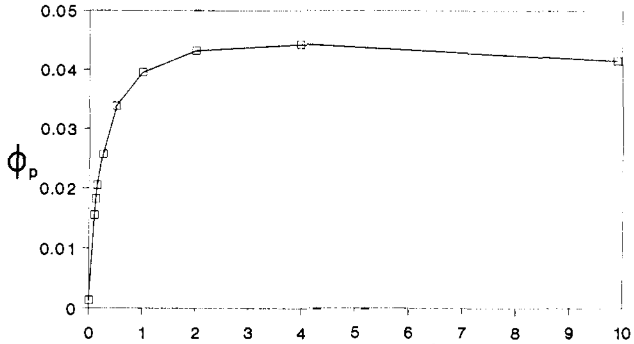


Figure 1. Photochemical isophorone deconjugation at various concentrations of acetic acid: [isophorone] = 0.145 M.

We report here our finding that the photochemical deconjugation reaction of 3-alkylcyclohexenones requires the presence of small amounts of weak acid in order to proceed and that many of the unusual features of the reaction are explained by a mechanism involving acid catalysis.

The quantum yield of deconjugation measured when benzene solutions of 3,5,5-trimethyl-2-cyclohexenone (isophorone, eq 2) were irradiated[6] was found to be variable and apparently depended upon the state of purity of the isophorone. Somewhat unexpectedly, the quantum yield declined when increasingly pure samples of isophorone were used. Addition of small amounts of acetic acid increased the quantum yield beyond that obtained with the least pure samples of isophorone, and a limiting upper value of efficiency was reached at approximately 4×10^{-3} M acid (Figure 1).[7] This suggests that an acidic impurity is present in crude samples of isophorone and that this impurity is required for deconjugation to occur. The presence of such an impurity may account for the earlier finding[5d,h] that the deconjugation of some enones is apparently second order in enone since increasing the concentration of the enone would increase the concentration of the impurity responsible for enhancing the efficiency of deconjugation. Similarly, the reported efficiency of the deconjugation reaction for isophorone in ethyl acetate[4d] may reflect the presence of low levels of acetic acid in this solvent.

Quenching of the deconjugation reaction with isoprene gave a linear Stern–Volmer plot with no curvature at high quencher concentrations. This suggests the involvement of a single excited state; the $k_q\tau$ value was 60 which implicates the lowest triplet excited state of isophorone in the reaction assuming typical values of cyclohexenone triplet lifetimes and rate constants for triplet quenching.[8]

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[1] Contribution No. 422 from the Photochemistry Unit, University of Western Ontario.

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[6] Preparative irradiations were performed in Pyrex with use of water-filtered light from a medium-pressure mercury lamp. Quantum yields were determined with a Photon Technology Inc. Quantacount Instrument. Solutions were 0.145 M in isophorone and were degassed by freeze–pump–thaw procedures. Conversions were determined by gas chromatography relative to an internal standard. No deconjugation occurred in the dark, and no reconjugation of the product occurred in irradiated solutions when allowed to stand in the dark. The deconjugated product was stable to the GC conditions of analysis used.

[7] The decline in quantum yield following attainment of the limiting value continues at higher acetic acid concentrations and is tentatively attributed to acetic acid dimer formation.

[8] Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090.

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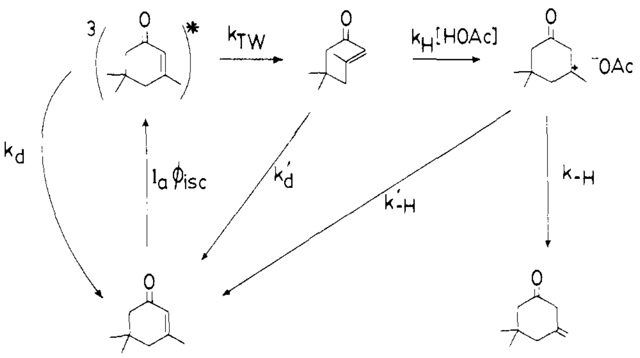
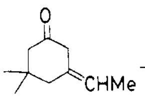
Scheme I



The quantum yield of deconjugation of isophorone solutions containing 4×10^{-3} M acetic acid showed a systematic decline from 0.044 to 0.035 when the isophorone concentration was gradually increased from 0.1 to 1 M. This is inconsistent with a mechanism of deconjugation which is bimolecular in isophorone but is attributable to self quenching of isophorone triplets by ground-state isophorone.[8]

The photochemical deconjugation reaction is reported to fail for 3-alkylcyclohexenones if a 3-methyl group is replaced by larger alkyl groups.[4b] However, we find that if 4×10^{-3} M acetic acid is present, then the reaction does proceed with 5,5-dimethyl-3-ethylcyclohexenone to give a mixture of (*E*)- and (**Z**)-**3**; **4** is also formed as a secondary (Norrish Type I) photoproduct at high conversions.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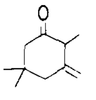
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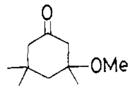
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The simplest explanation of our observations is that the carbon–carbon double bond of the triplet excited state of isophorone is protonated by the acid with Markovnikov regiochemistry to give a carbocation which eliminates to isophorone and the deconjugated product. However, this would require that interception of the triplet with 4×10^{-3} M acetic acid be much more efficient than triplet decay which would require a rate constant for protonation of the order of 10^{12} M^{-1} s^{-1} by acetic acid in benzene. Clearly a longer lived intermediate formed from the triplet is required for reaction with the acid. By analogy with the acid-catalyzed photochemical reactions of cyclohexenes[9] and the results of flash photolysis studies of the reaction of 4,4-dimethylcyclohexenone with alkenes[10] we suggest that the intermediate is a ground-state twisted cyclohexenone (a *trans*-cyclohexenone). This gives rise to the mechanism shown in Scheme I which in turn leads to eq 3 for the dependency of the deconjugation quantum yield, Φ_p, upon acid concentration.[11] The fit of the data from Figure 1 to eq 3 is shown in Figure 2. From the slope and the intercept of the plot the value of k_d'/k_H can be determined and is 1.9×10^{-4} M. The fastest value k_H can adopt is the rate of diffusion (1.5×10^{10} M^{-1} s^{-1} in benzene); and hence k_d' must be $\leq \sim 10^6$ s^{-1}. This corresponds to an intermediate with a lifetime greater than a microsecond which compares with 9 μs for *trans*-1-phenylcyclohexene.[9a]

$$\frac{1}{\Phi_p} = K\left\{1 + \frac{k_d'}{k_H[\mathrm{HOAc}]}\right\} \qquad (3)$$

$$\text{where } \frac{1}{K} = \Phi_{isc}\left\{\frac{k_{-H}}{k_{-H} + k_{-H'}}\right\}\left\{\frac{k_{TW}}{k_d + k_{TW}}\right\}$$

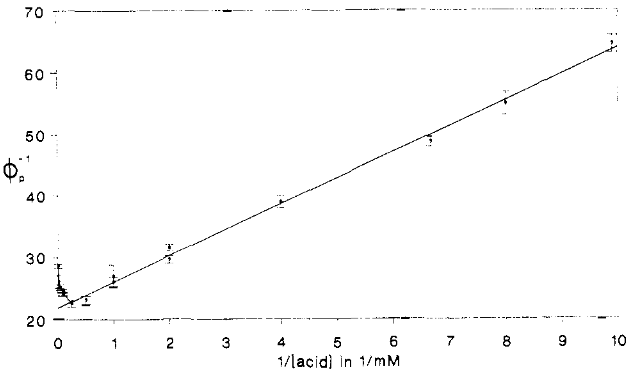

Figure 2. Photochemical isophorone deconjugation at various concentrations of acetic acid: [isophorone] = 0.145 M.

If a highly strained twisted enone or a carbocation are intermediates in the reaction, then they should be trappable by nucleophiles.[12] Indeed, irradiation of isophorone in benzene containing 10% methanol gave a mixture of deconjugated product **2** and the anticipated methyl ether **5** in the ratio 3:1.

Our observation of acid catalysis suggests that the previously reported[4,5] results for the photochemical deconjugation reaction of cyclohexenones need to be reexamined. In addition, our evidence for a twisted intermediate may have consequence for the other reactions of cyclohexenones such as rearrangement and cycloaddition where a similar intermediate has also been proposed;[10] the observation of acid catalysis may also be of relevance to the understanding of the mechanism of photochemical addition of nucleophiles to cyclohexenones and larger ring cycloenones.[12]

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Long-Range Electron Transfer in Structurally Engineered Pentaammineruthenium (Histidine-62)cytochrome *c*

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In many biological processes, long-range electron transfer (ET) plays a key role.[1] When the three-dimensional structures of proteins are accurately known, use of modified proteins[1a,2] and protein–protein complexes[3,4] provides an experimental approach

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