$-44°$ (Figure 1). Such observations indicate a decrease in the fluxional character of Cp_2Hg at these very low temperatures.

A further observation noted during these studies is that, at any particular concentration, the extent to which intermolecular exchange of Cp groups takes place increases in the CpHgX series in the order $X = Cp < Cl < Br < I$. Factors such as steric size of X and the nature of both the Cp–Hg and Hg–X bonds no doubt largely control the over-all rates of Cp group migration. Satellite broadening in the 22° spectrum of Figure 1 is due to intermolecular exchange of Cp groups in the CpHgCl–THF system.[16]

Computer-simulated nmr spectra have been obtained which closely resemble all the experimentally measured spectra, such as those shown in Figure 1. At this stage, however, unambiguous assignments cannot be made to the ^{199}Hg–H spin–spin coupling constants and, therefore, a definite conclusion is not possible at the moment regarding the role played by 1,2 and/or 1,3 shifts of the mercury atom around the Cp ring.

The physical properties of cyclopentadienylmercury compounds in different solvents are currently under investigation, as are the effects of various mono- and bidentate ligands. A full report on the nmr spectra of these and related organomercurials will be published soon.

Acknowledgments. The authors are grateful to Professor G. M. Whitesides, Massachusetts Institute of Technology, and Suzanne V. McKinley, the Dow Chemical Co., for assistance in this work. One of us (M. D. R.) also wishes to thank the National Science Foundation for a grant in partial support of this research program.

(16) We have observed this phenomenon proceeding in a reversible manner up to 120° in a solution of CpHgCl in diethylene glycol–methyl *t*-butyl ether (bp 185°), appreciable thermal stability being demonstrated up to this temperature.

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Received March 24, 1969

Intramolecular Photoreduction of Alkyl α-Diketones[1]

Sir:

Biacetyl (1) has often been employed as a probe for the mechanism of photoreactions in solution.[2–10] On the other hand, until recently[11,12] very little quantitative data[2,3] on the solution photochemistry of biacetyl and its derivatives had been published. The ability of **1** and other α-diketones[13] to phosphoresce with moderate efficiency ($\Phi_P \cong 0.1$) in fluid solution is exceptional and contrasts with the general lack of phosphorescence from fluid solutions of monoketonic compounds.[14] This unusual resistance of biacetyl triplets to radiationless deactivation has not been satisfactorily explained. The fact that (a) **1** has a relatively low triplet energy (E_3 = 56 kcal/mol)[4] and (b) **1** abstracts hydrogen atoms with a rate constant which is very small[2,11,12] relative to alkyl and aryl ketones[15] perhaps gives some hint to the origin of the stability of triplet **1** toward thermal deactivation, since it has been proposed that chemical[16a] or physical[16b] quenching may indeed limit the lifetime of many triplet states in solution.

α-Diketones undergo primary photochemical hydrogen abstraction,[11,17] addition to alkenes,[18] and, possibly, α cleavage.[19] The intramolecular hydrogen abstraction of alkyl α-diketones, possessing a γ carbon bearing a hydrogen atom, yields 2-hydroxycyclobutanones.[17a,b,20] We report here our studies of the rates for intramolecular abstraction of primary, secondary, and tertiary hydrogens for α-diketones **2**, **4**, and **6**, respectively, and compare our data with the intensely studied type II abstraction of branched alkyl ketones.[15,21]

Irradiation of 0.15 *M* benzene solutions of **2**, **4**, and **6** with 4350-Å light results in smooth, and essentially quantitative, formation of the cyclobutanones **3**, **5**, and **7**, respectively.[22] Each reaction is quenched by pyrene (E_3 = 48 kcal/mol),[23] a compound which is expected to be a diffusion-control quencher of triplets **2**, **4**, and **6** ($E_3 \cong$ 56 kcal/mol).[4] The Stern–Volmer plots (in benzene, acetonitrile, and *t*-butyl acohol), for quenching of the photorearrangements indicated in eq 1, are linear. The slopes of these plots may thus be equated to $k_q\tau$ where k_q is the bimolecular rate constant for quenching of α-diketone triplets by pyrene and τ is the α-diketone triplet lifetime. Table I lists $k_q\tau$ values, $1/\tau$ values (calculated from the assumption that $k_q = 5 \times 10^9$ M^{-1} sec^{-1} in benzene),[24] and quan-

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Table I. Photointramolecular Hydrogen Abstraction Reactions of **2**, **4**, and **6**

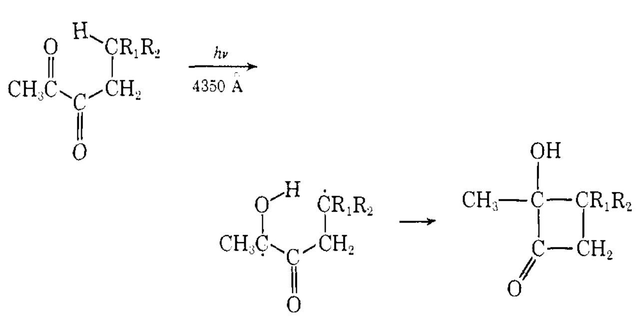
α-Diketone[a]	Solvent	$k_Q\tau$[b]	$1/\tau$[c]	k_r[d]	Φ_{cy}[e]
$CH_3COCOCH_2CH_3$ (**2**)	C_6H_6	1.07×10^5	4.7×10^4	2.5×10^3	0.054
2	C_6H_6	0.81×10^5[f]	6.2×10^4		
2	CH_3CN	1.6×10^5	7.0×10^4	4.4×10^3	0.062
2	$(CH_3)_3COH$	0.43×10^5	5.4×10^4	3.7×10^3	0.069
$CH_3COCOCH_2CH_2CH_2CH_3$ (**4**)	C_6H_6	1.8×10^4	2.7×10^5	1.3×10^5	0.50
$CH_3COCOCH_2CH(CH_3)_2$ (**6**)	C_6H_6	3.2×10^3	1.5×10^6	8.5×10^5	0.57
6	CH_3CN	8.5×10^3	1.3×10^6	8.5×10^5	0.66
6	$(CH_3)_3COH$	2.9×10^3	0.8×10^6	5.0×10^5	0.62

[a] 0.15 *M*, 4350-Å light, Hanovia 450-W lamp, Nonex glass, $CuSO_4$ in NH_4OH (40 g of $CuSO_4 \cdot 5H_2O$ in 68 ml of concentrated NH_4OH, then diluted to 1 l. with water), degassed to less than 10^{-3} mm. Irradiation performed on a "merry-go-round" apparatus. [b] From Stern–Volmer quenching of cyclobutanone formation by pyrene, except where indicated. Maximum error ±10%. [c] Calculated from the assumption that $k_q = 5 \times 10^9$ M^{-1} sec^{-1} in benzene, 11.0×10^9 M^{-1} sec^{-1} in CH_3CN, 2.3×10^9 M^{-1} sec^{-1} in $(CH_3)_3COH$. This rate represents the *maximum* rate constant for intramolecular photoreduction to form **8**, **9**, or **10**. [d] The *minimum* rate constant for intramolecular photoreduction calculated by multiplying $1/\tau$ by Φ_{cy}. [e] Quantum yield for cyclobutanone formation by ferrioxalate actinometry. Maximum error ±10%. [f] From Stern–Volmer quenching of the phosphorescence of **2** (0.05 *M*). Maximum error ±10%.

tum yields for the systems studied. In the case of **2**, Stern–Volmer quenching of the phosphorescence of **2** with pyrene was run. The result (Table I) demonstrates that the $k_Q\tau$ values from the two independent methods agree quite well, reinforcing the conclusion that only triplet α-diketones undergo this rearrangement[2,3,11,12,17b]

The salient features of our results are: (a) the order of magnitude increase in quantum yield in going from primary to secondary (or tertiary) hydrogen abstraction; (b) the remarkably *low* rate constants for intramolecular abstraction relative to alkyl monoketones[15] for which $k_r > 10^8$ sec^{-1}; (c) the relative insensitivity of the reaction rate and Φ_{cy} to solvent polarity and hydrogen bonding; (d) the increased reactivity from **2** to **4** to **6**.

Especially interesting is the low efficiency of rearrangement for **2**. The low values of Φ_{cy} could result from: (a) a low rate constant, k_r, for intramolecular abstraction for the process **2** → **8** relative to the rate constant, k_t, for inherent decay of triplet **2**, or (b) reversal of the hydrogen transfer which converts **8** back to **2**. The rate of triplet decay of biacetyl in benzene[25] under our conditions is 2–4 × 10^4 sec^{-1}. Since the *maximum* value of k_r from Table I is ~5 × 10^4 sec^{-1}, it appears that in contrast to the case for monoalkyl ketones, a major portion of the reaction inefficiency derives from a low value of k_r relative to k_t. A modest amount of hydrogen reversal is suggested by the modest increase in Φ_{cy} as one goes from benzene to more polar solvents. On the other hand, the inefficiency of **6** → **7** is due mainly to hydrogen reversion



2, $R_1 = R_2 = H$ ⟶ 8 ⟶ 3
4, $R_1 = H$, $R_2 = CH_2CH_3$ ⟶ 9 ⟶ 5 (1)
6, $R_1 = R_2 = CH_3$ ⟶ 10 ⟶ 7

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from the intermediate **10**, since even the minimum value of k_r for **6**, when coupled with the k_t expected in analogy to **1** and **2**, leads to an expected Φ_{cy} of unity if reversal is negligible. It should be noted that a moderate increase in Φ_{cy} is found as the solvent polarity increases, as is found for alkyl monoketones.[26]

It seems reasonable to assume that the stability of α-diketone triplets toward radiationless deactivation is probably related to the low reactivity of these molecules toward primary photochemical processes, such as hydrogen abstraction.[27] Furthermore, the relatively low energy of alkyl α-diketone triplets (E_3 = 56 kcal/mol) makes them considerably less accessible to impurity quenching[25] than are alkyl monoketones (E_3 = 78 kcal/mol).[28]

The low reactivity of alkyl α-diketones toward hydrogen abstraction relative to monoalkyl ketones is initially surprising since (a) the electron-withdrawing effect of the adjacent CO group is expected to enhance the reactivity of a n,π^* state[29] and (b) the intermediate biradicals (**8**, **9**, and **10**) are enolic and therefore resonance stabilized.[30] However, the low energy of the starting triplet may make biradical formation more endothermic than is the analogous case for triplet alkyl monoketones. This conclusion is corroborated by bond-energy calculations.[31] The same type of considerations would seem to rationalize the corresponding slow rate of intermolecular hydrogen abstraction by alkyl α-diketones.[12]

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Received June 27, 1969