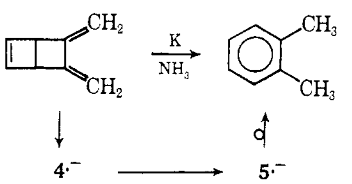
185–187° (MeOH); nmr ($CDCl_3$) τ 2.35–2.65 (m, 5 H), 2.7 (broad, 4 H), 5.2 (s, 4 H); mass spectrum *m/e* 279 (P); ir ($CHCl_3$) ν 1770, 1720, 910, 705, 650 cm^{-1}. The reaction with *N*-phenylmaleimide necessitates heating (DME, 80°, 15 min) and so leads directly to the ring-opened adduct **9**: nmr ($CDCl_3$) τ 2.6–2.85 (m, 9 H), 6.5–7.1 (m, 6 H).

In addition to its novel structure and potential as a source for *o*-xylylene, **4** was of interest because of the possibility that its anion radical would rearrange to **5**$\cdot^-$, a reaction which should be even more exothermic than the **4** → **5** transformation. Under conditions which readily afforded esr spectra of the anion radicals of **6** and other 1,2-diexocyclic dienes[9] (*intra muros* electrolysis in THF at −90° with n-$Bu_4N^+ClO_4^-$ electrolyte), **4** produced no esr signal at all. Since the conditions are sufficient for reduction (and current does flow) and since diene anion radicals are usually stable under these conditions, it may be that **4**$\cdot^-$ does indeed rearrange to **5**$\cdot^-$ which is unable to survive long enough to be detected. Alkali metal reductions also failed to yield esr signals. That Birch reduction (Scheme III) gives *o*-xylene but no 2,3-dimethyl Dewar benzene would also be in accord with the hypothetical rearrangement of **4**$\cdot^-$.

Scheme III



Acknowledgment. The authors are grateful to the National Science Foundation (GP-17596) and the Welch Foundation (F-149) for support.

[9] N. L. Bauld, F. Farr, and G. R. Stevenson, *Tetrahedron Lett.* 9, 625 (1970).

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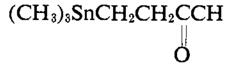
Intramolecular Energy Transfer in the Photochemistry of Keto Organotins

Sir:

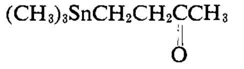
Our knowledge of the photochemistry of aliphatic ketones has increased greatly as a result of recent elegant investigations, and we are thus provided much insight into the behavior of photoexcited 2-alkanones with γ hydrogens.[1] Chemical consequences of photoexcitation may be cleavage of one of the carbon–carbon bonds at the carbonyl group (type I cleavage) or abstraction of a γ hydrogen by the carbonyl oxygen, followed by fragmentation to olefin and enol (type II process) or cyclobutanol formation.[2] In each case the atoms of the carbonyl group participate in the reaction. We have been interested in the question of whether the excitation energy can be transferred from the carbonyl group to another site in the molecule at which reaction might occur.[3] A promising reactive site would have one or more bonds weaker than the C–C or C–H bonds. Our first efforts involved the photochemistry of some keto organosilanes.[4] None of the compounds investigated (in which the carbonyl carbon and the silicon were separated by more than one carbon) showed special reactions which could be attributed to the presence of the silicon atom. We now report extension of these studies to keto organotins in which we do, in fact, find photoinduced reactions profoundly different from those of the ketosilanes and simple *n*-alkanones.

3-Oxobutyltrimethyltin (**1**) was prepared by treating the adduct of trimethyltin hydride with acrylonitrile (2-cyanoethyltrimethyltin) with methylmagnesium bromide. 4-Oxopentyltrimethyltin (**2**) was prepared similarly by treating the adduct of trimethyltin hydride with allyl cyanide (2-cyanopropyltrimethyltin) with methylmagnesium bromide.[5] Carbonyl absorptions of **1** were at 1710 cm^{-1} and 280 nm (ϵ 26) and those of **2** were at 1710 cm^{-1} and 280 nm (ϵ 35), indicating no significant perturbations due to the presence of the trimethyltin group.



$(CH_3)_3SnCH_2CH_2\overset{\displaystyle O}{\underset{\|}{C}}CH_3$

1



$(CH_3)_3SnCH_2CH_2\overset{\displaystyle O}{\underset{\|}{C}}CH_3$

2

Cyclohexane solutions of **1** in quartz vessels were degassed and irradiated with a medium-pressure lamp. A gas identified as methane by its infrared spectrum was evolved. The reaction solution contained no volatile products. When the solvent was removed, a viscous polymeric product remained which reacted rapidly with iodine. Subsequent addition of sodium hydroxide caused precipitation of dimethyltin oxide, which also precipitated when the reaction product mixture was treated directly with hydrogen peroxide. These observations indicate the presence of dimethyltin as a reaction product. Yields of methane ranged from 0.54 to 0.69 mol/mol of ketone reacted and yields of dimethyltin oxide collected ranged from 0.38 to 0.64 mol/mol of ketone. Results obtained with **2** under similar conditions yielded 0.39–0.41 mol of methane and 0.21–0.23 mol of dimethyltin oxide/mol of ketone reacted. When the nitriles from which the ketones were prepared were irradiated under similar conditions no methane was evolved and only a trace of precipitate which might be dimethyltin oxide was formed upon treatment of the photolysis product mixture with hydrogen peroxide. Neither methane nor dimethyltin was formed when tetramethyltin was irradiated with 2-butanone, benzaldehyde, acetophenone, or benzophenone in cyclohexane, nor when trimethyl-3-cyanopropyltin was irradiated with 2-butanone in the same solvent. Thus a substantial fraction of the tin atoms in each keto organotin suffers cleavage of two carbon–tin bonds, and

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[1] N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, 91, 7551 (1969).

[2] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, 5, 21 (1968).

[3] For other recent approaches to the problem of intramolecular transfer see: (a) H. Morrison, *J. Amer. Chem. Soc.*, 87, 932 (1965); (b) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, 87, 2322 (1965); P. A. Leermakers, J. Montillier, and R. D. Rauh, *Mol. Photochem.*, 1, 57 (1969); D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, 92, 2153 (1970).

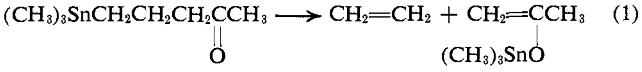
[4] H. G. Kuivila and P. L. Maxfield, *J. Organometal. Chem.*, 10, 41 (1967).

[5] All compounds had satisfactory elemental analyses, and nmr and infrared spectra were consistent with the assigned structures.

it may be inferred that the necessary energy is provided by an excited carbonyl group in the same molecule.

It was presumed that alkyl and organotin radicals were intermediates in these reactions. Therefore, irradiations were carried out (in Pyrex) using carbon tetrachloride, which should react with organotin radicals to form organotin chloride, as solvent. Ethyl mercaptan was also used as a solvent because it would be expected to trap alkyl radicals by hydrogen donation. It proved effective in trapping the organotin radicals as well. Control experiments were carried out with tetramethyltin in each of the solvents. Under the conditions of the photolytic experiments involving the ketones no detectable consumption of tetramethyltin occurred. Upon irradiation in carbon tetrachloride ketones **1** and **2** yielded 0.79 and 0.46 mol of trimethyltin chloride/mol of ketone consumed, respectively. In ethyl mercaptan **1** yielded 0.71 mol of 2-butanone and 0.64 mol of thioethyltrimethyltin [$(CH_3)_3SnSC_2H_5$]. Under similar conditions **2** yielded 0.59 mol of 2-pentanone and 0.44 mol of thioethyltrimethyltin.

By analogy with simple alkanones compound **1** might be expected to undergo α cleavage to give radicals which would react with ethyl mercaptan to form acetaldehyde and trimethylethyltin, neither of which was detected. Similarly compound **2** would be expected to undergo type II fragmentation or cyclobutanol formation, but no trimethylvinyltin was detected nor were any peaks present in the gas chromatogram of the photolysis product mixture which might be due to the expected cyclobutanol. An alternative to γ-hydrogen abstraction would be abstraction of the trimethyltin group on the γ carbon by the oxygen, eq 1. However,



$$(CH_3)_3SnCH_2CH_2CH_2\underset{\underset{O}{\|}}{C}CH_3 \longrightarrow CH_2{=}CH_2 + CH_2{=}\underset{\underset{(CH_3)_3SnO}{|}}{C}CH_3 \qquad (1)$$

there was no indication of a gaseous product (ethylene). Hence it is clear that the normal photochemistry of simple alkanones involving reactions at the atoms of the carbonyl group is substantially, if not completely, bypassed in the keto organotins in favor of reactions at sites two and three bonds removed.

Formation of the products isolated and characterized can be accounted for by eq 2–7. The major initial

$$(CH_3)_3Sn(CH_2)_n\overset{*}{C}OCH_3 \longrightarrow (CH_3)_3Sn\cdot + \cdot(CH_2)_nCOCH_3 \qquad (2)$$

$$(CH_3)_3Sn\cdot \longrightarrow CH_3\cdot + [(CH_3)_2Sn]_n \qquad (3)$$

$$CH_3\cdot + R\text{-}H \longrightarrow CH_4 + R\cdot \qquad (4)$$

$$\cdot(CH_2)_nCOCH_3 + C_2H_5SH \longrightarrow H\text{-}(CH_2)_nCOCH_3 + C_2H_5S\cdot \qquad (5)$$

$$(CH_3)_3Sn\cdot + CCl_4 \longrightarrow (CH_3)_3SnCl + \cdot CCl_3 \qquad (6)$$

$$(CH_3)_3Sn\cdot + C_2H_5S\cdot \longrightarrow (CH_3)_3SnSC_2H_5 \qquad (7)$$

chemical step is cleavage of the carbon–tin bond leading to formation of the trimethyltin and ketoalkyl radicals. The trimethyltin radicals tend to disproportionate to dimethyltin and methyl radicals in a hydrocarbon solvent, but react readily with carbon tetrachloride or thioethyl radicals. Similarly the ketoalkyl radicals tend to end up in polymeric products unless a good hydrogen donor such as ethyl mercaptan is present to trap them as the alkanones. Recovery of substantial yields of the latter suggests that the keto organotins undergo photolysis faster.

Concepts developed for the interpretation of radiationless relaxation processes can be used in interpreting photochemical reactions of alkanones.[6] One feature is the idea that the most reactive atoms in a simple organic molecule are those involved in high-frequency molecular vibrations (*e.g.*, C–H) because they can best accept energy from the high-frequency electronic vibrations. A second factor becomes important in the keto organotins. Since carbon–tin vibrations are of much lower frequency than any others in the molecules examined in this work the low dissociation energy of the carbon–tin bonds determines the course of reaction.

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(6) A. Heller, *Mol. Photochem.*, **1**, 257 (1969).

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Proton Affinity of Trimethylphosphine

Sir:

The recent determinations of the proton affinity of phosphine (185[1a] and 186[1b,c] kcal/mol) show it to be less basic than ammonia (207 kcal/mol).[2] Using ion cyclotron resonance spectroscopy,[3] we have determined the relative proton affinities of the trimethyl derivatives and find trimethylphosphine to have a higher proton affinity than trimethylamine. This is the first case to be encountered in which the substitution of a methyl group for a hydrogen in a binary hydride has resulted in a reversal of the order of proton affinities.[4]

The mass numbers and relative intensities of the principal ions observed in the positive-ion single-resonance spectrum of trimethylphosphine at 10^{-5} Torr and ionizing energies of 20–30 eV are 77 (s), 76 (s), 75 (m), 62 (vw), 61 (s), 60 (w), 59 (m), 58 (w), 57 (w), 48 (vw), 47 (w), 46 (w), 45 (vw), 41 (w), and 40 (vw).[5] Ions of mass above 100 were not initially looked for, but an ion of mass 137 was found in later studies at ionizing energies of 9 and 11 eV. Double-resonance spectra show 77, $(CH_3)_3PH^+$, results from reactions involving 47, 59, 61, and 62 and that all of the reactions involved have a negative dk/dE_{ion}, and thus may be assumed to be exothermic.

Double-resonance spectra were also obtained on the following mixtures: trimethylphosphine + trimethyl-

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(1) (a) D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969); (b) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969); (c) J. R. Eyler, *Inorg. Chem.*, **9**, 981 (1970).

(2) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969).

(3) See J. D. Baldeschwieler, *Science*, **159**, 263 (1969), for a discussion of the technique of cyclotron double resonance used in this study and ref 1a for the use of pressure-ion abundance data in establishing relative basicities.

(4) See ref 1b for the proton affinities of some other binary hydrides and their methyl derivatives.

(5) The symbols used for intensities are s for strong, m for moderate, w for weak, and vw for very weak.