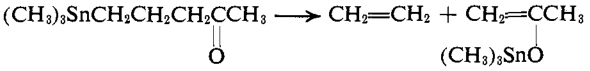
it may be inferred that the necessary energy is provided by an excited carbonyl group in the same molecule.

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.

Acknowledgment. Support of the work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

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

* To whom inquiries should be addressed.

Henry G. Kuivila,* Kuang-Hsin Tsai, Perry L. Maxfield
Department of Chemistry
State University of New York at Albany
Albany, New York 12203

Received June 5, 1970

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-

---

(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.

Table I

							dk/dE_{ion}
$(CH_3)_3NH^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	$(CH_3)_3N$	−
$(CH_3)_3PH^+$	+	$(CH_3)_3N$	→	$(CH_3)_3NH^+$	+	$(CH_3)_3P$	+
$(CH_3)_3P^+$	+	$(CH_3)_3N$	→	$(CH_3)_3NH^+$	+	C_3H_8P	+
$(CH_3)_3P^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	C_3H_8P	−
$(CH_3)_3N^+$	+	$(CH_3)_3N$	→	$(CH_3)_3NH^+$	+	C_3H_8N	−
$(CH_3)_2NCH_2^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	$(CH_3)N(CH_2)_2$	+
$(CH_3)_2NCH_2^+$	+	$(CH_3)_3N$	→	$(CH_3)_3NH^+$	+	$(CH_3)N(CH_2)_2$	+
$(CH_3)_3N^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	$(CH_3)_2NCH_2$	−
$(CH_3)_3N^+$	+	NH_3	→	NH_4^+	+	$(CH_3)_2NCH_2$	+
$(C_2H_5)_3NH^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	$(C_2H_5)_3N$	+
$(CH_3)_3PH^+$	+	$(C_2H_5)_3N$	→	$(C_2H_5)_3NH^+$	+	$(CH_3)_3P$	−
$(CH_3)_3PH^+$	+	$(C_2H_5)_3N$	→	$(C_2H_5)CNH^+$	+	$(CH_3)_3N$	−
$(CH_3)_3N^+$	+	$(C_2H_5)_3N$	→	$(C_2H_5)_3NH^+$	+	C_3H_8N	−
$(C_2H_5)_3NH^+$	+	$(CH_3)_3N$	→	$(CH_3)_3NH^+$	+	$(C_2H_5)_3N$	+
$(C_2H_5)_3N^+$	+	$(CH_3)_3N$	→	$(CH_3)_3NH^+$	+	$C_6H_{14}N$	+
NH_4^+	+	$(CH_3)_2NH$	→	$(CH_3)_2NH_2^+$	+	NH_3	−
$(CH_3)_3P^+$	+	$(CH_3)_2NH$	→	$(CH_3)_2NH_2^+$	+	C_3H_8P	+
$(CH_3)_3PH^+$	+	$(CH_3)_2NH$	→	$(CH_3)_2NH_2^+$	+	$(CH_3)_3P$	+
$(CH_3)_2NH_2^+$	+	$(CH_5)_3P$	→	$(CH_3)_3PH^+$	+	$(CH_3)_2NH$	−
$(CH_3)_2NH_2^+$	+	$(CH_3)_3N$	→	$(CH_3)_2NH^+$	+	$(CH_3)_2NH$	−
$(CH_3)_2NH^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	C_2H_6N	−
$C_2H_6N^+$	+	$(CH_3)_3P$	→	$(CH_3)_3PH^+$	+	C_2H_5N	−
$(CH_3)_3NH^+$	+	NH_3	→	NH_4^+	+	$(CH_3)_3N$	+

amine, trimethylphosphine + triethylamine, trimethylphosphine + dimethylamine + ammonia, ammonia + trimethylamine, trimethylamine + dimethylamine, and trimethylamine + triethylamine. The reactions and the dk/dE_{ion} which may be inferred from these spectra are shown in Table I.

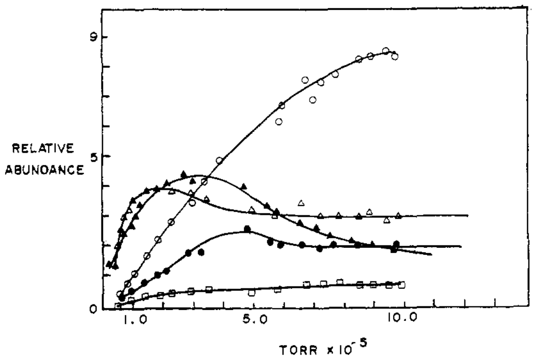


Figure 1. Variation of ion abundances with pressure for an equimolar $(CH_3)_3N$–$(CH_3)_3P$ mixture: □, $(CH_3)_5P_2^+$; ●, $(CH_3)_3NH^+$; △, $(CH_3)_3P^+$; ▲, $(CH_3)_3N^+$; ○, $(CH_3)_3PH^+$.

Combined with the known proton affinities of ammonia and phosphine, these data give the following order of proton affinities

$$(C_2H_5)_3N > (CH_3)_3P > (CH_3)_3N > (CH_3)_2NH > NH_3 > PH_3$$

In order to check the proton affinity of trimethylphosphine relative to trimethylamine we carried out a study of ion abundances in an equimolar mixture of the two compounds at low (9 and 11 eV) ionizing energies.[6]

The results at 11.0 eV are shown in Figure 1, where it may be seen that the $(CH_3)_3PH^+$ ion becomes the predominant species in the mixture of gases at pressures above 4 × 10^{-5} Torr.

There are at least three factors which may account for the greater effect of methyl substituents on the basicity of phosphines than on the basicity of amines: (1) B strain,[7] (2) hyperconjugation,[8] and (3) rehybridization energy.[9,10]

B strain was initially postulated to account for the weakness of trimethylamine compared to mono- and dimethylamine in aqueous solution. Although the results of Munson[11] and of Brauman and Blair[12] (and those obtained here) show that in the gas phase the base strength of the amines increases with an increase in the degree of alkylation, and hence the reversal of base strength in solution on trialkylation must be a solvent effect, B strain could still be important in trimethylamine. Since it would be expected to be relatively unimportant in trimethylphosphine, it could account for the reversal noted. The magnitude of the effect [at least 21 kcal/mol, *i.e.*, PA(NH_3)–PA(PH_3)] is larger, however, than one might expect for B strain.

Hyperconjugation involving the empty d orbitals of phosphorus might account for the difference. To test this possibility, α-deuterated trimethylphosphines were prepared and double- and single-resonance spectra obtained. The double-resonance spectra were ambiguous since 77 → 86 was *not* observed and other species could be coupled by electron exchange as well as proton exchange. The single-resonance spectra indicate that the basicity of the phosphines is not greatly affected by α deuteration. This failure to observe a large secondary deuterium isotope effect on the proton affinity of trimethylphosphine should not be interpreted as conclusive evidence that hyperconjugation is not important in the trimethylphosphonium ion. Halevi[13,14] suggests that in a molecule containing a fully

---

[6] We are grateful to a referee for suggesting this experiment.

[7] H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Amer. Chem. Soc.*, 66, 435 (1944).

[8] D. H. McDaniel, *Science*, 125, 545 (1957).

[9] J. H. Gibbs, *J. Chem. Phys.*, 22, 1460 (1954).

[10] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, p 151.

[11] M. S. B. Munson, *J. Amer. Chem. Soc.*, 87, 2332 (1965).

[12] J. I. Brauman and L. K. Blair, *ibid.*, 90, 6561 (1968).

[13] E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

[14] E. A. Halevi and B. Ravid, *Pure Appl. Chem.*, 8, 339 (1964).

developed positive charge the reduction of hyperconjugation on replacing hydrogen with deuterium may be counterbalanced by an increase in the electron releasing inductive effect of deuterium compared to hydrogen, and thus no isotope effect observed.

The bond angles of ammonia and trimethylamine suggest that the energy required for rehybridization on protonation is small; for phosphine the rehybridization energy may be large, while for trimethylphosphine it should be intermediate. The precise magnitude of the rehybridization energy has not been evaluated.

It is probable that the reversal in gas-phase basicity on methylating ammonia and phosphine is due to a composite of the above factors and possibly some further unrecognized factors.

Acknowledgment. We wish to thank Dr. Fred Kaplan for his helpful instruction in the early stages of our ion cyclotron resonance spectroscopy investigations.

* Address correspondence to this author.

Darl H. McDaniel,* Norman B. Coffman, John M. Strong
Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

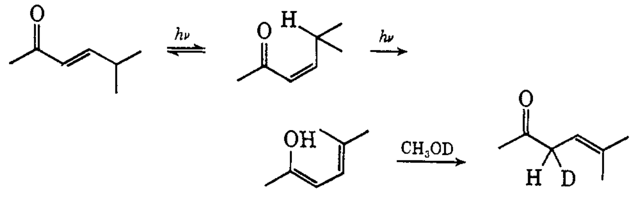
Received June 22, 1970

Photolysis of 1-Acetylcyclooctene. Direct Observation of Dienol Intermediate in Photochemical Deconjugation of α,β-Unsaturated Ketone

Sir:

The photochemical deconjugation of open-chain[1] and some cyclic α,β-unsaturated ketones[2] which bear γ-hydrogen atom(s) is well known. The intermediacy of a 1,3-dienol arising from a 1,5-hydrogen shift has been suggested since photolysis of 5-methyl-3-hexen-2-one in CH_3OD affords 5-methyl-4-hexen-2-one-3-*d* (Scheme I).[3] We wish to report the direct observation of 1,3-dienol formed in the photochemical reaction of 1-acetylcyclooctene (**1**).

Scheme I



A solution of **1** in carefully deoxygenated acetonitrile (*ca.* 5%) was irradiated using light of wavelength longer than 350 nm (aqueous $CuSO_4$ as a filter) at room temperature. The course of the reaction was monitored spectrometrically. After irradiation for 10 hr, **1** was consumed completely, and highly air-sensitive compounds (two components, *vide infra*) were obtained in 80% yield. The infrared spectrum showed no carbonyl absorption, but characteristic bands at 3450 (OH), 1656 (C=C), and 1191 cm^{-1} (C–O). The ultraviolet absorption exhibited a maximum at 255 nm (log ϵ *ca.* 4.0). The nmr signals due to the olefinic protons (Figure 1) are compatible only with a mixture of dienols **2a** and **3b** in a 5:1 ratio.[4,5] Appearance of the H_a signal at lower field than that of $H_{a'}$ is ascribed to the anisotropic effect of the enol oxygen. The hydroxyl signal at δ 5.68 disappeared upon addition of CH_3OD.[6] The assignments were ascertained by double resonance techniques.

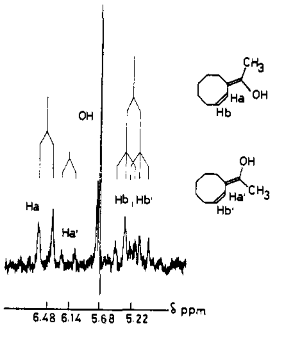
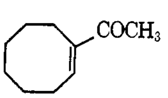
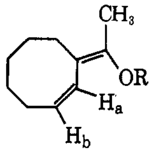


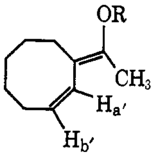
Figure 1. The nmr spectrum of the photolysate of **1** (5% CH_3CN solution, 60 MHz, TMS).



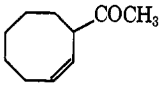
1



2a, R = H
b, R = COCH₃



3a, R = H
b, R = COCH₃



4

These new isomers in acetonitrile were fairly stable in the dark, and remained practically unchanged for 3 days at room temperature. Heating at 100° for 2 hr gave a mixture of 3-acetylcyclooctene (**4**)[7,8] and the starting enone **1** (83:17 ratio). Addition of a trace amount of sulfuric acid at room temperature caused instantaneous conversion to a mixture of ketones **4** and **1** (75:25), while exposure to potassium *tert*-butoxide in *tert*-butyl alcohol afforded **4** exclusively. Treatment with acetic anhydride–pyridine at −20° furnished the dienol acetates **2b**[9] and **3b**[10] (60% yield, 5:1 ratio)

---

(1) For a review see N. C. Yang in "Reactivities of the Photoexcited Molecule," Interscience, New York, N. Y., 1967, p 145.

(2) (a) H. Nozaki, T. Mori, and R. Noyori, *Tetrahedron*, **22**, 1207 (1966); (b) R. G. Carlson and J. H. Bateman, *Tetrahedron Lett.*, 4151 (1967).

(3) N. C. Yang and M. J. Jorgenson, *ibid.*, 1203 (1974).

(4) Silylation with *N,O*-bis(trimethylsilyl)acetamide followed by glpc analysis gave the same isomeric ratio.

(5) The splitting patterns show a close resemblance to those of 3-methylenecyclooctene prepared from 2-cyclooctenone and methylenetriphenylphosphrane: $J_{\mathrm{Ha-Hb}} = J_{\mathrm{Ha'-Hb'}} = 12$ Hz and $J_{\mathrm{Hb-C}H_2} = J_{\mathrm{Hb'-C}H_2} = 8$ Hz.

(6) The spectrum at higher field (in CD_3CN) is rather complicated by overlapping with signals of high molecular weight by-products (<20%) and CHD_2CN, but exhibits distinct singlets at δ 1.88 and 1.82 arising from methyl groups of **2a** and **3a**, respectively.

(7) All stable new compounds gave correct elemental analyses and molecular peaks in mass spectra.

(8) E. J. Corey and L. S. Hegedus, unpublished data; L. S. Hegedus, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1970.

(9) Spectral characteristics for **2b** are: uv (95% C_2H_5OH) 241 nm (log ϵ 4.15); ir (neat) 1755 and 1207 cm^{-1} (acetate); nmr (CCl_4, TMS) δ 1.59 (m, 6, CH_2), 1.87 (s, 3, $=C(OCOCH_3)CH_3$), 2.07 (s, 3, $COCH_3$),