10^{10} and $(5.3 \pm 0.5) \times 10^9$ M^{-1} sec^{-1}. The protonated form of the acrylate radical anion has[4] λ_{max} 260 nm and ϵ_{260} 7.7×10^3 M^{-1} cm^{-1} and is tentatively assigned the structure $CH_2\cdots CH\cdots C(OH)\cdots O\cdot^-$. This radical decays by first-order kinetics with $k = (4.0 \pm 0.5) \times 10^4$ sec^{-1}, to give a transient species A. On ionization of this radical, $pK_a = 7.0 \pm 0.1$ (ref 4), the spectrum at pH 9.5 of the radical dianion $CH_2\cdots CH\cdots CO_2\cdot^{2-}$ has λ_{max} 285 nm and ϵ_{285} 9.7×10^3 M^{-1} cm^{-1} (see Figure 1a). This radical decays by a first-order process with $k = (7.7 \pm 0.6) \times 10^4$ sec^{-1} at pH 9.5 and $\mu = 0.01$ M, to give the same transient species, A. Species A has completely different spectral characteristics, with λ_{max} 330 nm and ϵ_{330} 1.1×10^3 M^{-1} cm^{-1}. At pH 12.0, the only transient observed with our time resolution of ~0.1 μsec is identical with that produced at pH 9.5 by the decay of the $CH_2\cdots CH\cdots CO_2\cdot^{2-}$ radical dianion (see Figure 1a). Species A decays at both pH 9.5 and 12.0 by second-order kinetics with $2k = (1.0 \pm 0.2) \times 10^9$ M^{-1} sec^{-1}.

The physical parameters of species A are in excellent agreement with the previously reported[5] absorption spectrum of the $CH_3\dot{C}HCOO^-$ radical produced by the reaction

$$e_{aq}^- + CH_3CHClCOO^- \longrightarrow CH_3\dot{C}HCOO^- + Cl^-$$

More recent esr work on the interaction of e_{aq}^- with acrylate ion in a flow system at 20° reported[6] $CH_3\dot{C}HCOO^-$ as the only observable radical. These workers were apparently unable to observe the $(CH_2{=}CHCOO^-)^-$ radical owing to its relatively short lifetime.

The protonation of the dianion $CH_2\cdots CH\cdots CO_2\cdot^{2-}$ at the β position was found to be catalyzed by hydroxide ions (see Figure 1 and Table I) with $k = (7.7 \pm 0.3) \times 10^8$ M^{-1} sec^{-1} to give the $CH_3\dot{C}HCOO^-$ radical. In the pH range 7.8–9.5 (*i.e.*, at low hydroxide ion concentrations), this protonation reaction is catalyzed by NH_3, NH_4^+, $H_2PO_4^-$ (not HPO_4^{2-}), $HP_2O_7^{3-}$, and borate buffers; see Table I. This reaction is thus subject to general base and general acid catalysis. Weak acids would appear to favor protonation at the β-carbon atom in contrast to protonation on oxygen by H_3O^+. Since the corresponding acrylamide radical anion $CH_2\cdots CH\cdots CONH_2\cdot^-$ does not undergo catalysis of protonation by OH^- ions, the ionized carboxyl group in acrylate presumably affects the interaction with OH^- and the buffers examined.

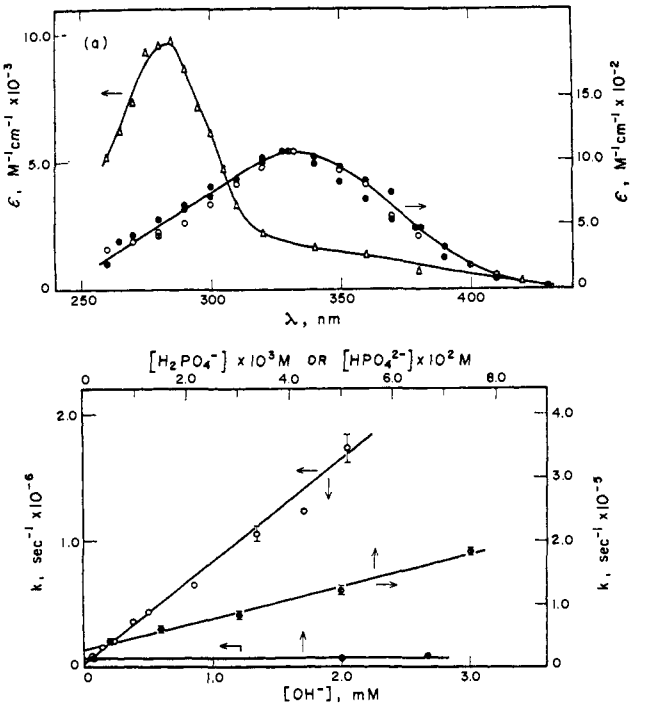

Figure 1. (a) Transient absorption spectra resulting from the action of e_{aq}^- on acrylate ion in air-free aqueous 1.0 M *tert*-butyl alcohol solutions at pH 10.0 (2 mM acrylate, ~8 krads/pulse, OD read at "zero time," Δ, and at 20 μsec after the electron pulse at pH 10.0, ●) and at pH 12.0 (5 mM acrylate, ~19 krads/pulse, read at "zero time," ⊗). Transient spectrum of the $CH_3\dot{C}HCOO^-$ radical, ⊙, produced from the action of e_{aq}^- on α-chloropropionic acid (50 mM, pH 9.2, 1.0 M *t*-BuOH, ~19 krads/pulse). (b) Dependence of the pseudo-first-order rate of decay of the acrylate radical dianion (5 mM acrylate, 1.0 M *t*-BuOH, dose ~8 krads/pulse) at 285 nm upon the concentrations of OH^- ions (⊙), $H_2PO_4^-$ (⊗), and HPO_4^{2-} · ions (●).

Table I. Second Order Rate Constants for the Protonation of the Acrylate Radical Dianion in Water by Various Buffers[a]

Buffer	Ionic strength, μ	Rate k, M^{-1} sec^{-1}
OH^-	0.03	$(7.7 \pm 0.3) \times 10^8$
$H_2PO_4^-$	0.22	$(2.0 \pm 0.2) \times 10^7$
HPO_4^{2-}	0.20	$\leq 4.0 \times 10^4$
$HP_2O_7^{3-}$	0.50	$(1.4 \pm 0.1) \times 10^6$
NH_4^+	0.10	$(9.0 \pm 0.5) \times 10^5$
NH_3	0.10	$(2.5 \pm 1.0) \times 10^6$
$B(OH)_4^-$	0.22	$(6.0 \pm 1.5) \times 10^5$
$B(OH)_3$	0.1–0.5	$(3.0 \pm 0.5) \times 10^5$

[a] Determined by following the pseudo-first-order decay of the acrylate radical dianion at 285 nm in presence of various concentrations of the buffers. In the presence of 1 mM buffers, the acrylate radical dianion decays at pH 8.2 with $k = (3.5 \pm 0.5) \times 10^4$ sec^{-1}. See also text and Figure 1.

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E. Hayon*
Pioneering Research Laboratory, U. S. Army Natick Laboratories
Natick, Massachusetts 01760

N. N. Lichtin, V. Madhavan
Department of Chemistry, Boston University
Boston, Massachusetts 02215

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(4) E. Hayon, N. N. Lichtin, and V. Madhavan, to be submitted for publication.
(5) P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, **73**, 4207 (1969).
(6) P. Neta and R. W. Fessenden, *J. Phys. Chem.*, **76**, 1957 (1972).

Reaction of *S*-(2-Pyridyl) Thioates with Grignard Reagents. A Convenient Method for the Preparation of Ketones

Sir:

Many reports on the synthesis of ketones from organometallic compounds and carboxylic acid derivatives[1] have appeared. The reactions of Grignard

(1) (a) D. A. Shirley, *Org. React.*, **8**, 28 (1954); (b) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954; (c) G. Posner and C. E. Witten, *Tetrahedron Lett.*, 4647 (1970); (d) A. Meyers and E. M. Smith, *J. Org. Chem.*, **37**, 4289 (1972); (e) A. Meyers and N. Nazarenko, *ibid.*,

reagents with acid chlorides, nitriles, acid amides, and acid anhydrides are frequently employed for this purpose. However, tertiary alcohols are invariably undesirable by-products except in the case of nitriles.

Staab and Jost[2] reported that Grignard reagents react with *N*-acylimidazoles to afford ketones in fairly good yields. Recently, Sakan and Mori[3] reported a convenient method for the synthesis of ketones from Grignard reagents and 8-acyloxyquinolines probably through an important intermediate of 8-acyloxyquinoline metal complex.

As part of our study on the carbon–carbon bond forming reaction by the use of 2-pyridyl sulfides,[4] we found that various *S*-(2-pyridyl) thioates (R^1COSPy)[5] react very rapidly with Grignard reagents (R^2MgBr) to give ketones in excellent yields by simple procedures. For example, to a solution of 5.26 mmol of *S*-(2-pyridyl) hexanethioate in 10 ml of dry THF was added a THF solution of phenylmagnesium bromide (approximately 1 mol equiv) until *S*-(2-pyridyl) hexanethioate disappeared (checked by tlc) at 0° under an argon atmosphere. By the addition of 0.2 ml of water, the solution turned yellow and a white precipitate immediately appeared. The reaction products, amyl phenyl ketone, 2-pyridinethiol, and 2,2′-dipyridyl disulfide (formed by air oxidation during work-up) were isolated by silica gel thin layer chromatography in 86, 52, and 44% yields, respectively. Alternatively, after the addition of water, the solvent was removed and the residue extracted with ether in the usual manner. The organic layer was washed with 1 *N* sodium hydroxide solution to remove 2-pyridinethiol and water, dried (Na_2SO_4), and distilled, after the removal of the solvent, to yield amyl phenyl ketone (83%, bp 134–137° (17 mm)).

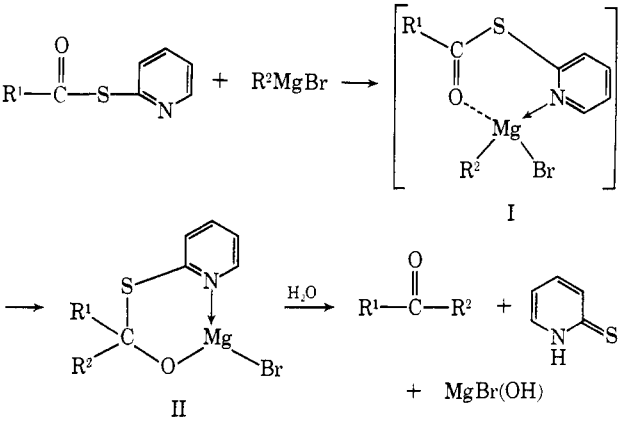
In a similar manner, aromatic ketones and primary and secondary aliphatic ketones such as benzophenone, *n*-butyl phenethyl ketone, cyclohexyl phenethyl ketone, *sec*-butyl phenethyl ketone, and acetophenone were obtained in excellent yields as shown in Table I. In addition, it was found that a diketone such as 1,4-dibenzoylbutane was obtained in 92% yield by treating bis[*S*-(2-pyridyl)] hexanebisthioate with phenylmagnesium bromide. In all cases, the amounts of tertiary alcohols were less than 1%.

The preferential formation of ketones may be explained by assuming initial formation of an "ate" complex I from the Grignard reagents and *S*-(2-pyridyl) thioates. The complex I is immediately converted to the second six-membered complex II as a result of the addition of Grignard reagents to the carbonyl group. Since the complex II, stabilized by the coordination of the nitrogen atom to the magnesium atom, reacts very sluggishly with Grignard reagents as compared with *S*-(2-pyridyl) thioates, further reaction with the Grignard reagents giving tertiary alcohols is prevented.

Table I. Reaction of *S*-(2-Pyridyl) Thioates with Grignard Reagents in THF

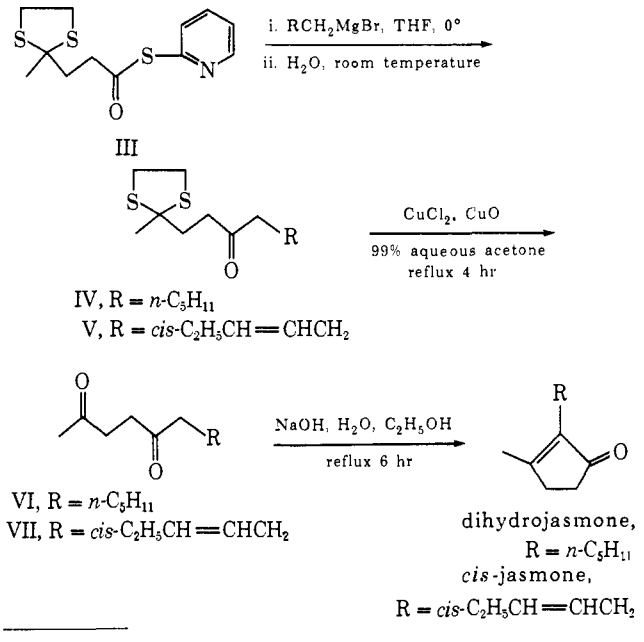
R^1	R^2	R^1COR^2, %[a]
Ph	Ph	94[b]
$PhCH_2CH_2$	n-C_4H_9	97
$PhCH_2CH_2$	c-C_6H_{11}	95
$PhCH_2CH_2$	*sec*-C_4H_9	83
CH_3	Ph	91
n-C_5H_{11}	Ph	86
$-(CH_2)_4-$	Ph[c]	92[d]

[a] Isolated yields by preparative tlc (silica gel). [b] To a benzene solution of *S*-(2-pyridyl) thiobenzoate was added a THF solution of phenylmagnesium bromide. [c] Two molar amounts of phenylmagnesium bromide were used. [d] The yield of 1,4-dibenzoylbutane.



The present ketone synthesis was successfully applied to the preparations of *cis*-jasmone and its analog through 1,4-diketone[6] starting from levulinic acid as shown in Scheme I. The thioate III was prepared

Scheme I



38, 175 (1973); (f) M. J. Jorgensen, *Org. React.*, **18**, 1 (1970); (g) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970); (h) J. E. Dubois and M. Boussu, *ibid.*, 2523 (1970).

(2) H. A. Staab and E. Jost, *Justus Liebigs Ann. Chem.*, **655**, 90 (1962).

(3) T. Sakan and Y. Mori, *Chem. Lett.*, 793 (1972).

(4) (a) T. Mukaiyama, K. Narasaka, K. Maekawa, and M. Furusato, *Bull. Chem. Soc. Jap.*, **44**, 2285 (1971); (b) T. Mukaiyama, S. Yamamoto, and M. Shiono, *ibid.*, **45**, 2244 (1972); (c) K. Narasaka, M. Hayashi, and T. Mukaiyama, *Chem. Lett.*, 259 (1972).

(5) The thioates listed in Table I were synthesized in good yields by the reaction of corresponding acid halides with 2-pyridinethiol in the presence of tertiary amines. After the usual work-up, the thioates were purified by distillation, recrystallization, or column chromatography.

(6) Other methods through a 1,4-diketone are found in the following references: (a) G. Büchi and H. Wüest, *J. Org. Chem.*, **31**, 977 (1966); (b) L. Crombie, P. Hemesley, and G. Pattender, *J. Chem. Soc. C*, 1924 (1969); (c) J. E. McMurry and J. Melton, *J. Amer. Chem. Soc.*, **93**, 5309 (1971); (d) R. A. Ellison and W. D. Woessner, *J. Chem. Soc., Chem. Commun.*, 529 (1972).

from levulinic acid by two steps[7] and isolated by silica gel column chromatography (97% based on levulinic acid). The ketone IV was obtained in 97% yield by the reaction of III with *n*-hexylmagnesium bromide, and the hydrolysis of IV by our method[8] afforded 1,4-diketone (VI) in 98% yield. Dihydrojasmone was obtained from VI according to the method of Hunsdieker[9] in 84% yield. Analogously, olefinic 1,4-diketone (VII) was isolated in 82% yield by the reaction of III with 3-*cis*-hexenylmagnesium bromide, followed by the hydrolysis[8] of the ethylene dithioacetal. VII was converted to *cis*-jasmone in 81% yield by the ordinary procedure.[9]

From the above results, it was assumed that thioates having a skeleton such as RCOSC(=N)— would preferably form ketones by treatment with Grignard reagents through the coordination intermediate. In fact, it was found that benzophenone was obtained in 98% yield by the reaction of 2-(benzoylthio)benzothiazole with phenylmagnesium bromide.

(7) The thioate III was prepared by the reaction of 4-oxovaleric acid ethylene dithioacetal, which was obtained from levulinic acid and ethanedithiol, with 2,2'-dipyridyl disulfide and triphenylphosphine in acetonitrile at room temperature for 10 min; T. Endo, S. Ikenaga, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **43**, 2632 (1970).

(8) K. Narasaka, T. Sakashita, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **45**, 3724 (1972).

(9) H. Hunsdieker, *Chem. Ber.*, **75**, 460 (1942).

Teruaki Mukaiyama,* Masashi Araki, Hisashi Takei
Laboratory of Organic Chemistry, Tokyo Institute of Technology Ookayama, Meguro-ku, Tokyo, Japan
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"Solvent Effects" on the Chemiluminescent Decomposition of Tetramethyl-1,2-dioxetane. Competitive Dark Pathways

Sir:

The kinetic parameters of the thermal decomposition of tetramethyl-1,2-dioxetane (TMD), which generates high yields of triplet acetone and very little excited singlet,[1] have recently been reported to be solvent dependent.[2] Thus, $\Delta H^{\ddagger}$ drops from 25 kcal in benzene to 13 kcal in methanol, while $\Delta S^{\ddagger}$ changes from -1 to -34 eu. The greatly altered activation parameters in methanol, assumed to belong to the same luminescent mechanism as in benzene, were taken to support a unique concerted, spin-forbidden process resulting in one excited triplet and one ground-state acetone molecule. The addition of amines[3] has recently been shown to catalyze, with a very similar lowering of the activation energy, the decomposition of *cis*-diethoxydioxetane[4] *via* a competitive "dark" pathway, superposed on the normal chemiluminescent decomposition. We present evidence here that TMD decomposes similarly by two competitive paths in methanol and ethanol, and that the *fast* reaction in these solvents produces no excited acetone, for (a) the faster the reaction, the lower the net luminescence yield, (b) the activation energy of the *luminescent* pathway is unchanged in the hydroxylic solvents, (c) the yield of reaction products from intercepted triplet acetone runs parallel to the chemiluminescence yield, and (d) exclusion of oxygen converts the benzene reaction from one of first order to one of second order in dioxetane, as predicted by a previous treatment,[5] but has no effect on the order of the alcohol reaction. In addition, we show that the very rapid dark reaction is not due to the alcohols themselves, but to a powerful catalyst present in traces even after careful distillation.

Table I. Activation Energy of Luminescent TMD Decomposition from Temperature Drop[a]

Solvent	Fluorescer	E_{chl}, kcal M^{-1} [b]	E_a, kcal M^{-1} [b]
Benzene	None added	27	27 } av 26.5
	DBA	22	26 }
Ethanol	None added	23	23 } av 25.7
	DBA	22	26 }
Methanol	DBA	24	28

[a] Air present; temperature range, 50–70°; [TMD], 0.04 or 0.08 M; $E_a = E_{chl} - E_{\Phi F'}$. [b] ±2 kcal.

In the chemiluminescent decomposition of TMD,[6] the initial luminescence intensity (acetone fluorescence; no fluorescer added) is proportional to the initial concentration of dioxetane multiplied by the rate constant for chemiluminescent cleavage, while the rate of decline of this intensity is proportional to the total decomposition rate of the TMD by all mechanisms. Thus it is possible to study a dark reaction by observing the intensity and decay rate of the competitive chemiluminescent reaction. Although the rates of decay of luminescence from TMD at 57° can be 100 times greater in methanol or ethanol than in benzene, the initial intensities are not larger and therefore the overall quantum yields are significantly smaller in the alcohols. When 9,10-dibromoanthracene (DBA) is added to the benzene or alcohol solution of TMD, the luminescence yields in both solvents are considerably increased (because DBA receives its excitation energy from triplet acetone, much the more abundant donor here), but again the yields are much higher in benzene (by two to three orders of magnitude over the yields in methanol). Thus, unless ethanol and methanol were effective quenchers of singlet and triplet acetone, which is not the case,[7] these results mean that fewer molecules of acetone are generated in excited states in these solvents.

The activation energy of the luminescent process is measured by quickly cooling,[8] from T_1 to T_2, a dioxetane solution undergoing chemiluminescent decomposition and measuring the light intensities immediately before, I_1, and after, I_2, the temperature drop.[3,4b] Because the

(1) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(2) (a) N. J. Turro and P. Lechtken, *ibid.*, **95**, 264 (1973); (b) *Pure Appl. Chem.*, **33**, 363 (1973).

(3) D. C.-S. Lee and T. Wilson, presented at the International Conference on Chemiluminescence, Athens, Ga., Oct 1972; in "Chemiluminescence and Bioluminescence," M. J. Cormier, D. M. Hercules, and J. Lee, Ed., Plenum Press, New York, N. Y., 1973, p 265.

(4) (a) This reaction, when uncatalyzed, also generates high yields of triplet carbonyl fragments; (b) see T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).

(5) P. Lechten, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973). We thank Dr. Turro for a prepublication copy of this manuscript.

(6) All chemiluminescence procedures as in ref 4. TMD was prepared according to Dr. K. R. Kopecky's procedure (private communication). All solvents were Mallinckrodt, AR, used without further purification unless indicated otherwise.

(7) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

(8) ~30 sec, so that the concentration of dioxetane can be considered constant throughout this interval.