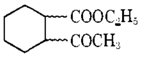
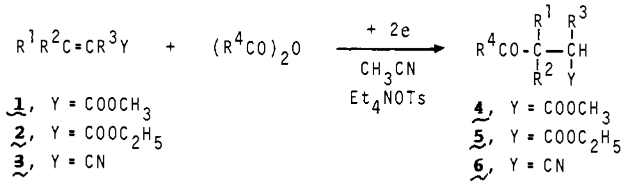
Table I. Electroreductive Acylation of α, β-Unsaturated Esters 1 and 2, and Nitriles 3 with Acid Anhydrides

Compd	Ester and Nitrile R^1	R^2	R^3	Acid anhydride, R^4	Product	No.	Yield, %[a]
1a	H	H	H	CH_3	$CH_3COCH_2CH_2COOCH_3$	4a	62
				n-C_3H_7	n-$C_3H_7COCH_2CH_2COOCH_3$	4b	63
				i-C_3H_7	i-$C_3H_7COCH_2CH_2COOCH_3$	4c	50
1b	CH_3	H	H	CH_3	$CH_3COCH(CH_3)CH_2COOCH_3$	4d	75
				n-C_3H_7	n-$C_3H_7COCH(CH_3)CH_2COOCH_3$	4e	82
				i-C_3H_7	i-$C_3H_7COCH(CH_3)CH_2COOCH_3$	4f	74
1c	CH_3	CH_3	H	CH_3	$CH_3COC(CH_3)_2CH_2COOCH_3$	4g	64
1d	CH_3	H	CH_3	CH_3	$CH_3COCH(CH_3)CH(CH_3)COOCH_3$	4h[b]	68
2a	C_6H_5	H	H	CH_3	$CH_3COCH(C_6H_5)CH_2COOC_2H_5$	5a[c]	58
				C_2H_5	$C_2H_5COCH(C_6H_5)CH_2COOC_2H_5$	5b	75
2b	H	$-(CH_2)_4^-$		CH_3		5c[d]	74
3a	CH_3	H	H	CH_3	$CH_3COCH(CH_3)CH_2CN$	6a	51
3b	C_6H_5	H	H	CH_3	$CH_3COCH(C_6H_5)CH_2CN$	6b	76

[a] Isolated yields. [b] Methyl 2-acetyl-2, 3-dimethyllevulinate was also formed in a 7% yield. [c] Ethyl 3-phenylpropionate and ethyl 2-acetyl-3-phenyllevulinate were also obtained in 14 and 8% yields, respectively. [d] A mixture of cis (18%) and trans (56%) isomers.



$$R^1R^2C{=}CR^3Y + (R^4CO)_2O \xrightarrow[\substack{CH_3CN\\ Et_4NOTs}]{+\ 2e} R^4CO\text{-}\overset{R^1}{\underset{R^2}{C}}\text{—}\overset{R^3}{\underset{Y}{CH}}$$

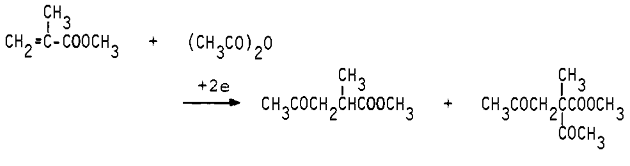
1, Y = $COOCH_3$
2, Y = $COOC_2H_5$
3, Y = CN

4, Y = $COOCH_3$
5, Y = $COOC_2H_5$
6, Y = CN

method seems one of the most promising methods of the syntheses of such compounds as may be expected to be formed from the reaction of acyl anion.

A typical procedure is described below. A solution of 20 g (0.067 mol) of tetraethylammonium p-toluenesulfonate in 80 ml of anhydrous acetonitrile was placed in cathodic (64 ml) and anodic (16 ml) chambers of a cell equipped with carbon rod electrodes, a reference electrode, and a ceramic diaphragm. To the catholyte was added 1.00 g (0.01 mol) of **1b** and 10.2 g (0.10 mol) of acetic anhydride. The catholyte was stirred with a magnetic bar and electrochemically reduced at the cathode potential of −2.3 to −2.5 V vs. SCE under the external cooling with a water bath until 4 F/mol of electricity was passed. The usual workup gave the γ-keto ester **4d** in a 75% yield (bp 96–98 °C (24 mm); lit[6] bp 82–83 °C (10 mm)). In a similar manner, γ-keto esters **4a–h** and **5a–c** and nitriles **6a,b** were obtained in satisfactory yields as shown in Table I.[7]

Generally, the acyl group was introduced exclusively to the β-carbon atoms of **1**, **2**, and **3**, and the formation of α,β-diacylated products was <2–3% except **1d** and **2a**. The electroreduction of methyl methacrylate under similar conditions, however, gave a mixture of a γ-keto ester and a α,β-diacylated ester in 43 and 50% yields, respectively, though the factors which controlled the α,β-diacylation were not known.



$$CH_2{=}\overset{CH_3}{C}\text{-}COOCH_3 + (CH_3CO)_2O \xrightarrow{+2e} CH_3COCH_2\overset{CH_3}{CH}COOCH_3 + CH_3COCH_2\overset{CH_3}{\underset{COCH_3}{C}}COOCH_3$$

The substitution of acid anhydrides by acid chlorides[8] in this electroreduction brought about generally a considerable decrease in the yields of **4** and **5**.[9] For instance, the electroreduction of **2a** in the presence of acetyl chloride and propionyl chloride gave **5a** (39%) and **5b** (56%), respectively. The controlled potential electrolysis (CPE) of **2a**[10,11] in the presence of acetic anhydride at −1.95 V vs. SCE[12] led to the formation of **5a**, while that at −1.40 V vs. SCE resulted in the almost complete recovery of **2a**. Similarly, the γ-keto ester **4d** was formed from the CPE of **1b** at −2.40 V vs. SCE.[10,11] These facts suggest that the electron transfer from the cathode to the activated olefins yielding anionic species is the initiation step of the reductive acylation. The detail of reaction mechanism will be the subject of future study.

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(5) (a) The electrochemical acylation of benzyl chloride with acid chlorides has been established by the authors: T. Shono, I. Nishiguchi, and H. Ohmizu, *Chem. Lett.*, 1021 (1977). (b) T. J. Curphey, T. D. Trivedi, and T. Layloff, *J. Org. Chem.*, **39**, 3831 (1974).

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(7) All the products described herein were identified by spectroscopic and elemental analyses and/or by the comparison with authentic samples.

(8) The molar ratio of acid chlorides to activated olefins was 3:1.

(9) The electroreduction of 1**b** in the presence of propionyl chloride gave methyl 3-methyl-4-oxohexanoate only in a 13% yield.

(10) The cyclic voltammetry of 1**b** and **2**a in 0.83 M $Et_4NOTs–CH_3CN$ showed reduction waves at −2.63 and −1.95 V (E_P) vs. SCE, respectively.

(11) The polarographic half-wave potentials ($E_{1/2}$) of ethyl crotonate and **2**a in 0.1 M Et_4NI–DMF were reported to be −1.84 and −1.27 V vs. Hg pool, respectively: J. P. Petrovich, *Electrochim. Acta*, **12**, 1429 (1967).

(12) The voltammetry of acetic anhydride in 0.83 M $Et_4NOTs–CH_3CN$ did not show any reduction wave until −2.8 V vs. SCE.

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Solvent Regulated Photochemical Behavior of a Tris(β-diketonate)rhodium(III) Complex

Sir:

Numerous studies[1,2] have established the general photoreactivity patterns of first row transition metal β-diketonate complexes (I). Thus visible or near-ultraviolet irradiation in-

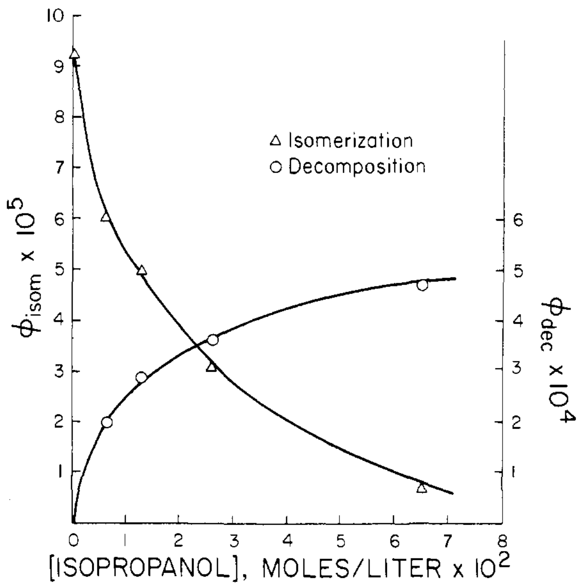
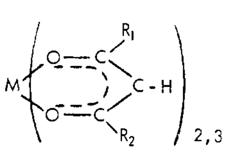


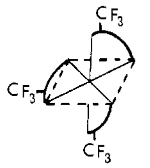
Figure 1. Photochemical quantum yields (254-nm irradiation) for the isomerization and decomposition of *trans*-Rh(tfa)$_3$ in mixed 2-propanol–cyclohexane solvents.



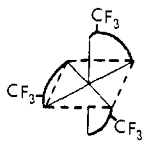
I

duces *either* stereochemical rearrangement (Cr) or redox decomposition (Mn, Fe, Co, Ni, Cu). We have recently observed that *trans*-Rh(tfa)$_3$ (tfa has $R_1 = CH_3$, $R_2 = CF_3$ in I) can undergo either or *both* processes, depending upon the nature of the solvent. Indeed we have been able to regulate the photochemical behavior by varying the solution composition over a narrow range. Our results, which constitute the first detailed photochemical study of a second row transition metal β-diketonate complex, are reported here.

Rh(tfa)$_3$ was prepared and separated into trans (II) and cis (III) isomers by a published procedure.[3] Irradiation at 254 nm was accomplished with a low pressure mercury (Pen-Ray) lamp whose output is 92% at this wavelength, while a high pressure mercury lamp and suitable filters were employed at other wavelengths. Light intensity was measured by ferrioxalate actionometry.[4]



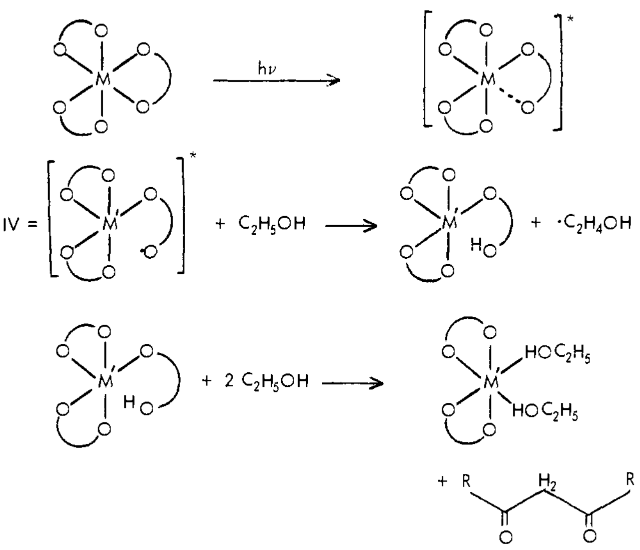
II



III

Since nanogram quantities of II and III are readily separated and identified by gas chromatography,[5] it has been possible to monitor both the steric and chemical transformations of the system. This flexibility has enabled us to detect either or both of two photoinduced processes, depending upon the solvent system employed. Thus trans to cis isomerization is the sole observable photoprocess ($\phi_{isom} = 9.2 \pm 0.4 \times 10^{-5}$) in deaerated cyclohexane upon 254-nm irradiation of *trans*-Rh(tfa)$_3$, while at wavelengths >302 nm the complex is photoinert within our detection limits ($\phi_{isom} < 6 \times 10^{-6}$). Sharply contrasting behavior obtains in deaerated 2-propanol in that only photodecomposition[6] of the complex occurs. The quantum efficiency of this process decreases with increasing wavelength of irradiation (ϕ_{dec} is $2.3 \pm 0.2 \times 10^{-3}$ at 254 nm, $4.4 \pm 0.3 \times 10^{-4}$ at 302 nm and $<1.5 \times 10^{-5}$ at 366 nm), but is unchanged at 254 nm upon addition of a 100-fold excess of LiCl or a 3-fold excess of H_2SO_4.

Scheme I[a]



[a] M' denotes the metal has undergone a one-electron reduction.

Table I. Effect of Solvent on the Photodecomposition of Analogous Cobalt and Rhodium Tris(β-diketonate) Complexes

	ϕ_{dec}, 254 nm		
	Alkane[a]	Ethanol	Cyclohexane + 0.01 M HSn(*n*-Bu)$_3$
trans-Co(tfa)$_3$	0.038[b]	0.12[b]	0.038-1[c]
trans-Rh(tfa)$_3$	$<6 \times 10^{-5}$	4.5×10^{-4}	~0.1

[a] Solvent is hexane for Co, cyclohexane for Rh. [b] From ref 2. [c] See footnote 12.

The key role of solvent in regulating the photochemical behavior of *trans*-Rh(tfa)$_3$ is particularly evident in mixed solvent systems. As illustrated in Figure 1, *both* isomerization and decomposition are observed upon 254-nm irradiation of the complex in cyclohexane solutions containing up to 0.065 M 2-propanol. The two processes are competitive as evidenced by the inverse responses of ϕ_{isom} and ϕ_{dec} to increasing alcohol content. Isomerization is completely suppressed in the presence of 0.24 M 2-propanol, and, significantly, the limiting value of ϕ_{dec} under these conditions is experimentally indistinguishable from that measured in the pure (~13 M) alcohol.

Both photoreactions are quenched by oxygen, but with decomposition being affected to the greater extent. Thus the quantum yield ratio, ϕ_{dec}/ϕ_{isom}, measured in cyclohexane solution containing 0.013 M 2-propanol decreases from 5.8 to 4.0 upon bubbling the sample with oxygen. Furthermore the ratio is wavelength dependent, increasing from 5.8 at 254 nm to >14.7 at 302 nm. Both observations provide compelling evidence for the existence of more than one photoactive excited state in *trans*-Rh(tfa)$_3$.[7]

While additional work is required to assign these photoactive states confidently, some insight as to their interaction with solvent can be offered. Thus the direct correspondence between ϕ_{dec} and 2-propanol concentration (see Figure 1) is reminiscent of the effect of alcohol in promoting the photoreduction of cobalt(III)[1a] and iron(III)[1b] β-diketonate complexes. The postulated mechanism[2] in these cases involves hydrogen atom donation from the alcohol to a monodentate bound ligand radical (IV) produced in the primary photochemical step (Scheme I). If this or a similar pathway were prominent in *trans*-Rh(tfa)$_3$, photodecomposition should be particularly favorable in the presence of a facile hydrogen atom donor such as $HSn(n\text{-}Bu)_3$.[8,9] Indeed we find that ϕ_{dec} rises to ~0.1 upon 254-nm irradiation of the complex in a cyclohexane solution containing 0.01 M hydride.[10] This result strongly implicates hydrogen atom abstraction as a key step in the photodecomposition of *trans*-$Rh(tfa)_3$. Furthermore we infer from such behavior that the population of at least one of the photoactive excited states imparts considerable radical character to the complex.[11] This premise is also consonant with the independence of ϕ_{dec} to changes in ionic strength or hydrogen ion concentration (vide supra), since any likely metal or ligand centered radical species are not expected to develop any significant charge separation or function as good Brønsted bases.

Finally, the present study allows the first comparisons to be drawn between the photochemical behavior of corresponding first and second row transition metal β-diketonate complexes. We note from Table I that while the photodecomposition of *trans*-$Rh(tfa)_3$ is generally less efficient than that of *trans*-$Co(tfa)_3$, it is also considerably more sensitive to the solvent environment. Thus the large disparity in ϕ_{dec} values measured in alkane solvents nearly disappears when the complexes are photolyzed in the presence of a potent hydrogen atom donor such as $HSn(n\text{-}Bu)_3$.[12] Flash photolysis studies currently underway should prove valuable in elucidating the factors responsible for this behavior.

Acknowledgment. We thank the Research Corporation for partial support of this work and Matthey Bishop, Inc., for a generous loan of rhodium trichloride. Some valuable discussions with Dr. Edward Sweet are also acknowledged.

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(6) Decomposition was monitored by comparing the total (trans + cis) gas chromatographic peak area of an irradiated sample with that of an unirradiated standard. No volatile Rh-containing photoproducts could be detected by gas chromatography. Analysis of the photolyzed solution by high pressure liquid chromatography, however, did reveal the presence of free H(tfa) ligand.

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(10) Sufficient *trans*-$Rh(tfa)_3$ is employed to absorb >99% of the irradiating light. Routine control experiments indicate the absence of any thermal reaction between the complex and $HSn(n\text{-}Bu)_3$.

(11) Two types of excited state, ligand to metal charge transfer and ligand localized $n-\pi^*$, are particularly attractive in this regard. The charge-transfer state can generate intermediate IV (see Scheme I), which should function as a hydrogen atom acceptor.[2] Similarly, $n-\pi^*$ states are known to be voracious hydrogen atom acceptors.[8,9]

(12) Although the quantum yield for photodecomposition of *trans*-$Co(tfa)_3$ in the presence of $HSn(n\text{-}Bu)_3$ has not been reported, it would presumably lie between 0.038 (the value in pure hexane[2]) and 1.

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Additions and Corrections

Thermal Stereomutation of Cyclopropanes [*J. Am. Chem. Soc.*, **98**, 122 (1976)]. By JEROME A. BERSON,* LARRY D. PEDERSEN, and BARRY K. CARPENTER, Department of Chemistry, Yale University, New Haven, Connecticut 06520.

We thank Professor W. R. Roth for pointing out that the right-hand curve (circles, expt 3) of Figure 1 is misplotted. The non-first-order nature of the system does not manifest itself in a correct plot of these data (Table VII), which shows good linear behavior with an apparent first-order rate "constant" slightly lower than that derived from the left-hand line (squares).

Anion Cryptates: Highly Stable and Selective Macrotricyclic Anion Inclusion Complexes [*J. Am. Chem. Soc.*, **98**, 6403 (1976)]. By ERNEST GRAF and JEAN-MARIE LEHN,* Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France.

Page 6404. For the first two entries of the first line in the table the error limits should have appeared as: ≥4.0 ± 0.5 and ≥4.5 ± 0.5.

Effect of Surfactant Micelles on the Stereochemistry and Rate of "Amsylate" Solvolytic Displacement Reactions in Water [*J. Am. Chem. Soc.*, **98**, 6613 (1976)]. By CHAIM N. SUKENIK and ROBERT G. BERGMAN,* Laboratories of Chemistry, California Institute of Technology, Pasadena, Calif. 91125.

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Reactions of Methylphenylcarbene and Phenylcarbene in Isobutene Matrices: Origins of the "Insertion" Products [*J. Am. Chem. Soc.*, **99**, 1262 (1977)]. By ROBERT A. MOSS* and MARTIN A. JOYCE, Wright and Rieman Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903.

Results in related systems (to be published separately) caused us to reinvestigate the photolysis of phenyldiazoethane in $^{13}CH_2{=}C(CH_3)_2$ (10 or 12 atom % enriched) at −196 °C (matrix). ^{13}C NMR analyses of *four* new, independent reactions (two different samples of labeled isobutene) showed that the ^{13}C label was 94–99% at C(1) of the product 2-methyl-4-phenyl-1-pentene, and only 1–6% at C(3). The new results