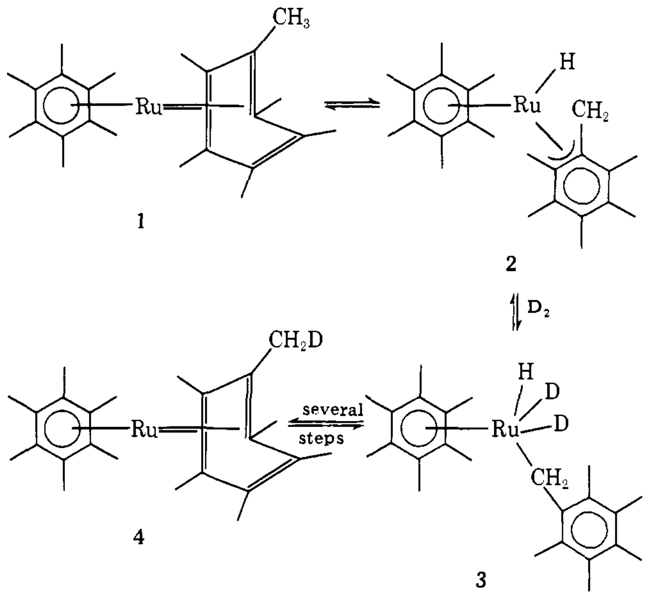
Scheme I



d_{12} were obtained from $C_6D_6 + H_2$ and $C_6H_6 + D_2$ with $C_6H_6D_6$ the major species in both reactions. Both the benzene recovered in the $C_6H_6 + D_2$ reaction and the hexamethylbenzene ligands in recovered catalyst contained deuterium. Most unexpectedly, the recovered xylenes from a D_2 hydrogenation reaction contained large amounts of deuterium and primarily consisted of the d_0 and d_1–d_6 species with relatively minor amounts of the d_7–d_{10} xylenes. A similar result was observed with the recovered toluene from a toluene–D_2 reaction system where the d_0 and the d_1–d_3 species predominated. Clearly, H–D exchange in the methyl groups is fast with respect to that of the aromatic hydrogen atoms. The distribution of deuterium in the hexamethylbenzene ligands of the recovered catalyst was unexceptional with $[d_0] > [d_1] > [d_2]$ and so on through $[d_{18}]$.

In the ruthenium system, the H–D exchange that involves the methyl substituents of the arenes would seem to require an intermediate similar to that postulated by Weber and Brintzinger[13] for thermal reactions of the analogous but less stable iron complex $[C_6(CH_3)_6]_2Fe$. This is illustrated in Scheme I. The η^1-benzyl form, **3**, for hexamethylbenzene might be much less stable because of steric factors than the analogue from *o*-xylene which then might account for the faster deuterium introduction in the methyl groups of the xylenes than in those of hexamethylbenzene. The H–D exchange of ring protons can be readily accounted for by a kinetically significant reversibility in some of the initial hydrogen addition steps in the hydrogenation cycle. Mechanistically, the hydrogenation cycle could be formally analogous to the allylcobalt system, and, in fact, the benzylruthenium-arene species **2** and **3** are very similar to the postulated allylcobalt-arene intermediates.[1-4] However, note that hydrogen transfer to the σ or π benzyl ligand in the ruthenium system does not lead to catalyst destruction as does hydrogen transfer to the allyl ligand in the allylcobalt system.

The scope and kinetic features of this catalytic arene hydrogenation system are under investigation. Further studies of arene-metal complexes in their reactions with hydrogen may provide the key identification of intermediates in this type of reaction.[14] For arene hydrogenations by coordination catalysis, there may be a commonality[15] in reaction mechanism with allylic or benzylic species as key intermediates. Thus? for catalyst longevity, permethylarenes or -cyclopentadienyls[16] should be optimal ligands since these ligands, which can yield benzylic or benzylic-like complexes, are very resistant to hydrogenation.

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(9) The arene–$Ru_6C(CO)_{14}$ complexes are obtained in low yield from the high temperature reaction of $Ru_3(CO)_{12}$ with an arene. Under present study is the reaction of $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{16}(PR_3)$ with arenes. Crucial to a catalytic system in this cluster system may be a facile arene exchange capability in some $Ru_6C(CO)_xL_y$ species. A catalytic hydrogenation of arenes with ruthenium carbonyls has been reported to proceed at 100 °C (100 atm): P. Frediani, M. Bianchi, and F. Piacenti, *Chim. Ind.* (*Milan*), **53,** 80 (1971). Our investigations of $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ as arene hydrogenation catalysts showed no hydrogenation to 150 °C (5 atm). Above this temperature, ruthenium metal was formed and hydrogenation then proceeded: K. G. Caulton, M. G. Thomas, B. A. Sosinsky, and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.*, **73,** 4274 (1976); E. L. Muetterties and J. W. Johnson, unpublished data.
(10) A complete understanding of this transition metal group arene chemistry will require analogous studies of arene–$M(CO)_xL_{3-x}$ with L a more effective donor molecule like a phosphine or phosphite.
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(15) At least there may be one dominant type of reaction mechanism.
(16) It would be of interest to determine whether the methyl groups of $C_5(CH_3)_5$ ligands in the rhodium catalyst, described by Maitlis, et. al.,[6] incorporate deuterium in the $C_6D_6 + H_2$ reaction.
(17) NSF Energy Related Postdoctoral Fellow, 1976–1977.

J. W. Johnson,[17] E. L. Muetterties*
Department of Chemistry, Cornell University
Ithaca, New York 14853

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A Novel Acylation of Some Activated Olefins by an Electroreductive Method[1]

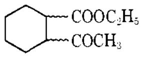
Sir:

Owing to its wide potentiality in organic syntheses, the generation of acyl anion or its chemical equivalents, though most of them are rather complex species, has attracted much attention in recent years.[2] On the other hand, electrochemical reduction has been known as a powerful tool in the generation of active species which may difficultly be formed by conventional chemical methods.[3] Although the electroreductive acylation of heteroatoms has been studied extensively,[4] only few have been known in the acylation of carbon atom.[5]

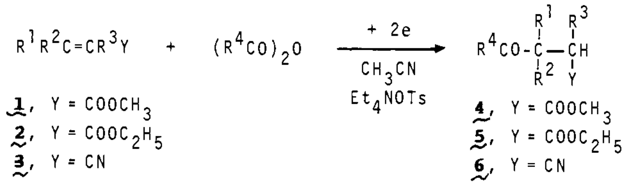
We wish to report herein a novel electrochemical acylation of activated olefins **1, 2,** and **3,** in which the products, γ-keto esters **4** and **5** and nitriles **6,** are just the same as those formed from the addition of acyl anion to the activated olefins, though this electrochemical reaction may not involve the acyl anion itself as the active species.

In view of its simplicity and generality, the electroreductive

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

	Ester and Nitrile						
Compd	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
				$n\text{-}C_3H_7$	$n\text{-}C_3H_7COCH_2CH_2COOCH_3$	4b	63
				$i\text{-}C_3H_7$	$i\text{-}C_3H_7COCH_2CH_2COOCH_3$	4c	50
1b	CH_3	H	H	CH_3	$CH_3COCH(CH_3)CH_2COOCH_3$	4d	75
				$n\text{-}C_3H_7$	$n\text{-}C_3H_7COCH(CH_3)CH_2COOCH_3$	4e	82
				$i\text{-}C_3H_7$	$i\text{-}C_3H_7COCH(CH_3)CH_2COOCH_3$	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.



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

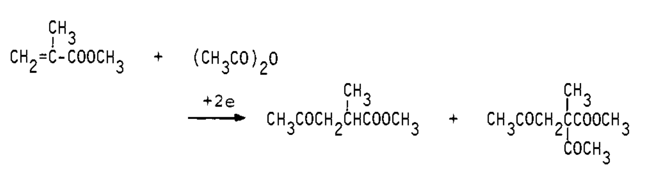
1, Y = $COOCH_3$
2, Y = $COOC_2H_5$
3, Y = CN

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.



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}\text{-}COOCH_3 \quad + \quad (CH_3CO)_2O \xrightarrow{+2e} CH_3COCH_2\overset{\overset{CH_3}{|}}{C}HCOOCH_3 \quad + \quad CH_3COCH_2\underset{\underset{COCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}COOCH_3$$

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

(10) The cyclic voltammetry of **1b** 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.

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Tatsuya Shono,* Ikuzo Nishiguchi, Hiroshi Ohmizu
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Sakyo, Kyoto 606, Japan

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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 (**1**). Thus visible or near-ultraviolet irradiation in-