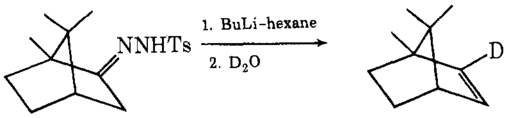
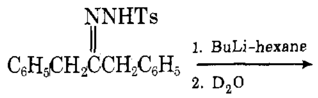
when the reaction is quenched with D_2O, 2-bornene-2-d_1 containing 95% deuterium (mass spectrometry) is obtained. The yield of alkene is inferior to that obtained in ether, probably because of the insolubility of the tosylhydrazone in hexane.

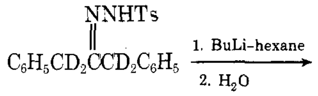


Attempts to incorporate deuterium into several other alkenes employing this technique, however, were far less successful. For example, the cis and trans isomers of 1,3-diphenylpropene generated from 1,3-diphenyl-2-propanone tosylhydrazone[4] after D_2O quenching give a mixture of labeled and unlabeled alkene.[5] Moreover, 1,3-diphenyl-2-propanone-1,1,3,3-d_4 tosylhydrazone gives a mixture of d_3 and d_4 alkenes.



$$C_6H_5CH_2\overset{NNHTs}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow[2.\ D_2O]{1.\ \text{BuLi-hexane}}$$

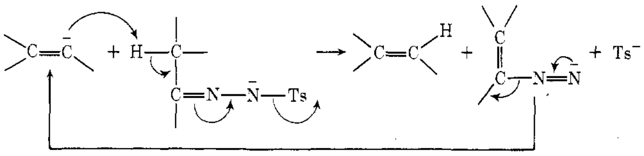
$C_6H_5CH{=}CHCH_2C_6H_5$ + d_1 alkene[6]
(cis and trans) (cis and trans)



$$C_6H_5CD_2\overset{NNHTs}{\overset{\|}{C}}CD_2C_6H_5 \xrightarrow[2.\ H_2O]{1.\ \text{BuLi-hexane}}$$

$C_6H_5CD{=}CDCD_2C_6H_5$ + d_3 alkene[6]

A carbene mechanism would give the d_4 alkene, but must be precluded by the high cis to trans ratio of the product.[4] It is therefore proposed that the third mechanism of vinyl anion neutralization involves proton abstraction from the α position of a tosylhydrazone salt in a chain reaction.



The reaction of 1,3-diphenyl-2-propanone tosylhydrazone, and similar acyclic systems, with alkyllithium reagents is further complicated by the fact that the geometric isomer ratio is affected by solvent changes and by reaction times. Investigations of the factors affecting these reactions are in progress at present. In light of the results with acyclic systems, it appears that the vinyl anion generated from camphor tosylhydrazone is reluctant to attack the tosylhydrazone salt, presumably for steric reasons.

Experimental Section

2-Bornene-2-d_1. To a suspension of camphor tosylhydrazone[7] (3.2 g, 0.01 mol) in 50 ml of dry hexane was added 15 ml of n-butyllithium in hexane (2.0 M, 1.92 g, 0.03 mol) over 30 min. The suspension, which turns orange-yellow, was allowed to stir for 16 hr at room temperature and excess D_2O was carefully added. Water and ether were added and the layers were separated. The 2-bornene was isolated as previously described[2] and the yield was 643 mg (47%), mp 105-110°. A low-voltage mass spectrum (15 eV) showed the 2-bornene to be 95% d_1 and 5% d_0. The position of the deuterium was determined by pmr. Unlabeled 2-bornene shows a one-proton doublet at 5.62 ppm (J = 6 Hz) and a one-proton multiplet at 5.85 ppm. The labeled 2-bornene obtained in this experiment shows a one-proton broadened doublet centered at 5.85 ppm. 2-Bornene-3-d_1[1] obtained from camphor-3,3-d_2 tosylhydrazone[8] and methyllithium shows a one-proton broadened singlet at 5.60 ppm.

Registry No.—Camphor tosylhydrazone, 10224-32-5; n-butyllithium, 109-72-8; 2-bornene-2-d_1, 51472-55-0.

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(3) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, **89**, 5736 (1967).
(4) R. H. Shapiro, *Tetrahedron Lett.*, 345 (1968).
(5) *The full details of this study will appear in a subsequent publication.*
(6) The relative positions of the hydrogens and deuteriums have not been determined.
(7) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).
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Molybdenum Hexacarbonyl Catalyzed Acylation of Ferrocene

Howard Alper* and Steven M. Kempner

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

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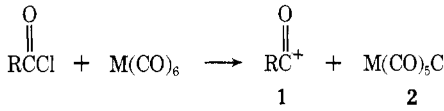
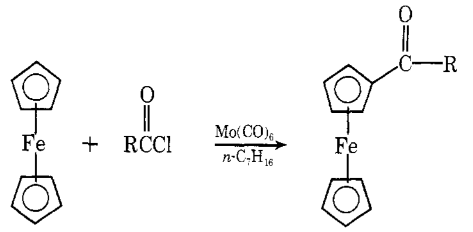
One of us recently showed that group VI metal carbonyls, particularly molybdenum hexacarbonyl [$Mo(CO)_6$], are useful catalysts for the reaction of ethers and acid halides.[1] The reaction was proposed to occur *via* initial formation of an acylium ion (**1**) and a metal pentacarbonyl halide anion (**2**). If such a process indeed occurs, then it



$$R\overset{O}{\overset{\|}{C}}Cl + M(CO)_6 \longrightarrow \underset{\mathbf{1}}{R\overset{O}{\overset{\|}{C}}{}^+} + \underset{\mathbf{2}}{M(CO)_5Cl^-}$$

should be possible to acylate metallocenes such as ferrocene. We now wish to report that Friedel-Crafts acylation of ferrocene, and presumably other metallocenes, can be effectively catalyzed by $Mo(CO)_6$.

Treatment of a series of acid chlorides with ferrocene in n-heptane, and using a catalytic quantity of $Mo(CO)_6$, gave reasonable to very good yields of acylated ferrocenes (**3**).



3

The yields and melting points of the products are listed in Table I. In several instances (*e.g.*, **3**, R = 1-adamantyl)[2] the yields obtained are superior to those reported

Table I
Yields and Melting Points of Acylated Ferrocenes

3, R =	Yield,[a] %	Mp, °C	Lit. mp, °C
CH_3	76	84.0–85.0	85.0–86.0[b]
$(CH_3)_2CH$	41	Oil	Oil[c]
Cyclohexyl	50	76.0–78.0	79[d]
1-Adamantyl	76	144.5–145.5	147.0–148.0[e]
C_6H_5	73	109.0–110.0	108.1–108.3[b]

[a] Yields are of pure **3** and are based on unrecovered ferrocene. [b] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969. [c] R. J. Stephenson, British Patent 864,197 (1961); *Chem. Abstr.*, **55**, 17647 (1961). [d] T. Leigh, British Patent 819,108 (1959); *Chem. Abstr.*, **54**, 7732*d* (1960). [e] Reference 2.

using other catalysts. Diacylated ferrocenes were not isolated from any of these reactions.

The mechanism of this metal carbonyl catalyzed reaction, assuming initial generation of **1**, is likely similar to those proposed for other catalysts.[3]

Experimental Section

General Procedure for $Mo(CO)_6$-Catalyzed Acylation of Ferrocene. A mixture of ferrocene (10–20 mmol), acid chloride (1.05/1.00 mole ratio of acid chloride/ferrocene), and $Mo(CO)_6$ (5–10 mol %) in *n*-heptane (80–200 ml) was refluxed with stirring under nitrogen for 1–2 days. The solution was cooled and filtered, and the filtrate was flash evaporated. The residue from flash evaporation was dissolved in benzene (or 1:1 hexane–benzene) and chromatographed on silica gel. Elution with benzene or hexane–benzene (1:1) gave unreacted ferrocene. The acylated ferrocene (**3**) was obtained on elution with benzene or benzene–ether. No diacylated ferrocene was isolated when ether, methylene chloride, or chloroform were used as eluents. The yields and melting points of **3** are listed in Table I. The acylated ferrocenes were identified on the basis of melting points, as well as infrared, nuclear magnetic resonance, and mass spectral results.

Acknowledgments. This research was supported by the Research Foundation of the State of New York. We are pleased to acknowledge gifts of generous quantities of $Mo(CO)_6$ by the Climax Molybdenum Co.

Registry No.—**3** (R = CH_3), 1271-55-2; **3** [R = $(CH_3)_2CH$], 41406-84-2; **3** (R = cyclohexyl), 51364-96-6; **3** (R = 1-adamantyl), 34699-71-3; **3** (R = C_6H_5), 1272-44-2; $Mo(CO)_6$, 13939-06-5; ferrocene, 102-54-5; acetyl chloride, 75-36-5; isobutyryl chloride, 79-30-1; cyclohexanecarbonyl chloride, 2719-27-9; adamantane-1-carbonyl chloride, 2094-72-6; benzoyl chloride, 98-88-4.

References and Notes

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(2) J. J. McDonnell and D. J. Pochopien, *J. Org. Chem.*, **36**, 2092 (1971).
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Epimerization of Mestranol Acetate on Alumina

Ramesh M. Kanojia,* Linda Yarmchuck, and Irving Scheer

Division of Chemical Research, Ortho Research Foundation, Raritan, New Jersey 08869

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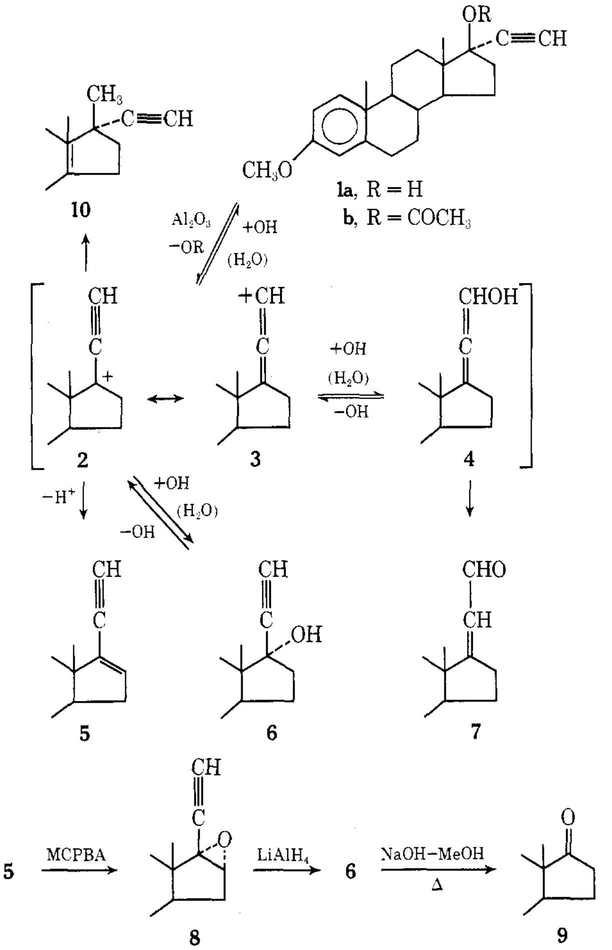
The preparation of 3-methoxy-19-nor-17α-pregna-1,3,5(10)-trien-20-yn-17β-ol (**1a**, mestranol) by ethynylation of the corresponding 17-ketone **9** is well known.[1] However, the epimeric 17β-ethynyl-17α-ol compound **6** (epimestranol) has apparently not been characterized.[2] During the course of a continuing investigation of the reactions of steroidal tertiary 17β-acetates on alumina, we observed the formation of other polar products in addition to the previously reported enynes arising from deacetoxylation.[4] We wish to report the formation of epimestranol **6** by an unexpected epimerization of mestranol acetate (**1b**) on alumina.

When a benzene solution of **1b** was allowed to remain in contact with a column[5] of neutral alumina[6] at room temperature for 5–10 days, the principal transformation product **5** (30–50%) was eluted as the least polar component, followed by a mixture of unchanged acetate **1b**, two closely moving products **6** and **7**, and finally by mestranol (**1a**). Repeated chromatography of this mixture on silica gel, followed by fractional crystallization, afforded **6** and **7**, each in 5% yield.



The absence of acetoxy bands in the ir and nmr spectra of **5** indicated that it was a product of deacetoxylation. The presence of a vinylic proton at δ 6.13 and a deshielded ethynyl proton at δ 3.07 in the nmr spectrum, as well as an augmented uv absorption at 225 nm (ϵ 19.200), established the conjugated enyne structure for **5**. The same enyne was obtained by treatment of **1a** with $POCl_3$ in pyridine.[7] An isomeric enyne detected by nmr in trace amounts in the mother liquors from **5** was identified as the product **10** formed by Wagner–Meerwein migration of the C_{13} methyl group to C_{17}, by comparison with an authentic sample obtained by dehydration of **1a** with formic acid.[8] Compound **6** appeared to be an ethynylcarbinol on the basis of its microanalysis and ir and nmr spectral data. The location of the ethynylcarbinol functions of **6** at C_{17} became evident from its conversion to the 17-ketone **9** *via* the base-induced reversal[10] of ketone ethynylation. Finally, **6** was also prepared by an alternate synthesis. Treatment of enyne **5** with *m*-chloroperoxybenzoic acid (MCPBA) afforded the epoxide **8**[11] (49%), which on reduction with $LiAlH_4$ furnished **6** (~15%), identical with that obtained by transformation of mestranol acetate (**1b**) on alumina. These results confirmed the epimeric relationship of **6** and **1a** at C_{17}. A conjugated aldehyde structure for **7**, as suggested by its spectral properties, was confirmed by comparison with authentic material.[9] Unlike the acetate **1b**, the parent carbinol **1a** failed to give transformation products on alumina.

The formation of the observed alumina-transformation products from **1b** can be explained by invoking a carbonium ion mechanism. The mesomeric carbonium ion **2** ↔ **3** can be formed by a loss of acetate ion[12] on the dipolar[13] surface of alumina. Formation of the conjugated aldehyde **7** *via* the enol **4**, by reaction of the allenic form **3** of the mesomeric cation with water from alumina, is recogniz-