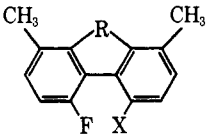
Table I. Coupling Constants for Derivatives of 4,5-Difluoro- and 4-Methyl-5-fluorophenanthrenes[a,b]



Compd type	R	X = F; J_{F-F}, Hz	X = CH_3; J_{H-F}, Hz	X = CH_3; J_{C-F}, Hz	$(J_{F-F})/170$	$(J_{H-F})/11.9$	$(J_{C-F})/24.0$
1	HC=CH	170	11.9	24.0	1	1	1
2	HOCHCHOH	92.9	7.6	15.7	0.55	0.64	0.65
3	O=CC=O	106.5	8.1	16.1	0.63	0.67	0.67
4	O=COC=O	46.7	3.7	(~7)[d]	0.28	0.30	(~0.30)[e]
5	O=C	(~85–100)[d]	7.3[c]	(~15)[d]	(~0.61)[e]	0.61	(~0.61)[e]

[a] Determined from ^1H, ^{19}F, and ^{13}C nmr spectra at various spectrometer frequencies. [b] All coupling constants are reported in hertz. [c] Value obtained from the literature: G. W. Gribble and J. R. Douglas, Jr., *J. Amer. Chem. Soc.*, 92, 5764 (1970). [d] Predicted coupling constants. [e] The same ratio as was observed from H–F couplings was assumed.

from planarity should be smaller for the parent phenanthrene **1**-CH_3 than its derivatives, **2**-CH_3 and **3**-CH_3. The consequence should be a greater proximity of atoms at positions 4 and 5. The proximity of the 4-methyl to the 5-fluoro group seems to produce a downfield shift of the methyl carbon in **1**-CH_3 relative to **2**-CH_3 and **3**-CH_3 ($\delta_{4\text{-}C}{}^{1\text{-}CH_3} - \delta_{4\text{-}C}{}^{2\text{-}CH_3} = 3.4$ ppm; $\delta_{4\text{-}C}{}^{1\text{-}CH_3} - \delta_{4\text{-}C}{}^{3\text{-}CH_3} = 3.2$ ppm).[9]

The changes in proximity of the groups at the 4 and 5 positions are also reflected in changes in the fluorine coupling constants. It was previously demonstrated[2] that the decrease in J_{F-F} can be taken as a standard fractional decrease in through-space coupling as a consequence of this structural variation, $J_{F-F}{}^{2\text{-}F}/J_{F-F}{}^{1\text{-}F} = 0.55$. The observation that ^{13}C–F coupling decreases by a comparative amount, $J_{C-F}{}^{2\text{-}CH_3}/J_{C-F}{}^{1\text{-}CH_3} = 0.64$, implies that through-space interactions contribute substantially to the 4-carbon–5-fluorine coupling constant. This conclusion is reinforced by comparing the ratios $J_{F-F}{}^{3\text{-}F}/J_{F-F}{}^{1\text{-}F} = 0.63$ and $J_{C-F}{}^{3\text{-}CH_3}/J_{C-F}{}^{1\text{-}CH_3} = 0.67$. Furthermore, the observation that H–F coupling and ^{13}C–F coupling decrease by proportionately the same amount permits the prediction of coupling constants in related compounds. For example, using the observed ratio $J_{H-F}{}^{4\text{-}CH_3}/J_{H-F}{}^{1\text{-}CH_3} = 0.30$ leads to a prediction for the ^{13}C–F coupling constant in **4**-CH_3 of ~7.0 Hz. Similarly, the ^{13}C–F coupling in **5**-CH_3 is predicted to be ~15 Hz.

The fact that the ratios of H–F couplings and ^{13}C–F couplings are essentially identical supports our earlier proposal that the coupling between methyl hydrogen and fluorine may result from interactions centered on the fluorine and methyl carbon rather than on the fluorine and hydrogen nuclei.[10,12] Further studies of fluorine coupling in these and related systems are currently in progress and will be reported shortly.

Acknowledgment. We wish to thank the Research Corporation for financial assistance. Grants from the National Science Foundation aided in the purchase of nmr spectrometers used in this work.

(9) This downfield shift appears to arise from paramagnetic deshielding of the carbon resulting from proximity of the group at the 5 position. A similar deshielding effect was observed for the fluorine resonances in 1,8-dimethyl-4,5-difluorophenanthrene; ref 2.

(10) This might contribute to the unusual dihedral angle dependence of H–F coupling in *o*-alkylfluorobenzenes.[11]

(11) The α-H–F coupling in *o*-alkylfluorobenzenes appears strongest when the α-H is not proximate to fluorine: P. C. Myhre, personal communication.

(12) A similar through-oxygen coupling has been proposed: F. A. L. Anet, A. J. R. Brown, P. Carter, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 5249 (1965).

(13) National Science Foundation Trainee, 1968–1970; National Aeronautics and Space Administration Fellow, 1970–1971.
(14) Alfred P. Sloan Research Fellow, 1969–1972.

F. R. Jerome,[13] K. L. Servis*[14]
Department of Chemistry, University of Southern California
Los Angeles, California 90007
Received May 5, 1972

The Claisen Rearrangement of Allyl Esters[1]

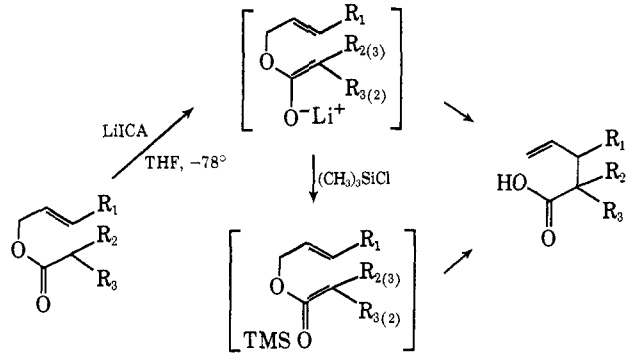
Sir:

The recent investigations of Rathke[2] have made possible the generation of ester enolates free of complicating condensation reactions. The possibility that the enolate anions formed from allyl esters under these conditions would undergo a Claisen-type rearrangement on warming has fascinating consequences for both the scope and general applicability of this useful sigmatropic reaction. While the base-catalyzed rearrangement of a few allyl esters has been previously observed,[3] the harsh conditions, low yields, and specialized character of the esters belie the generality of the process. Current investigation of the reaction under these new conditions has resulted in efficient means for the conversion of allyl esters to the corresponding γ,δ-unsaturated acids under surprisingly mild conditions.

Representative examples of a series of the simplest, and hence most demanding, esters are presented in Table I. The esters **1**, **2**, and **5** of tertiary and secondary acids rearranged rapidly at room temperature or slightly above as their lithium enolates, but the acetates **3** and **4** rearranged sufficiently slowly under these conditions that undesired side reactions (aldol-type condensation, ketene formation?) became predominant. Particularly in these cases it was found advantageous to quench the lithium enolate at −78° with trimethylsilyl chloride[4] before warming. The resulting ketene acetals now rearrange quite rapidly. A small amount (2–6%)

(1) The support of this work by the National Science Foundation is gratefully acknowledged.
(2) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, 93, 2318 (1971).
(3) R. T. Arnold and C. Hoffman, *Syn. Commun.*, 2, 27 (1972), and earlier work; S. Julia, M. Julia, and G. Linstrumelle, *Bull. Soc. Chim. Fr.*, 2693 (1964).
(4) Y. Kuo, F. Chen, C. Ainsworth, and J. J. Bloomfield, *Chem. Commun.*, 136 (1971).

Table I. Conditions for Rearrangement of Allyl Esters



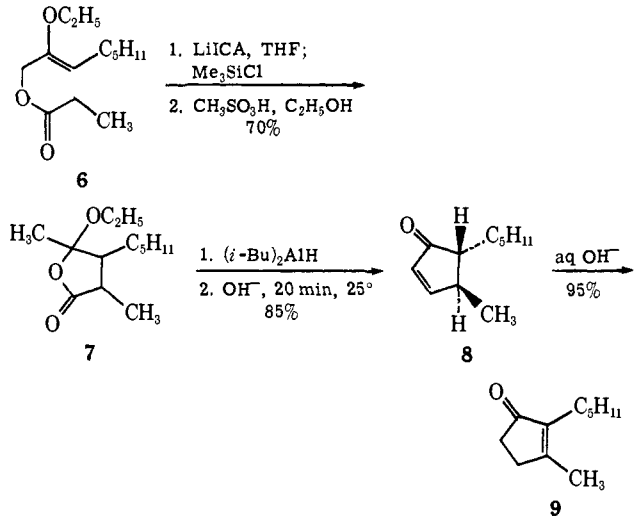
No.	R_1	R_2	R_3	Reagents[a]	Time, min[b]	Temp, °C	% yield
1	CH_3	CH_3	CH_3		10	25	80
1	CH_3	CH_3	CH_3	Me_3SiCl	10	25	78[c]
2	CH_3	CH_3	H		60	25	75
2	CH_3	CH_3	H	Me_3SiCl	30	67	75[c]
3	CH_3	H	H	Me_3SiCl	90	67	70[c]
4	H	H	H	Me_3SiCl	120	67	66[c]
5	CH_3	*trans*-CH=CHC_2H_5	H		180	25	69

[a] All esters were enolized with 1.05 equiv of lithium isopropylcyclohexylamide (LiICA), at −78°. [b] In all cases the reaction mixture required an additional 30 min to rise from −78° to the temperature indicated. [c] In cases where Me_3SiCl was used the rearranged product contained 2–6% C-silylated material.

of the acids produced in this manner were found to be C-silylated, probably as a result of enolization and silylation of the rearranged silyl esters by the slight excess of reagents used. The pure γ,δ acids were prepared[5] from these mixtures by esterification (CH_2N_2) and then base hydrolysis ($NaOCH_3$, CH_3OH; H_2O) (**3** in 50% and **4** in 57% overall yield).

The facility with which these rearrangements take place is particularly striking in view of the conditions required by alternate procedures. The amide acetal,[6] orthoacetate,[7] and standard vinyl ether[8] reactions are all reported to require temperatures above 100° for the comparable transformation. In addition, the present procedure, initiated from readily prepared and stable allyl esters, requires no preequilibration of the allylic alcohol with excess reagent, as do the foregoing methods, and is conducted entirely under basic or neutral conditions in contrast to the orthoacetate[7] and vinyl ether[8] procedures.

These modifications may be put to good use when *both* the allylic alcohol *and* the acid portion of the system are available only in restricted quantities, and/or where acid labile groups are present. By way of exploring these advantages for the synthesis of prostoglandin-like systems, we have effected the rearrangement of the ester **6**[9] and converted the product to the dihydrojasmone structure **9**. In this case rearrangement was best effected through the trimethylsilyl ketene acetal,



6 **7** **8** **9**

and the product was isolated as the ethoxylactones **7** after acidification of the reaction mixture. Formation of the *trans*-cyclopentenone **8** was efficiently accomplished after reduction and aqueous base treatment of this stereoisomeric lactone mixture **7**. Transformation of this cyclopentenone to dihydrojasmone structure **9** followed the recorded procedure.[10,11]

Further exploration of the utility of these conditions for the synthesis of prostoglandins and related substances is being actively pursued.

(5) J. R. Gold, L. H. Sommer, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 70, 2874 (1948).

(6) A. E. Wick, D. Felix, K. Steen, and A. Eschenmoser, *Helv. Chim. Acta*, 47, 2425 (1964).

(7) W. S. Johnson, L. Wethemann, W. R. Bartlett, T. J. Brockson, T. Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, 92, 741 (1970).

(8) A. W. Burgstahler and I. C. Nordin, *ibid.*, 83, 198 (1961); G. Saucy and R. Marbet, *Helv. Chim. Acta*, 50, 2091 (1967); K. Sakai J. Ide, O. Oda, and N. Nakamura, *Tetrahedron Lett.*, 1287 (1972).

(9) Prepared from 2-ethoxy-2-nonen-1-ol by esterification with propionic anhydride in pyridine solution. The alcohol was prepared by the method of W. Grell and H. Machleidt, *Justus Liebigs Ann. Chem.*, 699, 53 (1966).

(10) G. Stork, G. L. Nelson, F. Rouessac, and O. Gringore, *J. Amer. Chem. Soc.*, 93, 3091 (1971).

(11) All new compounds encountered in this work were characterized by ir and nmr spectroscopy and gave satisfactory combustion analyses.

Robert E. Ireland,* Richard H. Mueller

Contribution No. 4468
Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received June 1, 1972