the ultraviolet irradiation of $(NH_3)_5CoNO_2^{2+}$ results in the formation of the linkage isomer, $(NH_3)_5CoONO^{2+}$, in addition to the direct generation of Co^{2+};[13] formate, HCO_2^-, is isoelectronic with NO_2^-. N-Bonded nitrite has a higher ligand field strength than does the O-bonded isomer and shows blue-shifted d–d bands in a manner similar to that observed for LL.[13]

C-Bonded formate is apparently both thermodynamically and kinetically unstable with respect to Co^{2+} with protonation of the free carboxylate end serving to retard the rate of transfer of a ligand electron to the metal center; it should be noted that formate is a more powerful reducing agent than is formic acid.[14] It is clear that a facile pathway to Co^{2+} exists for these compounds that is not available for the usual Co(III)–amine complexes which are kinetically stable. It is not immediately clear what the structural parameter is which permits intramolecular electron transfer; unfortunately, the number of cases of simple Co(III) complexes in which such a process occurs is extremely limited. The activation energy of 23 kcal mol^{-1} for the formation of Co^{2+} can be viewed as the energy required to promote a ligand electron to a charge-transfer excited state of the complex and thence to an e_g orbital of the metal center. This thermal activation process is clearly independent of the state of protonation of the formate and the nature of the other ligands.

These results require that the mechanisms previously proposed[15] for the photolysis of oxalato complexes of Co(III) be reexamined, and that the implications to electron transfer processes involving Co(III) be explored.

Acknowledgment. The authors thank Professor J. N. Armor for assistance in the separation and characterization of en-LL and Dr. E. Rotlevi for his help in obtaining the data for $(NH_3)_5CoO_2CCO_2H^{2+}$.

(13) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 7, 1398 (1968).

(14) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952, p 130.

(15) T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, 228, 252 (1955); G. B. Porter, J. G. W. Doering, and S. Karanka, *J. Amer. Soc.*, 84, 4027 (1962); H. Way and N. Filipescu, *Inorg. Chem.*, 8, 1609 (1969).

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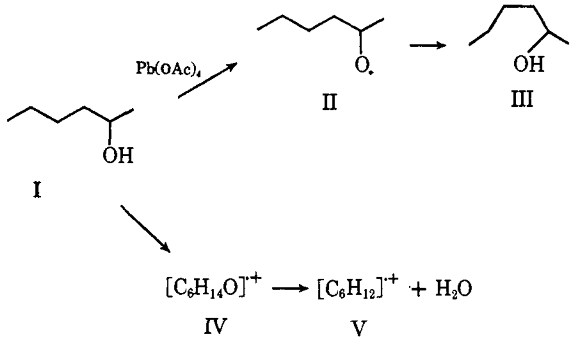
Electron Impact Induced 1,4 Elimination. The Barton Reaction in Disguise

Sir:

Transfer to oxygen of a hydrogen located on a carbon δ to the carbinol grouping (II → III and IV → V in Scheme I) characterize both the Barton reaction[1] and the mass spectral elimination of water[2,3] (Scheme I).

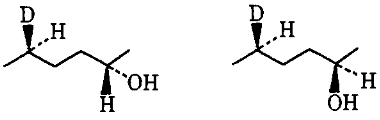
Scheme I[a]



[a] Various reagents will effect this reaction (I to II). Some of these go on to produce furans while others lead to differing final products. See ref 1.

Although the products of the Barton reaction are compelling evidence for the accepted gross structure of the intermediate II no such product information is at hand to assign structure to the species IV which lives for less than 1 μsec in the mass spectrometer. The comparative dynamic stereochemistry of the hydrogen transfer steps (II → III and IV → V), uncovered in the present work, provides strong evidence of similar structures for II and the previously inaccessible IV. The diastereomers exhibited in Chart I, with deuterium substituted in turn for the C-5 diastereotopic hydrogens of 2-hexanol, are the molecules necessary to effect such a stereochemical comparison. As outlined in Scheme II acetol and lactic acid served as effective precursors to put these molecules (VI and VII) and their enantiomers in hand.

Chart I



VI VII

As shown (Scheme II), (*R*)-(−)-propylene glycol and its enantiomer were obtained from acetol[4] and (*S*)-(−)-ethyl lactate, respectively.[5] In each case, primary hydroxyl group tritylation[6] prior to tosylation[7] followed by lithium aluminum deuteride reduction yielded the labeled enantiomeric 1-propanols (IX, one enantiomer shown).[8,9] Alkylation of the derived bromide[10] yielded

(1) M. Akhtar, *Advan. Photochem.*, 2, 263 (1964), is a general review of this reaction. Also see: K. Heusler and J. Kalvoda, *Angew. Chem., Int. Ed. Engl.*, 3, 525 (1964). For more recent papers with leading references see: M. LJ. Mihailović, Ž. Čeković, and J. Stanković, *Chem. Commun.*, 981 (1969); A. Deluzarche, A. Maillard, P. Rimmelin, F. Schue, and J. M. Sommer, *ibid.*, 976 (1970); A. C. Cope, M. A. McKervey, N. M. Weinshenker, and R. B. Kinnel, *J. Org. Chem.*, 35, 2918 (1970); M. LJ. Mihailović and Ž. Čeković, *Synthesis*, 209 (1970).

(2) A recent comprehensive article containing leading references is: M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, 92, 3076 (1970).

(3) The highly site specific 1,4 abstraction is deduced from the products in the Barton reactions. See discussion and references in Akhtar's review article (ref 1 herein). In the mass spectrometer, deuterium labeling revealed the highly specific (>90%) 1,4 abstraction; see: W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, 86, 2375 (1964); S. Meyerson and L. C. Leitch, *ibid.*, 86, 2555 (1964).

(4) P. A. Levene and A. Walti, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 545.

(5) J. Jacobus, Z. Majerski, K. Mislow, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 91, 1998 (1969).

(6) J. Jary and K. Kefurt, *Collect. Czech. Chem. Commun.*, 31, 1803 (1966).

(7) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1180.

(8) Lithium aluminum deuteride displacement of tosylate is known to proceed with inversion of configuration; see: G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, 22, 479 (1957). Apparently the trityloxy group does not participate since the product trityl ether of 2-deuteriopropanol may be isolated. In addition no 2-propanol is obtained.

(9) All deuterated materials were shown to be identical with authentic protium compounds by vpc comparison.

(10) C. S. Marvel and F. D. Hager, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 248.

Scheme II

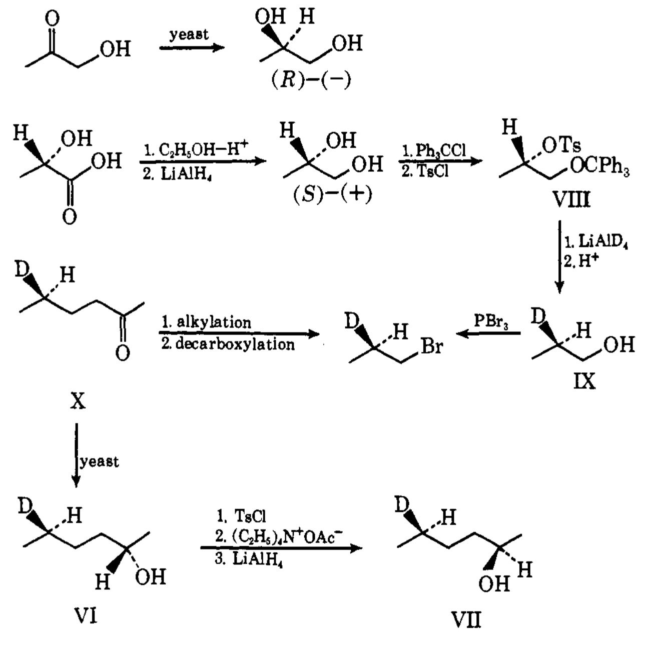
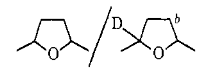
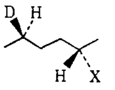
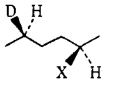
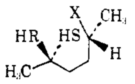


Table I[a]

	 Pb(OAc)$_4$ (X = OH)[c]	Ag$_2$O/Br$_2$ (X = OH)[d]	$\frac{M-DOH}{M-HOH}$ 70 eV (X = OH)[e]	$\frac{M-DCl}{M-HCl}$ 70 eV (X = Cl)[f]
	20/100	17/100	68/100	26/100
	27/100	22,100	74/100	36/100

[a] The numbers are average values of numerous runs with standard deviations of ±1. [b] The cis and trans isomers of the product 2,5-dimethyltetrahydrofurans were separated by vpc and analyzed separately by mass spectrometry of the M − 15 peak for d_0/d_1 content. The deuterium incorporation was independent of furan stereochemistry. [c] Carried out heterogeneously in hydrocarbon solvent at 81°. [d] Carried out heterogeneously in hydrocarbon solvent at 25°. See ref 1 for details of these reactions. [e] Temperature of the ion source was about 100°. At 15 eV (nominal) the deuterated diastereomers exhibited identical mass spectra presumably due to scrambling (for a recent discussion and leading references, see: I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **92**, 3797 (1970)). [f] Ion source at about 100°.

Table II[a]

		X = OH			X = Cl
		Pb(OAc)$_4$	Ag$_2$O Br$_2$	70 eV[b]	70 eV[b]
	k_R/k_S	1.16	1.14	1.10	1.28

[a] See the text for explanation of calculation. Data derived from Table I. Approximate deviation ±0.05. [b] The *EI* rate constants are average values over the range of accessible energy states.

the deuterated ketones X. Yeast converted this ketone to the desired optically pure[11] alcohol VI of known configuration.[12] Inversion[13] of the hydroxyl center as shown yielded the necessary diastereomeric alcohol VII with an optical rotation, $[\alpha]^{21}D$ −12.2° (C_2H_5OH), nearly equal but opposite in sign to VI. The antipodes could not be distinguished in either the Barton reactions or the mass spectral eliminations.

Table I summarizes the experimentally determined deuterium retention in the four reactions studied.

Curtin's procedure[14,15] allows the transposition of the data on the Barton reactions in Table I into the relative rates of transfer of the C-5 diastereotopic hydrogens of 2-hexanol.[16] In the electron impact induced eliminations which are not C-5 site specific the relative intensities at M − HX and M − DX are proportional to $k_R/Ik_S + k_i$ from one diastereomer and $k_S/Ik_R + k_i$ from the other where I is the isotope effect and k_i is the relative rate for abstraction of hydrogens from other carbons in the chain.[17] Since elimination of water and hydrogen chloride under electron impact are always attended by isotope effects near unity,[2] simple division of M − DX by M − DX + M − HX will yield the relative rates k_R/k_S. Table II presents the results of these manipulations.

The time scales for the four reactions under discussion (Table II) range from hours ($Pb(OAC)_4$) to minutes (Ag_2O/Br_2) to fractions of a microsecond (electron impact). The electron impact induced reactions take place under high vacuum (10^{-7} mm) while the Barton reactions occur in hydrocarbon solvent. Nevertheless, when presented with the subtle difference between the diastereotopic hydrogens on C-5, (*R*)-2-hexanol preferentially abstracts the pro-(*R*) hydrogen in all cases. The only reasonable interpretation for such data is that these apparently diverse reactions possess a common driving force,[18,19] and, heavier, that there must exist a considerable degree of structural similarity, including all the conformational factors pertinent to the C-5 hydrogen discrimination, among the various intermediates and transition states.

This work adds to recent accumulating evidence[20] suggesting that extrapolation of accessible phase molecu-

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(11) L. Hub and H. S. Mosher, *J. Org. Chem.*, **35**, 3691 (1970), and references therein.

(12) R. MacLeod, H. Prosser, L. Fikentscher, J. Lanyi, and H. S. Mosher, *Biochemistry*, **3**, 838 (1964).

(13) A. C. Cope and R. B. Kinnel, *J. Amer. Chem. Soc.*, **88**, 752 (1966).

(14) D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953).

(15) M. M. Green, J. M. Moldowan, D. J. Hart, and J. M. Krakower, *ibid.*, **92**, 3491 (1970).

(16) K. Mislow, and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

(17) In ref 15 above may be found a detailed discussion of the effect on the calculation of k_i and the relationship of ion intensity to relative rate constants.

(18) These data do not support proposals of variant mechanism between $Pb(OAc)_4$- and Ag_2O/Br_2-catalyzed tetrahydrofuran formation from alcohols; see: A. Deluzarche, A. Maillard, P. Rimmelin, F. Schue, and J. M. Sommer, *Chem. Commun.*, 976 (1970), and references therein.

(19) Since the Barton reactions are driven by the reactivity of the oxygen radical, the results suggest that the positive charge does not play an essential role in the mass spectral eliminations. This is in support of theories of reactivity on even and odd electron ions; see: F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966, p 78 ff.

(20) J. Deutsch and A. Mandelbaum, *J. Amer. Chem. Soc.*, **91**, 4809 (1969); M. M. Green and R. B. Roy, *ibid.*, **92**, 6368 (1970); ref 2 and 15 herein; M. E. Munk, C. L. Kulkarni, C. L. Lee, and P. Brown, *Tetrahedron Lett.*, 1377 (1970); E. Gil-Av, J. H. Leftin, A. Mandelbaum, and S. Winstein, *Org. Mass Spectrom.*, **4**, 475 (1971); C. C. Fenselau and C. H. Robinson, *J Amer. Chem. Soc.*, **93**, 3070 (1971).

lar structural parameters to gaseous molecular ions is right on.

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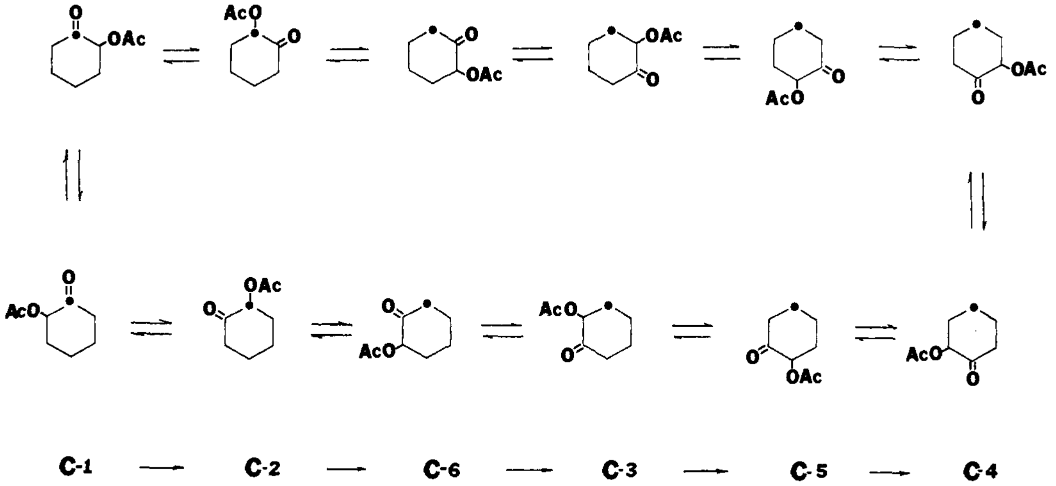
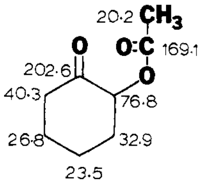
A ^{13}C Nuclear Magnetic Resonance Study of the Interchange–Transfer Rearrangement of α-Acyloxy Ketones[1,2]

Sir:

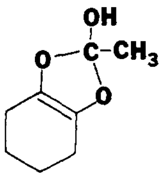
Recently, presumptive evidence for a degenerate rearrangement of α-acyloxycycloalkanones was found in the fact that all hydrogen atoms in a series of such compounds were labile in acetic acid-d_4.[3] The mechanism suggested (Scheme I) for the complete deuterium exchange involved both an enediol derivative **2** for *interchange* of the two oxygen functions and an allylic rearrangement of the enol **3** to *transfer* the acyloxy group from the α to the α′ position. By means of ^{13}C nmr spectroscopy we have now been able to provide strong support for this mechanism and to acquire additional information not readily discernible by other means.

Scheme I

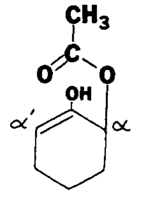




1



2



3

The proposed migration of oxygen functions around the intact carbon skeleton requires that a labeled carbon atom be equally distributed among all positions of the ring at equilibrium. The ^{13}C nmr signals from each carbon atom of 2-acetoxycyclohexanone (**1**) are well separated and assignable (see **1**).[4] 2-Acetoxycyclohexanone-*1*-^{13}C (60% enriched) was prepared in 66% yield by successive enol acetylation and epoxidation of cyclohexanone-*1*-^{13}C, which was made in 55% yield by the reaction of 1,5-dilithiopentane with $^{13}CO_2$.

After treatment of **1**-*1*-^{13}C in HOAc–KOAc at 142° for 12 hr, the recovered **1** had the excess ^{13}C label equally distributed between C-1 and C-2. With the same temperature and time, unlabeled **1** in DOAc-d_3–KOAc-d_3 incorporated up to five D atoms at C-2, C-3, and C-6.[5] Unlabeled **1** in propionic acid–KOAc (135°, 24 hr) gave recovered **1** but no 2-propionoxycyclohexanone. However, when the temperature of the reaction of **1**-*1*-^{13}C in HOAc–KOAc was raised to 218° for 22 hr, the recovered **1** now had the label equally distributed among all six carbon atoms of the ring. Furthermore, the ratio of the ring carbon signals to the acetate methyl signal was 10:1 as demanded by the suggested mechanism. Thus, in the HOAc–KOAc medium at the lower temperature, enolization and intramolecular functional group interchange occur readily, whereas the $\alpha \rightarrow \alpha'$ transfer occurs at a detectable rate only at temperatures above ~200°.

Whether the $\alpha \rightarrow \alpha'$ transfer in HOAc was intra- or intermolecular could not be established by substitution of propionic acid because acyl exchange occurred at temperatures much above 140°, but it was possible to show that the HOAc is not essential and also to provide strong evidence that the allylic rearrangement can be intramolecular. A dilute toluene solution (100 mg/5 ml) of **1**-*1*-^{13}C in a sealed glass tube at 240–250° for 75 hr[6]

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(1) Part XVIII in the series ^{13}C Nuclear Magnetic Resonance Studies.

(2) Part XVII: P. de Mayo, J. B. Stothers, and M. C. Usselman, *Can. J. Chem.*, in press.

(3) I. S. Y. Wang and E. W. Warnhoff, *Chem. Commun.*, 1158 (1969).

(4) The ^{13}C spectra were determined for benzene-d_6 solutions of **1** using a Varian XL-100-15 system. With proton noise decoupling and time averaging, satisfactory spectra could be obtained with samples of *ca.* 50 mg in 1.5 ml, although more concentrated solutions were employed for precise integrations. The shieldings were measured relative to internal TMS. The well-established additivity of substituent effects for ^{13}C chemical shifts allowed estimates of the shieldings for C-3, -4, -5, and -6 in **1** from the data for the monosubstituted cyclohexanes. The assignments for the carbonyl, carbinyl, and methyl carbons are unambiguous.

(5) Location of deuterium at C-3 and C-6 was established by comparison of the proton-decoupled ^{13}C nmr spectra of **1** and the ring-pentadeuterated **1**.

(6) Compound **1** in a sealed tube without solvent under these conditions undergoes considerable decomposition. Similarly, if **1** is heated in toluene solution in a sealed tube from which oxygen has not been removed, extensive decomposition occurs. However, removal of oxygen