between 19 and 27 °C, using an external reference of 1 M $H^{15}NO_3$ in D_2O. Chemical shifts, corrected to 25 °C, are reported upfield of this reference in parts per million.

Proton noise-decoupled ^{13}C spectra were obtained at 15.09 MHz with our Brukarian DFS-60 pulse Fourier transform modified spectrometer[19] on 1 M solutions in dimethyl-d_6 sulfoxide. Shifts were measured relative to internal cyclohexane (2.5% by volume) and referenced to Me_4Si.

Low-temperature proton spectra were recorded with a Varian A-56/60 spectrometer, using about a 0.5 M solution of sulfonethanamide **16** in sulfuryl chloride fluoride and in dichlorofluoromethane. Temperatures were measured before and after recording each spectrum by replacing the sample tube in the probe with a tube containing a thermometer in carbon disulfide precooled in dry ice–acetone.

The sulfonamides were synthesized by standard techniques[7,20] and purified by recrystallization from 70% aqueous isopropyl alcohol. Dimethyl sulfoxide was dried over calcium hydride and distilled prior to use.

Registry No.—**1**, 63-74-1; **2**, 98-10-2; **3**, 5339-67-3; **4**, 837-18-3; **5**, 67723-08-4; **6**, 3237-31-8; **7**, 37441-50-2; **8**, 1709-50-8; **9**, 5033-22-7; **10**, 28859-91-8; **11**, 5033-23-8; **12**, 67723-09-5; **13**, 67723-10-8; **14**, 81-07-2; **15**, 5661-14-3; **16**, 67723-11-9; **17**, 67723-12-0; **18**, 7471-26-3; **19**, 312-63-0; **20**, 6311-65-5; **21**, 16468-97-6; **22**, 1678-25-7; **23**, 67723-13-1; **24**, 1829-81-8.

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$^3J_{CH}$ Coupling Constants in Oxiranes, Thiiranes, and Cyclopropanes

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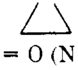
Three-bond coupling constants are reported between carbon and hydrogen in oxiranes, thiiranes, and cyclopropanes, plus limited data on aziridines. These coupling constants appear to be sufficiently regular to aid in assigning stereochemistry, although substantial differences occur with change in heteroatom. The increase in $^3J_{CH}$ in the order O, N, S, and CX_2 parallels the increase in bond length of the ring C–C bond. No effect of hybridization of the coupling carbon is evident.

In recent years, the NMR spectra of small ring compounds have attracted increasing interest.[1] The ^{13}C spectra of azirines,[1e] oxaziridines,[1d] oxiranes,[2] and aziridines[3] have been reported, as well as ^{13}C coupling constants for certain nitrogen heterocycles.[4,5] The importance of the orientation of the lone pair on nitrogen on the magnitude of various types of coupling constants has been elucidated.[4] A number of ^1H-NMR studies of small rings of general structure 1 have



1, X = O (N), S, CR_2

appeared.[6–14] In particular, Manatt, Brois, and Elleman reported that vicinal ^1H coupling constants increased in the order X = O, N, S, CR_2, although thiiranes (X = S) rather poorly obeyed attempted correlations with electronegativity.[15] Two- and three-bond coupling constants are of the same sign in oxiranes and aziridines, but of opposite sign in thiiranes and cyclopropanes.[15]

On the other hand, Ohtsura and Tori found that ^1H coupling constants were of larger magnitude in thiirane 1-oxides (and 1,1-dioxides) than in thiiranes. The results were interpreted in terms of the Pople–Bothner-By model for spin coupling.[17] However, the *larger* ^3J values for 1 (X = SO) were ascribed to *greater electronegativity* of the SO.

The present study emphasizes coupling constants between carbon and hydrogen. The purpose of this work was to determine whether a geometric dependence of $^3J_{CH}$ was present in three-membered rings and whether this dependence was sufficiently regular to be of use in predicting or substantiating configuration.[18] Scheme I illustrates the coupling constant data for certain oxiranes and thiiranes having a similar substitution pattern. The $^3J_{CH}$ values for *cis*-CH_3 and -H ring substituents are substantially larger than for trans substituents, where at best the coupling is barely observable. The data in Scheme I show that carbon–hydrogen coupling constants are rather similar to hydrogen–hydrogen coupling constants in their geometric dependence. Chertkov and Sergeyev,[19] as well as Perlin *et al.*,[20] have studied the geometric dependence of $^3J_{CH}$, and the general indications are that a Karplus relationship is obeyed for carbon–hydrogen nuclei.[21] However, Lemieux and co-workers have expressed reservations.[22] In **2–4** *cis*-CH_3 and -H exhibit $^3J_{CH}$ values from 2–3 Hz whereas trans nuclei show values of 0.5–1.8 Hz in fair agreement with expectations. Thus, the dihedral angle between cis nuclei is 0°, whereas the dihedral angle between trans nuclei is ca. 120°.

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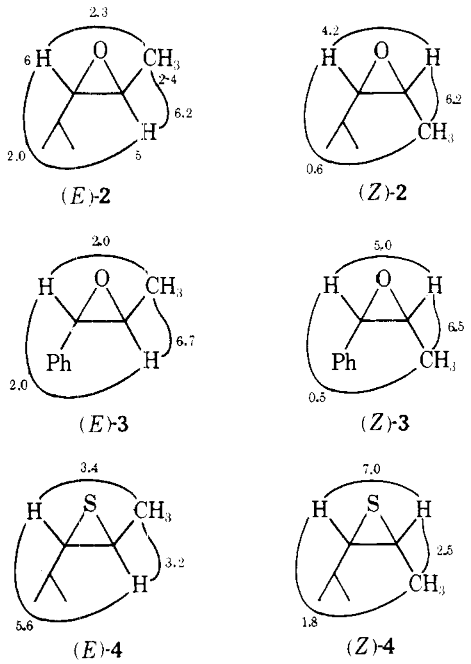
Scheme I

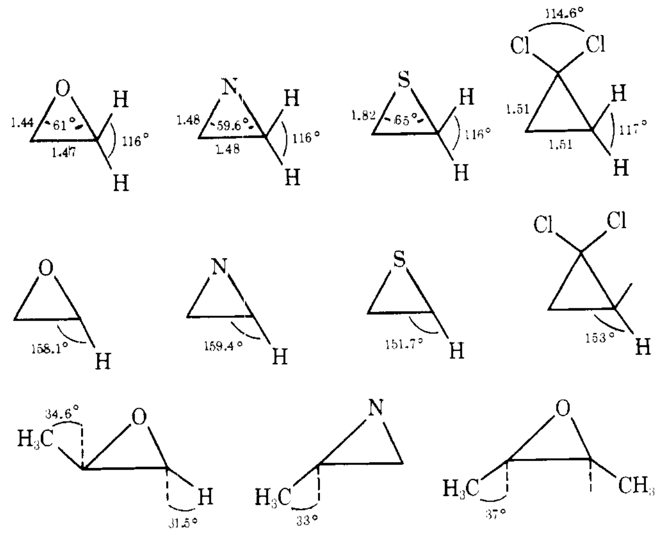


A large $^3J_{CH}$ value would be expected in the former case and a near minimum value in the latter.[23] However, the $^3J_{CH}$ values are larger for X = S than for X = O. As will be shown later, $^3J_{CH}$ is larger still for cyclopropane derivatives.

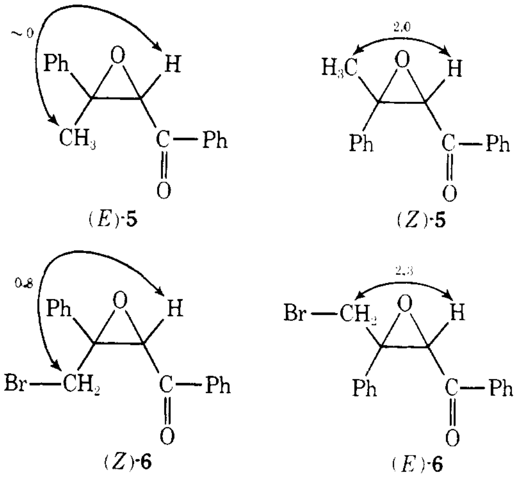
The geometries of similar small ring compounds are shown in Scheme II.[24] These data show that alkyl-substituted oxiranes are similar in angular relationships to hydrogen-substituted oxiranes, although small adjustments have occurred to minimize the additional steric hindrance.[23] The progression from X = O to S to CR_2 involves a lengthening of the ring C–C bond through which coupling occurs. Previous workers have considered oxiranes to have $sp^{2.22}$ hybridization for exocyclic bonds, whereas thiiranes were believed to have slightly greater p character, $sp^{2.27}$.[25] The values for X = N and CR_2 exocyclic bonds are roughly similar.[5,26]

The trisubstituted oxiranes, as in Scheme III, are the type of molecule where $^3J_{CH}$ may ultimately become useful as a guide to configuration, since few other methods are available.[18] These trisubstituted oxiranes proved to be rather similar to the less highly substituted molecules shown in Scheme I with regard to $^3J_{CH}$: i.e., $^3J_C \simeq 2$ Hz and $^3J_T \simeq 0$ Hz. The effect of electronegative substituents on exocyclic carbons is shown by **6E** and **6Z**. Similar to alkenes, the $BrCH_2$ group has a slightly larger $^3J_{CH}$ value than CH_3.[18,27] However, the magnitude of $^3J_{CH}$ seems relatively constant in a variety of structures, and therefore useful as an indication of configuration, although large changes in electronegativity or ring strain would be expected to produce divergences in $^3J_{CH}$ values from the data in Schemes I and III.

Scheme II



Scheme III

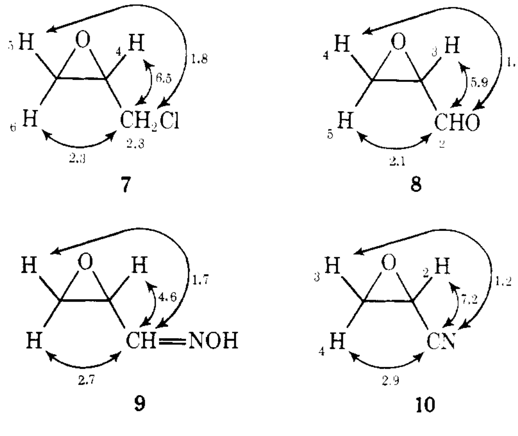


The effect of hybridization on $^3J_{CH}$ in a group of monosubstituted oxiranes is shown in Scheme IV. The carbon nucleus in question changes from sp^3 (CH_2Cl) to sp^2 (CO) to sp^1 (CN) in **7**, **8**, and **10**. In each case, the carbon is attached to one electronegative group. The total range of values is quite small. The lack of a significant effect of hybridization is in marked contrast to the findings in alkenes (i.e., CC=CH couplings) where an increase in $^3J_{CH}$ is found as s character (and nuclear-electron spin recognition) increases, as predicted by Karabatsos in 1962, and later observed by Marshall and others.[28]

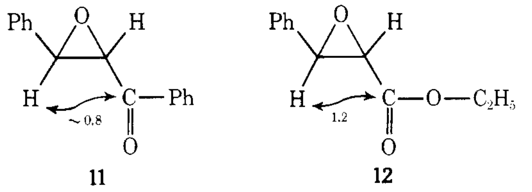
In alkenes, substantial variations in $^3J_{CH}$ were observed among various types of carbonyl groups (i.e., RCOC=CH). The general order of increasing $^3J_{CH}$ was ketones < esters ~ acids < aldehydes. In oxiranes (Schemes IV and V) a similar variation is found, although the range of $^3J_{CH}$ is small.

Scheme VI illustrates the coupling constants observed in a series of substituted cyclopropanes plus limited data on aziridines.[29] The cyclopropanes **13** and **14** were particularly attractive for study, as the ^1H spectrum was simple and the ^{13}C spectra therefore could be solved without too much difficulty. The $^3J_{CH}$ values for sp^3 (CH_3), sp^2 (CO), and sp^1 (CN) carbon nuclei show small differences. The ^{13}CN coupling constant to a cis vicinal proton is indeed quite sizable in **16**, but in **15**, this coupling constant is not as large as the ^{13}CO coupling constant to *cis*-^1H in **14**. In addition, the ketone ^{13}CO

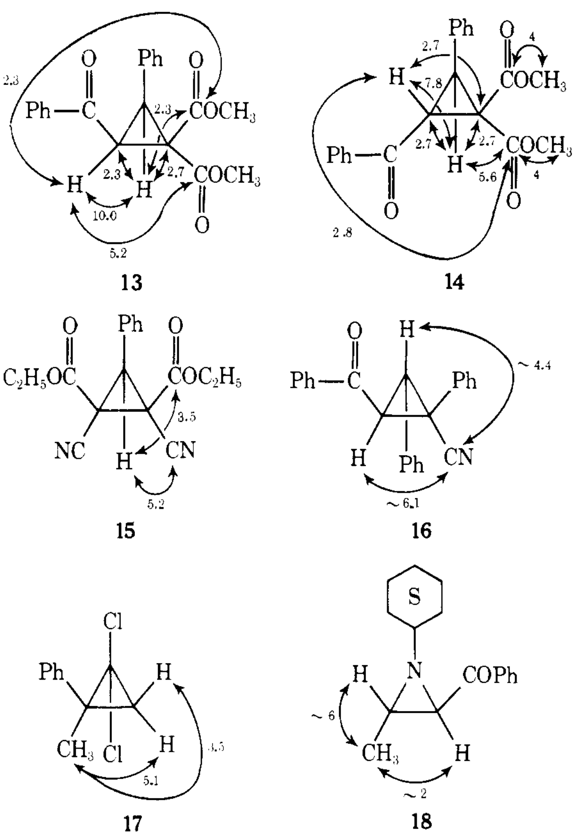
Scheme IV



Scheme V



Scheme VI



value in **13** is similar to the sp^3 $^{13}CH_3$ coupling in **17.** Thus, the dependence of $^3J_{CH}$ on hybridization is hardly straightforward in these cases.

In conclusion, we would again draw attention to the general order of magnitude of $^3J_{CH}$, namely, X = O (N), S, and CR$_2$. The magnitude of $^3J_{CH}$ roughly parallels $^3J_{HH}$ in this series of compounds.[30] In both cases, an increase in ^3J is found as the electronegativity of X decreases. However, Tori and coworkers found the opposite effect for X = S, SO, SO$_2$.[16] On the other hand, in both sets of data, the increase in ^3J parallels an increase in the C–C bond distance for the bond across the ring from X (cf. Scheme II).

Solkan and Sergeyev and others have given a mathematical relationship that predicts a *decrease* in spin coupling magnitude as bond length increases:

$$^3J_{HH} = {}^3J_0[1 - 2.9(r_{C-C} - 1.350)] \quad \text{for HC=CH}$$

This idea seems well established in NMR,[31] but it is clearly not obeyed for the three-membered rings of this study.

In thiirane 1,1-dioxides, Hoffmann et al. have interpreted the increase in bond length (compared to thiiranes) in terms of a weakening of the C–C bond across the ring from SO$_2$ due to a back-donation of electrons from SO$_2$ into the C–C antibonding orbital.[32] It is possible that the lone pairs on nitrogen and oxygen undergo a similar back donation.[32] Perhaps the reason for the increased magnitudes of spin coupling (X = O (N), S, CR$_2$) may be sought in the lower excitation energies likely to be present in molecules having weak bonds.[33]

Experimental Section

NMR Spectra. The ^{1}H spectra were taken on a Varian A-60D or a Varian XL-100 instrument. Expanded spectra of the ^{1}H regions of interest were used for computer simulation purposes. The ^{13}C spectra were taken on the XL-100 operating at 25.2 MHz. For chemical shift purposes, a 5K spectral width was used, with an 0.8 s acquisition time (leading to use of the maximum number of data points, i.e., 8192); a 0.2 s pulse delay was used with noise decoupling at 5–7 W of power. The tipping angle used was about 50° (30-μs pulse width on this instrument). In order to observe coupling constants to ^{1}H, the gated mode of decoupler operation was used, with about 1.5 to 2.0 s pulse delay; a 1K spectral width was used usually with a 500 Hz filter, and a 4 s acquisition time. The sample concentration was usually about 100–170 mg/mL of CDCl$_3$ (solvent). The reliability of the data is ±0.25 Hz for the $^3J_{CH}$ values.

The ^{1}H spectra were simulated using the LAOCON3 program adapted for computer-generated plots of the simulated spectrum. Parameters were varied until the simulation was superimposable on the original spectrum. Using the ^{1}H data thus obtained, the ^{13}C spectra were similarly simulated. For the oxiranes, $^2J_{CH}$ and $^3J_{CH}$ were taken as the same in sign. For cyclopropanes and thiiranes, opposite signs were used, which, incidentally, necessitates very careful simulations, as deceptive simplicity is near at hand. Microwave spectra suggested very similar geometries in substituted and unsubstituted oxiranes, and the signs of the ^{1}H and ^{13}C coupling constants are likely to be similar.[28,34]

For the iterative simulations of the observed ^{13}C spectra that were successful, that for epichlorohydrin (**7**) showed a root mean square error of 0.150, with probable errors in the data sets: J_{12} = 7.748; J_{13} = 7.638; J_{14} = 0.119; J_{15} = 0.064, and J_{16} = 0.064 [the ^{13}C is always numbered "1"]. For glycidaldehyde (**8**) the rms error was 0.051; probable errors of data sets: J_{12} = 0.021; J_{13} = 0.021; J_{14} = 0.024, and J_{15} = 0.024. For **10,** the rms error was 0.215, with probable errors: J_{12} = 0.251, J_{13} = 0.258, and J_{14} = 0.257. For **2E,** the rms error was 0.221, with probably errors: J_{12} = J_{13} = J_{14} = 0.031, J_{15} = 0.051, and J_{16} = 0.051. For **12,** the quaternary carbon and carbomethoxy groups displayed first-order spectra that were not simulated. For C3, the rms error was 0.004, with probable errors: J_{12} = 0.006 and J_{13} = 0.006. For **13,** several types of couplings were again first-order; for C3, however, simulation showed a rms error of 0.003, with probable errors: J_{12} = 0.004 and J_{13} = 0.004. For **14,** the AX spectrum, of course, is first-order. However, in the case of **15,** there was great difficulty in obtaining reasonable data, because of the superposition of H2 and H3, which led to the observation of "averaged" couplings in the ^{13}C spectrum. Protons 2 and 3 were broken apart with Eu(fod)$_3$ and the ^{13}C spectrum taken on the same solution where the ^{1}H spectrum indicated a reasonable separation of ^{1}H resonances. The data are, however, approximate.

The remaining materials were not successfully simulated by the iterative technique. Particularly for compounds with degenerate peaks, and/or a small amount of data available for an iterative fit, the program failed to converge to reasonable values. The computer repeatedly indicated changes in line numbers. These compounds were fitted by trial and error, as discussed earlier.

Compounds. (*E*)-2,3-Epoxy-4-methylpentane [(*E*)-2]. To 5 g (0.059 mol) of the commercial trans alkene in 25 mL of CH$_2$Cl$_2$ at 0 °C, a solution of 12 g (0.069 mol) of *m*-chloroperoxybenzoic acid in CH$_2$Cl$_2$ was added dropwise over 2 h. The solution was filtered, and the solid was washed with additional CH$_2$Cl$_2$. The combined CH$_2$Cl$_2$ solutions were extracted with saturated NaHCO$_3$ solution, dried (MgSO$_4$), and distilled through a short pass still, bp 101–102 °C (ca. 760 mm) (lit.[37] bp 102–103 °C), yielding 5.2 g of product (88% yield).

(*Z*)-2,3-Epoxy-4-methylpentane [(*Z*)-2]. was similarly prepared, bp 94–95 °C (lit.[37] bp 96–97 °C), in 83% yield.

1,2-Epoxy-1-phenylpropanes [(*E*)-3 and (*Z*)-3]. The *E* isomer was available from a previous study,[38] but was redistilled through a short pass still before spectral determination, bp 87–88 °C (20 mm) (lit.[38] bp 85 °C (20 mm). The *Z* isomer was prepared from commercial cis alkene using essentially the procedure for (*E*)-**2**, bp 94–95 °C (20 mm) [lit.[39] bp 91 °C (14 mm)].

(*Z*)-2,3-Epithio-4-methylpentane [(*Z*)-4]. To 10 g (0.1 mol) of (*E*)-2 in 20 mL of water, 10 g (0.13 mol) of NH$_4$SCN was added plus sufficient methanol to effect solution of all components. The reaction mixture was stirred at ca. 35 °C overnight, then 5 g (0.065 mol) of NH$_4$SCN was again needed, and the resulting mixture was stirred for 4 days.[40] The organic product was salted out by adding 50 mL of saturated NaCl solution, the organic material was then extracted with 6 × 50 mL portions of ether and dried ($MgSO_4$), and the ether was evaporated. The reaction product was separated from starting material by VPC using a 10% Apiezon M on DMCS treated Chromosorb W (column length ca. 3 m), at a column temperature of 80 °C and He flow rate of 60 mL/min. The retention time was 3.2 min. The NMR spectrum of the crude reaction product indicated a 75% yield of product.

(*E*)-2,3-Epithio-4-methylpentane [(*E*)-4] was prepared similarly and also purified by VPC (10% Apiezon on Chromosorb W column) similar to (*Z*)-4. The retention time was 4.8 min.

(*E*)-2,3-Epoxy-1,3-diphenyl-1-propanone (11). Chalcone was prepared by the procedure in ref 41, mp 54–56 °C. To 10.4 g (0.05 mol) of chalcone in a three-necked flask equipped with dropping funnel, reflux condenser, and stirrer, 50 mL of methanol and 50 of mL of 1 N NaOH was added, followed by warming to ca. 3.5 °C and addition of 6.4 mL of 30% H_2O_2 over a 30 min period. The solution changed from yellow to colorless. The reaction mixture was cooled and the product removed by filtration. The product was recrystallized from ethanol, mp 89–89.5 °C (lit.[42] mp 89–90 °C), giving 8.7 g (77% yield) of **11**.

2,3-Epoxy-3-methyl-1,3-diphenyl-1-propanones [(*E*)-5 and (*Z*)-5]. Dypnone was prepared by the procedure in ref 43, bp 155 °C (1 mm). Dypnone was epoxidized with H_2O_2 by the procedure used for **11**, in which both the *E* and *Z* isomers were formed. These were separated by fractional recrystallization from ethanol; (*E*)-**5**, mp 94–95 °C (lit.[44] mp 94–95 °C), in 81% yield, and (*Z*)-**5**, mp 162–163 °C (lit.[44] 163–164 °C), in 10% yield.

3-Bromo-2,3-epoxy-1,3-diphenyl-1-propanones [(*E*)-6 and (*Z*)-6]. These materials were prepared by the method of Wasserman giving (*Z*)-**5**, mp 136–137 °C (lit.[45,46] mp 135–136 °C), and (*E*)-**5**, mp 159–161 °C (lit.[45] mp 160–161 °C). Note that the compounds **5** and **6** of similar stereochemical nature have opposite Kahn–Ingold–Prelog designations due to a change in priority, which is a serious drawback to the *E*,*Z* system.

1-Chloro-2,3-epoxypropane (7) and 2,3-epoxypropanal (8) were commercial materials that appeared quite pure in the ^1H and ^{13}C NMR spectra. These were therefore used as received.

2,3-Epoxypropylidenazanyl acetate (9) was prepared by the method of Payne, bp 54 °C (0.3 mm) (lit.[46] bp 60–65 °C, 1 mm), in 62% yield.

2,3-Epoxypropanenitrile (10) was prepared from **9** by the method of Payne, bp 47 °C (20 mm) (lit.[46] bp 47–48 °C, 20 mm), in 55% yield.

Dimethyl 2-Benzoyl-3-phenylcyclopropane-1,3-dicarboxylates (13 and 14) were prepared by the method of Kohler.[47] The *Z* isomer (**13**) was obtained in 82% yield, mp 91–92 °C (lit.[47] mp 94 °C). The *E* isomer (**14**) was obtained in 95% yield, mp 72–73 °C (lit.[47] mp 72 °C).

3-Benzoyl-1,2-diphenyl-1-cyclopropanecarbonitrile (16) was prepared by the method of Kohler and Allen, mp 166–168 °C (lit.[48] mp 168 °C). In the case of this compound, the ^1H signals were superposed, but separable with $Eu(fod)_3$. By dehydrobromination resulting in ring closure of 4-bromo-5-oxo-2,3,5-triphenylpentanenitrile, an isomeric cyclopropane of **16** (mp 173 °C, lit.[40] mp 172 °C) was obtained. The ^1H signals were again superposed, but treatment with $Eu(fod)_3$ did not have the desired effect. The coupled ^{13}CN spectrum was nondescript. An isomer of mp 114 °C was also obtained, but in insufficient quantity for NMR analysis.

Diethyl 1,2-dicyano-3-phenyl-1,2-cyclopropanedicarboxylate (15) was prepared by essentially the method of Zhurinov and Val'fson, mp 98–99 °C (lit.[41] mp 96–97 °C). The NMR equivalence of the cyanides proved this material to have the stereochemistry shown in Scheme VI.

The aziridine **18** was generously provided by Dr. Phil Tarburton and Dr. N. H. Cromwell.

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Registry No.—(*E*)-**2**, 2390-95-6; (*Z*)-**2**, 3204-02-2; (*E*)-**3**, 23355-97-7; (*Z*)-**3**, 4541-87-1; (*E*)-**4**, 56078-18-3; (*Z*)-**4**, 56078-17-2; (*E*)-**5**, 19804-81-0; (*Z*)-**5**, 19804-64-9; (*E*)-**6**, 23265-28-3; (*Z*)-**6**, 23265-29-4; **7**, 106-89-8; **8**, 765-34-4; **9**, 67722-96-7; **10**, 4538-51-6; **11**, 7570-86-7; **13**, 67489-05-8; **14**, 67489-04-7; **15**, 67772-81-0; **16**, 67773-25-5; **18**, 67772-82-1; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-4-methyl-2-pentene, 691-38-3; chalcone, 94-41-7; *cis*-1-phenyl-1-propene, 766-90-5; dypnone, 495-45-4.

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Novel Decarboxylative Oxidation of α-Hydroxy-β-keto (or -β-imino) Acid Salts of Mercury(II)

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Mercury(II) salts or methylmercuric salts effect oxidative decarboxylation of α-hydroxy-β-keto (or -β-imino)carboxylate anions to convert the hydroxy to keto groups, with concomitant deposition of mercury(0). With certain reactant stoichiometries, mixed hydroxy and keto products are obtained. Dimethylmercury is produced additionally when methylmercuric salts are utilized as oxidant. Possible mechanisms are discussed. These results are important in considering (1) that metals involved in organic reactions may serve dual roles (catalysis and redox) and (2) *that the production of biacetyl, which accompanies anaerobic fermentation of sugars to acetoin, probably occurs* via an intervening nonenzymatic oxidation of the enolate anion generated upon decarboxylation of acetolactic acid.

Mercury(II) is known to oxidize many classes of organic compounds. The free aqueous ion is a fairly strong oxidant, as shown by the reduction potentials given below:

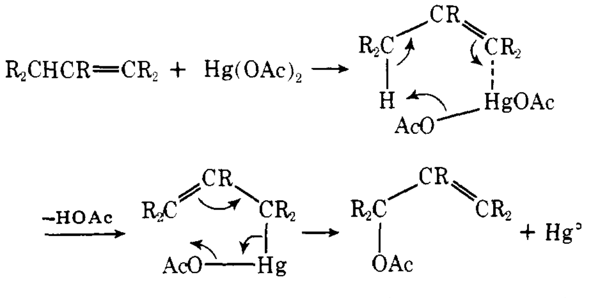
$$Hg^{2+} + 2e^- \rightarrow Hg^\circ \qquad E^\circ_{298} = +0.851\ \text{V}$$

$$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+} \qquad E^\circ_{298} = +0.905\ \text{V}$$

$$Hg_2^{2+} + 2e^- \rightarrow 2Hg^\circ \qquad E^\circ_{298} = +0.796\ \text{V}$$

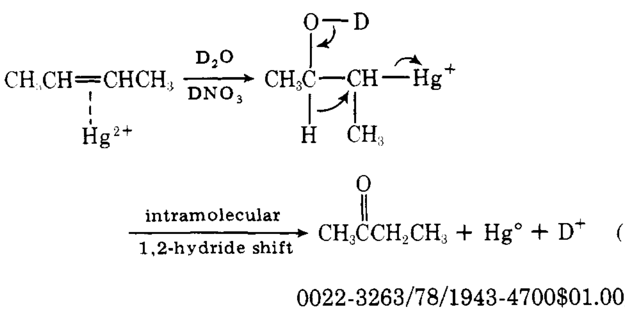
However, as indicated by the reaction mechanisms suggested in the literature (shown below), initial complexation of Hg(II) to a nucleophilic center (>C=C< or a donor lone-pair) is apparently a prerequisite for a kinetically observable redox reaction:

(i) Allylic acetoxylation of olefins (mercuric acetate in hot acetic acid)[1]



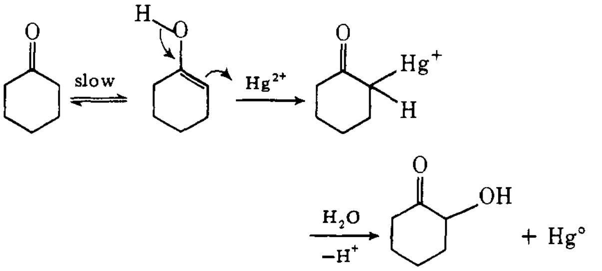
(1)

(ii) Oxidation of olefins to ketones (mercuric nitrate in warm aqueous nitric acid)[2,3]



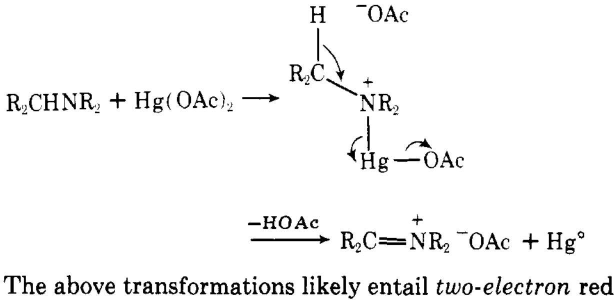
(2)

(iii) α-Hydroxylation of ketones (mercuric perchlorate in aqueous perchloric acid)[4]



(3)

(iv) Oxidation of tertiary amines (mercuric acetate in hot aqueous acetic acid)[5]



(4)

The above transformations likely entail *two-electron* redox reactions and the experimentally observed production of Hg(I), as of an apparent one-electron reduction, is attributable to the mercury(II) oxidant reacting with the initial Hg° product to form mercury(I) compounds:

$$Hg^\circ + HgX_2 \rightarrow Hg_2X_2 \qquad (5)$$

Reported herein is the novel finding that mercury(II) effects an oxidative decarboxylation of α-hydroxy-β-keto (or -β-imino)carboxylate anions (the conjugate acids of which are not isolable,[6,7] vide infra). The following stoichiometries have been demonstrated:

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