Table IV

Time, min	Absorbance at 1740 cm^{-1} 1	2
0	0	0
19	0.031	0.027
34	0.053	0.048
49	0.084	0.079
65	0.107	0.106
80	0.132	0.131
107	0.178	0.180
123	0.204	0.205

Table V

Time, min	Absorbance at 1740 cm^{-1} 3	4
0	0	0
19	0.017	0.010
34	0.024	0.017
50	0.032	0.022
72	0.045	0.031
94	0.058	0.044
110	0.061	0.051
124		0.055
132		0.061
149		0.066

value for k_2'/k_2 based upon the expected radical stabilities. Radical 4 is produced exclusively in both the di-*tert*-butyl peroxide catalyzed addition of propylene oxide to 1-octene[14] and the photochlorination of propylene oxide.[15] Radicals 3 and 4 have been prepared by photolysis of di-*tert*-butyl peroxide in propylene oxide at −40 °C.[16] From the reported ESR spectrum, one can estimate a 4/3 ratio of ~2.6. At 70 °C or higher,[14,15] 4 is essentially the only radical formed. Radicals 3 and 4 would be expected to open to α-carbonyl radicals. This has been observed for 4.[14,16] The free-radical chain process is completed by the α-carbonyl radicals abstracting a hydrogen atom from propylene oxide.

As the pressure is increased, the primary photoprocess, shown in Scheme I, is quenched thus decreasing propanal formation. Furthermore, the free-radical chain route becomes more significant as the pressure is increased; however, the absolute amount of free-radical chain route does not change significantly under the conditions studied. We propose that the majority of the propanal is formed via Scheme I, while the majority of the acetone is formed via Scheme II.

Experimental Section

General. The propylene oxide was purified by two distillations through a fractionating column and its purity checked by gas chromatography. The irradiations were carried out using a low-pressure mercury arc constructed of Suprasil quartz to allow use of the 1849-Å line. The lamp was mounted inside a 66-l. cell which also serves as the housing for a long path infrared optical system. A 66-l. reference cell was also used so that crossed-beam analysis could be carried out. The system was entirely mercury free (oil diffusion pumps, electronic pressure gauges, etc.) to ensure that mercury photosensitization could not be occurring. A Perkin-Elmer Model 21 spectrophotometer was used to obtain all spectra. The system was monitored as to the rate of formation of carbonyl products by following the increase in absorbance of the carbonyl band at ~1740 cm^{-1}. After irradiation the entire sample was trapped at −196 °C and then subjected to GLC analysis. Each product was collected on a Perkin-Elmer Model 154-L vapor fractometer and identified by direct comparison with authentic material.

Irradiation of Propylene Oxide. The photolysis cell was charged with 0.5 mm of propylene oxide and monitored by following the increase in carbonyl absorbance. The results of two representative runs at 0.52 mm are shown in Table IV.

Irradiation of Propylene Oxide with Inert Gas. The photolysis cell was charged with 0.52 mm of propylene oxide and various pressures of helium and nitrogen. The photolysis was monitored by following the increase in carbonyl absorbance. Ketene was formed in the presence of inert gas as indicated by its absorption spectrum. Two representative runs, with 35 mm added helium (3) and 177 mm added helium (4), are shown in Table V.

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Registry No.—Propylene oxide, 75-56-9.

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Configurational Stability of the Unsubstituted Cyclopropyl Radical in the Hunsdiecker Reaction

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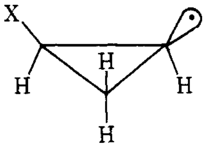
The stereochemistry of the cyclopropyl radical has been studied in a wide variety of situations, including the Hunsdiecker reaction of cyclopropanecarboxylic acids,[1] the reduction of cyclopropyl halides with organotin hydrides[2] or sodium borohydride,[3] and the photolysis or thermolysis of cyclopropanecarboxylic acid peroxy esters.[4] The various configurational results that have been observed include retention, partial retention, partial inversion, and complete thermodynamic equilibration. All cyclopropyl radicals examined hitherto, however, possess one or more β substituents (1) to monitor the configuration, and most also have an α substituent (2). Substitution can alter the final configurational



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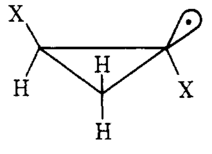

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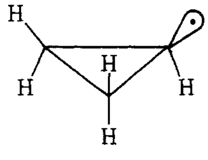

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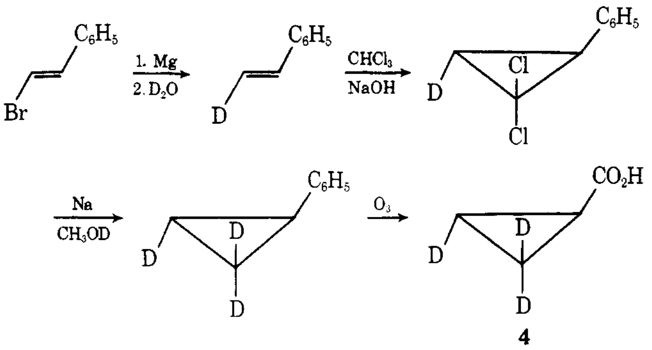
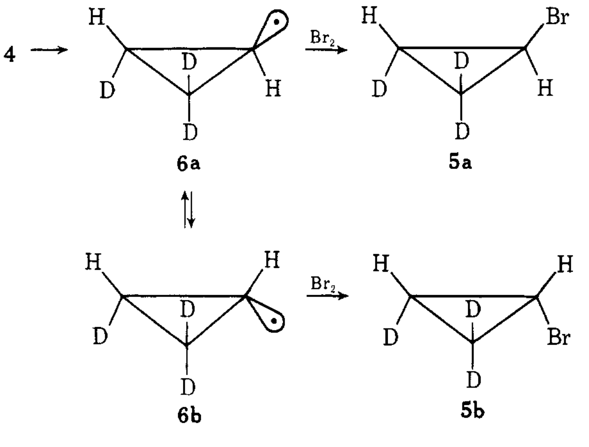
result by steric interaction with the incoming reagent, by steric interaction with other substituents (reflecting the thermodynamic stability of diastereoisomers), and by electronic effects on the inversion rate of the radical. Recent MINDO/3 studies show that both α and β substitution can affect inversion barriers.[5] In this note we wish to report the first chemical investigation of the configurational stability of the completely unsubstituted cyclopropyl radical (**3**).

The cyclopropyl radical was generated by the Hunsdiecker reaction,[6] and the stereochemical outcome of the reaction was determined by means of the deuterium label in cyclopropane-*trans*-2,2,3-d_3-carboxylic acid (**4**), which was prepared according to the illustrated stereospecific route.[7] Configuration was monitored by the single deuterium (trans in the starting carboxylic acid) at the 3 position, and NMR spectral analysis was simplified by incorporation of the additional pair of deuterium atoms at the 2 position. The NMR spectrum of the acid **4** showed a simple AB quartet at δ 1.2 and 1.5 with a coupling constant of 4.5 Hz, characteristic of trans stereochemistry.[8] The Hunsdiecker reaction was carried out with equimolar Br_2 and **4** in the presence of red mercuric oxide at 70 °C.[9]



The configuration of the product, bromocyclopropane-2,2,3-d_3 (**5**), was determined from its deuterium-decoupled NMR spectrum (Figure 1). The four-peak low-field resonance (δ 2.9) is from the 1 proton (α to bromine), which is identical (except for small isotopic differences) in the two possible configurational modifications, **5a** (retention) and **5b** (inversion), and has essentially the same chemical shift. The doublet with the larger (about 7 Hz)[8] splitting from the cis isomer **5b** is superimposed on top of the doublet with the smaller (about 3.5 Hz) splitting from the trans isomer **5a**. The two doublets, within experimental error (±2% over 12 runs), have equal areas. The four-peak high-field resonance (δ 0.9) is from the 2 proton, which is cis to the bromine in **5a** and trans in **5b**. Thus the small and large 2-proton doublets have different chemical shifts. The ratio of the doublets again is 1.00 ± 0.02.



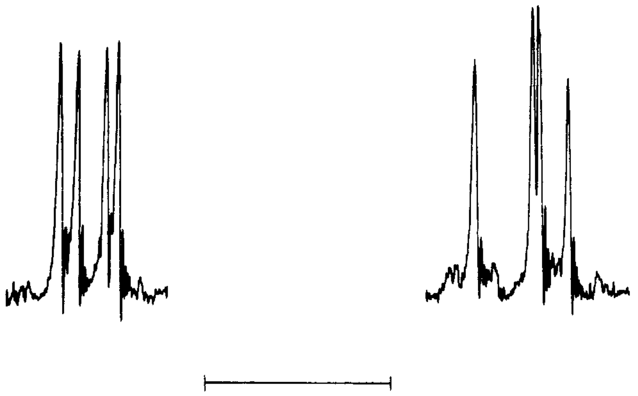


Figure 1. The 60-MHz proton magnetic resonance spectrum of bromocyclopropane-2,2,3-d_3 (**5**) obtained from the Hunsdiecker reaction of cyclopropane-*trans*-2,2,3-d_3-carboxylic acid (**4**). The peaks are sharpened by double irradiation at the deuterium frequency. The calibration bar represents 20 Hz.

There should be no difference in the rate of bromine attack on the isotopically isomeric radicals, **6a** and **6b**, since deuterium isotope effects should be negligible. The observed product distribution (**5a**/**5b**) of unity demands that interconversion of the radicals (**6a** ⇌ **6b**) be much faster than reaction with bromine. Consequently, the ratio **5a**/**5b** does not depend on the concentration of bromine. The ratio of the cyclopropyl radicals (**6a**/**6b**) must correspond to that of the products (**5a**/**5b**), i.e., unity. Thus the radical in the unsubstituted cyclopropyl system produced by the Hunsdiecker reaction undergoes complete thermodynamic equilibration of configuration. Either the radical is planar or atomic inversion is extremely fast. This result is consistent with an ESR study,[10] with the predictions of CNDO/2[2d] and MINDO/3[5] calculations, and with inferences from Ando's work on norcarane-7-carboxylic acid[1b] and Applequist's work on methylcyclopropanecarboxylic acids.[1c] The latter two studies also reported complete diastereomeric configurational equilibration. Our results therefore indicate that the alkyl substituents used by these workers did not alter the overall results. Incomplete equilibration observed in other substituted systems[1-4] must result from steric effects on reactivity or from electronic effects of substituents on the barrier to radical inversion.

Experimental Section

NMR spectra were taken on Perkin-Elmer R20B and Varian T60 spectrometers. Deuterium decoupling was carried out on the R20B.

Styrene-*trans*-β-*d*.[11] A mixture of *trans*-β-bromostyrene (91.5 g, 0.5 mol, purified from the Aldrich mixture), 82 g (0.75 mol) of ethyl bromide, and 800 ml of tetrahydrofuran (THF) was added dropwise to a mixture of 34 g (1.4 mol) of Mg and 100 ml of THF with stirring over a 3.5-h period. The temperature was kept below 30 °C by occasional cooling with a water bath. After completion of the addition, the solution was stirred for 30 min more, and 30 g (1.5 mol) of D_2O was added carefully. The products were extracted with ether, dried ($MgSO_4$), and distilled under aspirator pressure (39–40 °C) to give 31.5 g (61%) of styrene-*trans*-β-*d*. The NMR spectrum showed the sample to be at least 90% isomerically pure.

1,1-Dichloro-2-phenylcyclopropane-*d*. To a mixture of 70.7 g (0.65 mol) of styrene-*trans*-β-*d*, 180 g (1.6 mol) of $CHCl_3$, and 140 ml of 50% aqueous NaOH, 1.3 g of benzyltriethylammonium chloride was added. The mixture was stirred for 2 h, with the temperature maintained at 30–40 °C. The mixture was diluted with 600 ml of H_2O, extracted three times with ether, and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was distilled [62–65 °C (1 mm)] to give 110.5 g (90%) of the product. The NMR spectrum showed this sample to be at least 87% isomerically pure: NMR (CCl_4) δ 1.68 (d, J = 9 Hz, 1 H), 2.73 (d, J = 9 Hz, 1 H), 7.09 (s, 5 H).

Phenylcyclopropane-*trans*-2,2,3-d_3. 1,1-Dichloro-2-phenylcyclopropane-*3-d* (30 g, 0.16 mol) was placed with 300 ml of anhydrous ether in a 1-l., three-necked flask cooled in an ice bath. Metallic Na (40 g) was added in roughly 1-cm^3 pieces during the course of the reaction. At the same time, wet methanol (15 ml of D_2O and 90 ml of MeOD) was added dropwise with vigorous stirring. The addition of wet methanol required 2.5 h, but the addition of Na was finished in 2 h (the addition of Na should be faster than that of wet methanol). After completion of the reaction, any excess Na was removed by filtration with a Büchner funnel. The solution was washed with H_2O, and the ether layer was dried ($MgSO_4$). Distillation [60–62 °C (9 mm)] yielded 15 g (78%) of the product. The isomeric purity was over 87% by NMR analysis: NMR (CCl_4) δ 0.58 (d, J = 5 Hz, 1 H), 1.72 (d, J = 5 Hz, 1 H), 6.95 (m, 5 H).

Cyclopropane-*trans*-2,2,3-d_3-carboxylic Acid (4).[7] A solution of 15 g (0.124 mol) of phenylcyclopropane-*trans-2,2,3*-d_3 in 200 ml of HOAc and 20 ml of H_2O was placed in a 500-ml flask equipped with a sintered glass cylinder as an ozone inlet, as well as a gas outlet. Ozone was produced by electric discharge from a Welsbach T 23 ozonator and bubbled through the solution at 0 °C. Excess O_3 was decomposed by bubbling the exit gas through an aqueous solution of NaI. After a reaction period of 36 h, the starting material has almost gone, as indicated by the NMR spectrum of the total reaction mixture. Hydrogen peroxide (30%, 40 ml) was then added to the ozonolysis mixture, which was allowed to stand overnight at room temperature. Some palladium on charcoal was added to decompose any remaining peroxide. After the complete decomposition of the peroxide (overnight), the palladium/charcoal was filtered off with a Büchner funnel. The solvent was removed under reduced pressure at about 40 °C, and the residue was distilled to give 4.1 g of the cyclopropane-d_3-carboxylic acid: NMR (CCl_4) δ 1.2 (d, J = 4.5 Hz, 1 H), 1.5 (d, J = 4.5 Hz, 1 H).

Bromocyclopropane-*2,2,3*-d_3 (5). A mixture of 30 ml of 1,1,2,2-tetrachloroethane, 13.7 g (0.063 mol) of red mercuric oxide, and 10.8 g (0.125 mol) of cyclopropane-*trans-2,2,3*-d_3-carboxylic acid was placed in a 100-ml, three-necked flask equipped with a distilling receiver, a thermometer, and a stirrer. The mixture was heated to remove about 4 ml of H_2O and solvent. The solution was then cooled to about 70 °C, the distilling receiver was removed, and 20 g (0.125 mol) of Br_2 was added dropwise with stirring over a period of 15–20 min. Carbon dioxide evolved vigorously but ceased about115 min after the addition was completed. The condenser was replaced by a distillation column, and the mixture was distilled with stirring. The distillate below 75 °C was collected (4.5 g, 29%).

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Registry No.—4, 61377-11-5; **5a**, 61377-12-6; **5b**, 61377-13-7; *trans-β*-bromostyrene, 588-72-7; styrene-*trans-β-d*, 6911-81-5; 1,1-dichloro-2-phenylcyclopropane-*d*, 61377-09-1; phenylcyclopropane-*trans-2,2,3*-d_3, 61377-10-4.

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Favorskii-Type Rearrangement of Chlorinated Acetylacetone Monomethyl Enol Ethers. Presumptive Evidence for a Cyclopropane Dimethyl Acetal Intermediate

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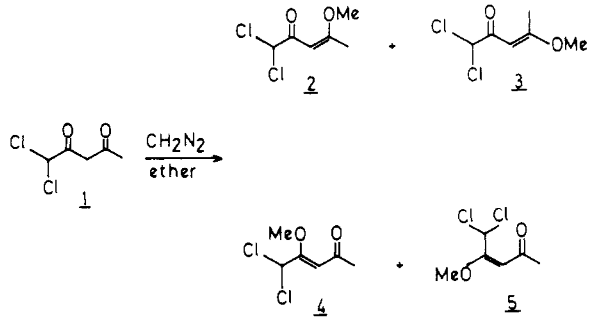
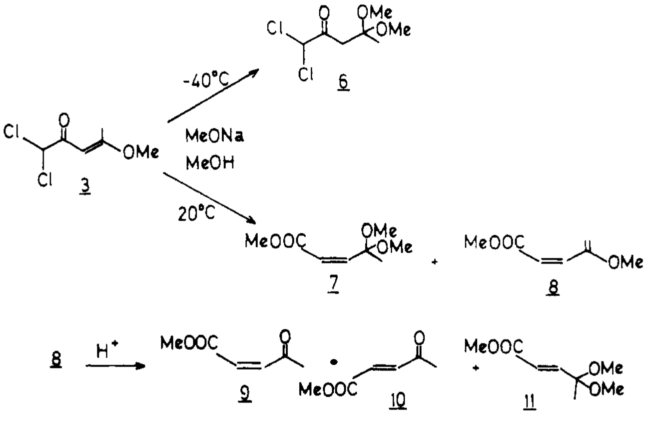
Our interest in the Favorskii rearrangement of dichlorinated methyl ketones[3,4] and the reactions of chlorinated 1,3-cyclohexanedione monomethyl enol ethers with sodium methoxide[5] prompted us to explore the reactivity of dichlorinated aliphatic β-diketone monomethyl enol ethers.

As model compounds the monomethyl enol ethers of 1,1-dichloro-2,4-pentanedione (**1**), prepared by condensation of methyl dichloroacetate and acetone in the presence of sodium using the method of Panizzi,[6] have been selected. Treatment of **1** with ethereal diazomethane initially gave four compounds: (*Z*)- and (*E*)-1,1-dichloro-4-methoxy-3-penten-2-one (**2, 3**); (*Z*)- and (*E*)-5,5-dichloro-4-methoxy-3-penten-2-one (**4, 5**)



(14, 27, 6, and 24%, respectively). On distillation the *Z* compounds were completely isomerized into the more stable *E* compounds **3** and **5**, which, however, were thermally labile and decomposed on standing.

Treatment of (*E*)-1,1-dichloro-4-methoxy-3-penten-2-one (**3**) with 4 equiv of sodium methoxide in methanol (2.5 N) at −40 °C gave the methanol addition product 1,1-dichloro-4,4-dimethoxy-2-pentanone (**6**). At room temperature a mixture of *cis*-methyl 4,4-dimethoxy-2-pentenoate (**7**) and *cis*-methyl 4-methoxy-2,4-pentadienoate (**8**) was produced in a 1:4 ratio. Treatment of **8** with dilute acetic acid afforded a mixture of *cis*- and *trans*-methyl 4-oxo-2-pentenoate (**9** and **10**) and *trans*-methyl 4,4-dimethoxy-2-pentenoate (**11**).



As found in the case of dichloromethyl ketones[3,4] the unsaturated esters **7** and **8** are in the cis configuration, which is in accordance with the mechanism proposed by Bordwell's