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Energies of the Cycloalkyl and 1-Methylcycloalkyl Free Radicals by the Decarbonylation Method

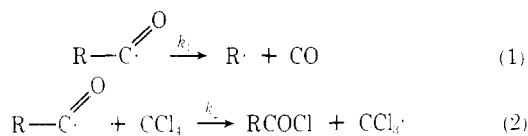
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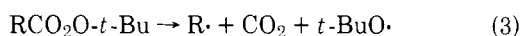
The relative rates of formation of cycloalkyl and 1-methylcycloalkyl free radicals by decarbonylation of the corresponding acyl radicals have been measured for ring sizes 3-6. The relative rates at 135 °C for cycloalkyl radicals in descending order of ring size from 6 to 3 are 0.268, 0.316, 0.0795, and 0.0121. For the 1-methylcycloalkyl radicals of the same ring sizes they are 14.1, 11.1, 1.18, and 0.542. The relationships of these values to other measures of cycloalkyl radical stabilities are presented and discussed.

The first quantitative measurements of the energies of simple bridgehead radicals were reported by Applequist and Kaplan in 1965.¹ Their method was to measure by analysis of products the competition between decarbonylation of acyl radicals (eq 1) and capture by carbon tetrachloride (eq 2). The



rate for eq 2 was assumed constant (independent of R), for which supporting facts and arguments were presented. The acyl radicals were generated from the corresponding aldehydes by reaction with di-*tert*-butyl peroxide. Values of k_1/k_2 were found to correlate with known values of the dissociation enthalpies ($D_{\text{R-H}}$) of simple alkanes to form alkyl radicals, and this correlation was used to propose values of $D_{\text{R-H}}$ for the bridgehead position studies of the following radicals: 90.1 kcal for 1-adamantyl, 91.0 kcal for 1-bicyclo[2.2.2]octyl, and 97.7 kcal for 1-norbornyl.

Subsequently, three groups have investigated the same bridgehead series using a better-known method, the rates of decomposition of *tert*-butyl peresters (eq 3).²⁻⁴ In Table I are



shown their results in the form of relative rates, together with the earlier k_1/k_2 values from decarbonylation. Viewed in this form, the results of the two approaches are strikingly similar, which supports the validity of both methods. The adamantyl, *tert*-butyl, and 1-bicyclo[2.2.2]octyl radicals have roughly the same stability, while the 1-norbornyl radical is destabilized. Some authors^{2,3} have attempted to extract evidence for geometric destabilization of even the adamantyl and bicyclo[2.2.2]octyl radicals by factoring out the inductive stabilization of the perester transition states leading to these radi-

cals, but the meaning of such geometric destabilization is unclear now that the geometry of the *tert*-butyl radical is known to be pyramidal and probably close to tetrahedral.^{5,6} The point remains, however, that the perester transition states are subject to inductive effects and therefore may be polarized to such an extent that the rates may to some degree reflect carbonium ion stability in addition to radical stability. The extent of such influences in the decarbonylation transition states is entirely unknown, but by the aforementioned technique of empirical correlation with known $D_{\text{R-H}}$ values any polar contribution may be automatically canceled.¹

In addition to the tenuous advantage of the decarbonylation method in avoiding polar kinetic effects, the method has a large advantage over perester thermolysis in that the latter changes mechanism to a one-bond (-O-O-) cleavage when the alkyl radical is of high energy, and it seems likely that the 1-norbornyl radical is about at (if not beyond) the limit of the range of radicals that can be studied this way.^{4,7} The decarbonylation method has been extended to the less stable 1-triptycyl radical⁸ ($D_{\text{R-H}} = 98.3$ kcal) and even further in the present work (vide infra).

Other kinetic approaches to the measurement of bridgehead free-radical energies have also been employed and deserve mention here.

Rüchardt⁹⁻¹⁴ has measured the rates of the unimolecular decompositions of symmetrical azo compounds, RN=NR. When the R groups were the bridgehead radicals listed in Table I, the rates at 300 °C in benzene were, relative to each other, much like those in the perester thermolysis: the relative rates of 1-adamantyl/1-bicyclo[2.2.2]octyl/1-norbornyl were (1.00):0.36:0.071.¹⁵ The interpretation is clouded, however, by the fact that even the 1-adamantyl case is slower than the *tert*-butyl case (2,2-azoisobutane) by a factor of 0.02.¹⁵ Rüchardt concluded that the bridgehead cases are slower because the transition state in the endothermic azo decomposition is more advanced so that planarity at the radical center is more closely approached.⁹ But to explain the similar relative rates

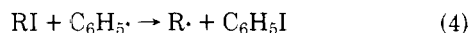
Table I. Relative Rates of Reactions Forming Free Radicals at 135 °C^a

Radical	Decarbonylation ^b	Perester thermolysis
1-Adamantyl	2.48	2.00, ^c 1.66, ^d 4.57 ^e
<i>tert</i> -Butyl	(1.00)	(1.00)
1-Bicyclo[2.2.2]octyl	1.24	0.245, ^c 0.225 ^e
1-Norbornyl	0.0068	0.0149, ^c 0.0135 ^e

^a The perester rates were all taken at lower temperatures but extrapolated to 135 °C by least-squares fitting to the Eyring equation using all reported rate constants²⁻⁴ with equal weights. ^b Reference 1. ^c Reference 3. ^d Reference 2. ^e Extrapolated rate constants from ref 4 relative to the average rate at 135 °C for *tert*-butyl (0.065 s⁻¹) from ref 2 and 3.

within the bridgehead series for azo compounds and peresters he suggested¹¹ that most of the strain increase is already present in transition states in which the bridgehead bonds are only slightly broken. This interpretation is difficult to accept even in terms of planar tertiary radicals, but if the radicals are indeed pyramidal then something else must surely be invoked to account for the azo data.¹⁶ The rates of azo decomposition do not appear to have been correlated with known energies of alkyl radicals (but see further discussion below). The method must be regarded as one with some promise but with hazards in interpretation.

Danen¹⁷ determined the relative rates of iodine atom abstraction by a phenyl radical (eq 4). The empirical correlation



of these rates with known aliphatic $D_{\text{R-H}}$ values gave a line from which the following values for the bridgehead positions were read off: 92.2 kcal for 1-adamantyl, 93.2 kcal for 1-bicyclo[2.2.2]octyl, and 99.4 kcal for 1-norbornyl. These values are 1.7–2.2 kcal larger than the decarbonylation figures¹ (vide supra). The reason for the discrepancy is not evident. The iodine atom abstraction method should be tested further.

The purpose of this publication is to present the results of measurement of the energies of cycloalkyl and 1-methylcycloalkyl radicals by the decarbonylation method. Values of k_1/k_2 and values of $D_{\text{R-H}}$ inferred from them by the previous correlation¹ are listed in Table II.

Discussion

All of the radical studies in this work have also been investigated by R uchardt and co-workers using the perester thermolysis.¹⁹ To facilitate comparison of their rates with the decarbonylation data, all rates have been converted to relative rates with the six-membered rings as the standard (Table III). As in the bridgehead series, the data are very similar. The most obvious differences are that the cyclopentyl and 1-methylcyclopentyl radicals are formed more easily in the decarbonylation method than in the perester thermolysis, by a factor of about 2 in each case, and that the 1-methylcyclopropyl radical is formed much faster by decarbonylation than by perester thermolysis.

Both sets of data are in contrast with the rates of solvolysis of cycloalkyl tosylates²⁰ and the rates of decomposition of azobiscycloalkane nitriles,²¹ in both of which the 5-ring case goes considerably faster than the 6-ring case. These examples were easily understood in terms of transition states approaching planarity where eclipsing would be relieved in the cyclopentanes but increased in the cyclohexanes. In order to interpret the free-radical reactions in a way consistent with planar free radicals, it is necessary to propose early transition states (still tetrahedral) in the perester thermolysis and decarbonylation. If the radicals are actually tetrahedral or insensitive to out-of-plane distortion, then the transition states

for their formation could be tetrahedral no matter how far bond breaking had gone. A small degree of polarization in the transition state might produce some transient flattening toward carbonium ion geometry, and such an effect could be contributing to the differences between the two methods. Alternatively, if the transition state for decarbonylation is more advanced than that for perester thermolysis, then eclipsing involving the leaving group in the starting material might be more relieved in the former and produce the relatively faster reaction in the cyclopentyl cases.

The large discrepancy between the decarbonylation rate and perester thermolysis rate for formation of the 1-methylcyclopropyl radical is not fully explainable with the information at hand. If the perester data are for two-bond cleavage transition states, then the cyclopropyl radical is only slightly stabilized, if at all, by an α -methyl group: the rate constants for cyclopropyl and 1-methylcyclopropyl were 4.2×10^{-5} and 7.4×10^{-5} s⁻¹, respectively, at 110 °C.¹⁹ On the other hand, the data in Table II (decarbonylation) show an acceleration factor due to methyl of 45 in the cyclopropyl case, compared with 15, 35, and 53 in the cyclobutyl, cyclopentyl, and cyclohexyl cases, respectively. Perhaps the cyclopropyl and 1-methylcyclopropyl cases in the perester series have gone beyond the expected stability limit where the mechanism shifts to the one-bond cleavage (O-O), which would be insensitive to the α -methyl substituent. This would still leave unexplained the relatively easy formation of 1-methylcyclopropyl from decarbonylation since a competing one-bond mechanism for perester thermolysis should make the rate *larger* than expected from the radical stability.

If conformational and strain effects are of only small importance in determining the values of $D_{\text{R-H}}$ or the correlated rate constants, then one must ask what determines the general reaction orders shown in Tables II and III (ring sizes $6 \cong 5 > 4 > 3$). R uchardt¹⁹ has pointed out that the logarithms of the perester rates give rough linear correlation with values of $J_{13\text{C-H}}$ for the corresponding cycloalkanes.²² The decarbonylation data in Table II for secondary radicals correlate about as well as the perester data (ring sizes 3–6) with $J_{13\text{C-H}}$ (correlation coefficients $r = 0.972$ and 0.961 , respectively) but not as well for the tertiary radicals ($r = 0.864$ and 0.997 for decarbonylation and perester thermolysis, respectively). Although the hybridization state of carbon as measured by $J_{13\text{C-H}}$ is clearly not the sole determinant of radical stability, it may be the principal contributor to the differences within the cycloalkyl or 1-methylcycloalkyl series up through the six-membered ring.

Some of the 1-methylcycloalkyl radicals have also been investigated by the azoalkane decomposition method.²³ The relative rates at 200 °C in benzene for formation of 1-methylcyclohexyl, 1-methylcyclopentyl, and 1-methylcyclobutyl radicals were (1.00):1.66:0.076.¹⁵ These results are not very different from the decarbonylation and perester results (Table III), but they do show still another small enhancement of the 5 ring relative to the other two ring sizes.

The values of $D_{\text{R-H}}$ for the secondary cycloalkyl radicals have been determined by gas phase kinetic studies of the reactions of cycloalkanes with various free radicals. The best values as selected by Ferguson and Whittle¹⁸ are shown in Table II. The values are similar to those derived from decarbonylation and show the same relative stabilities, which further supports the validity of the decarbonylation method.

The relative stabilities of cyclopentyl and cyclohexyl radicals (as well as larger ring sizes) have been studied by Bunce and Hadley²⁴ by measuring the relative reactivities of the cycloalkanes with various hydrogen-abstracting radicals: chlorine and bromine atoms, *tert*-butoxy, phenyl, and trichloromethyl. The relative reactivities per methylene group vary from near unity to about a factor of 4 in favor of the cy-

Table II. Energies of Cycloalkyl Radicals by the Decarbonylation Method

Registry no.	Radical	k_1/k_2 (135 °C) ^a	Runs	D_{R-H} (25 °C) ^b	D_{R-H} (lit.) ^c
3170-58-9	Cyclohexyl	0.268 ± 0.050	5	96.2 ± 0.3	95.5
3889-74-5	Cyclopentyl	0.316 ± 0.039	8	96.0 ± 0.2	94.2
4548-06-5	Cyclobutyl	0.0795 ± 0.0164	3	97.8 ± 0.3	96.5
2417-82-5	Cyclopropyl	0.0121 ± 0.0032	3	100.2 ± 0.4	100.7
16998-65-5	1-Methylcyclohexyl	14.1 ± 2.9	5	91.1 ± 0.3	
33968-73-9	1-Methylcyclopentyl	11.1 ± 3.0	4	91.4 ± 0.4	
53249-17-5	1-Methylcyclobutyl	1.18 ± 0.12	3	94.3 ± 0.2	
65338-31-0	1-Methylcyclopropyl	0.542 ± 0.144	3	95.3 ± 0.4	

^a Experimental error is the average deviation from the average of all runs. ^b In units of kcal/mol. ^c From gas phase kinetic studies summarized in ref 18.

clopenty radical. The reactivity ratios were sensitive to solvent as well as the attacking radical. It would be difficult to draw firm conclusions about the relative stabilities of the two cycloalkyls from these complicated data, but the numbers are at least not in obvious conflict with the other data described above.

A modification of the decarbonylation method, apparently not yet applied to the cycloalkyl cases, is the use of an efficient acyl radical trap, such as nitrosoisobutane, in order to reduce the risk of variation of k_2 with structure.²⁵ A problem with this method seems to be the difficulty of maintaining a known concentration of the trap low enough to permit any decarbonylation of acyl radicals which would produce primary alkyl or comparably unstable radicals. The method is thus apparently restricted to approximately the same range of radical types as the perester thermolysis method.

Experimental Section

All boiling points and melting points are uncorrected. Infrared spectra were obtained on Perkin-Elmer Infracord and Model 237 grating infrared spectrometers and calibrated with the 1603-cm⁻¹ band of polystyrene. All NMR spectra were measured with Varian Models A56/60, A60A, and T-60 spectrometers at 60 MHz. Chemical shifts are expressed in parts per million relative to an internal standard of Me₄Si. Preparative vapor phase chromatography was performed on a Varian Aerograph Model A-700 Autoprep instrument. Quantitative vapor phase chromatography was performed on an F and M Model 300 instrument. Elemental analyses were performed by Mr. J. Nemeth and his associates. Mr. Robert Thrift assisted in operation of the NMR spectrometers.

Materials. Carbon tetrachloride (Baker, spectrophotometric grade) was distilled under argon from phosphorus pentoxide through a 1.7 m Podbielniak column and collected at 76.0–76.2 °C (751 mm). Di-*tert*-butyl peroxide (Matheson Coleman and Bell, practical grade) was distilled under argon through a 1.7 m Podbielniak column and collected at 40.0–40.5 °C (60 mm) [lit.²⁶ bp 37 °C (48 mm)]. *o*-Dichlorobenzene (Eastman, reagent grade) was distilled through a 1.7 m Podbielniak column and collected at 95.8–96.3 °C (55 mm). *p*-Chlorotoluene (Eastman, reagent grade) was distilled through a 1.7 m Podbielniak column and collected at 75.0–75.2 °C (27 mm). 1,2-Dimethoxyethane (Eastman, reagent grade) was distilled through a 30 cm glass helices packed column and collected at 82.0–82.7 °C (748 mm). Ethanol (U.S.I., absolute) was distilled from magnesium ethoxide²⁷ under argon and collected at 78.2–78.4 °C (753 mm); the product was stored under argon. Methanol (Baker, reagent grade) was distilled from magnesium methoxide²⁷ under argon and collected at 64.3–64.6 °C (751 mm); the product was stored under argon. Hexachloroethane (Aldrich Chemical Co.) was recrystallized from ether and melted at 187–188 °C (sealed capillary) [lit.²⁸ mp 189 °C (sealed capillary)]. *tert*-Butyl chloride (Aldrich Chemical Co.) was distilled through a 30 cm spiral wire column and collected at 49.3–49.8 °C. Tetrahydrofuran (Baker, reagent grade) was dried over calcium hydride, distilled from lithium aluminum hydride, and collected at 63.8–64.7 °C (750 mm); the product was stored under argon. Cyclohexyl chloride (Aldrich Chemical Co.) was distilled through a 30 cm glass helices packed column and collected at 140.8–141.3 °C (742 mm) [lit.²⁹ bp 40.3 °C (21 mm)]. Cyclopentyl chloride (Columbia Organic Chemicals) was distilled through a 30 cm glass helices packed column and collected at 114.2–114.8 °C (750 mm) (lit.³⁰ bp 114.5–115.0 °C). 1-Methylcyclohexene (Aldrich Chemical Co.) was distilled under argon through a 30 m glass helices packed column and collected at

Table III. Comparison of Decarbonylation and Perester Thermolysis Data for Formation of Cycloalkyl Free Radicals

Radical	Rel. k_1/k_2 from decarbonylation at 135 °C	Rel. k from perester thermolysis ^a
Cyclohexyl	(1.00)	(1.00)
Cyclopentyl	1.18	0.468
Cyclobutyl	0.297	0.233
Cyclopropyl	0.045	0.061
1-Methylcyclohexyl	(1.00)	(1.00)
1-Methylcyclopentyl	0.787	0.334
1-Methylcyclobutyl	0.084	0.119
1-Methylcyclopropyl	0.038	0.0017

^a Data at 110 °C for the secondary radicals and 80 °C for the tertiary radicals.

108.0–108.6 °C (750 mm) (lit.³¹ bp 110.2–110.4 °C). Cyclopropanecarboxylic acid (Aldrich Chemical Co.) was distilled through a 15 cm Vigreux column and collected at 96.0–97.0 °C (40 mm) [lit.³² bp 97–98 °C (40 mm)]. Cyclohexanecarboxylic acid (Aldrich Chemical Co.) was distilled through a 15 cm Vigreux column and collected at 113.1–114.2 °C (10 mm) [lit.²⁹ bp 110 °C (8 mm)]. Cyclopropane (Matheson, high purity grade) was used without further purification.

Impurities in compounds directly used for the decarbonylation experiments and product determination studies were less than 0.5% as determined by NMR and infrared spectral or vapor phase chromatographic analyses.³³

Vapor Phase Chromatographic Analyses. The vapor phase chromatographic analyses were performed on an F and M Model 300 instrument with helium as the carrier gas. The separations were carried out on the following 0.25-in diameter columns: (A) 15 ft 10.5% SE-30 on Chromosorb P-AW-DMCS, (B) 15 ft 5.0% SE-30 on Chromosorb P-AW-DMCS, (C) 15 ft 20.0% Carbowax 20M on Anakrom ABS 60–70 mesh, and (D) 12 ft 20.0% Carbowax 20M on Anakrom ABS 100–110 mesh. Collections of products for identification purposes were carried out on the above columns or on the following two preparative columns: (1) 15 ft × 0.375 in 19.5% SE-30 on Chromosorb P-AW-DMCS and (2) 15 ft × 0.375 in 20.0% Carbowax 20M on Chromosorb P-AW-DMCS.

Quantitative analyses were performed using temperature programming. Peak areas were measured for each analysis by a disc chart integrator and a polar planimeter and finally checked by cutting out the peaks and weighing them. Decarbonylation products were usually identified by comparison of retention times and by comparison of infrared spectra of collected materials with those of authentic compounds, the preparations of which are described below.

Relative response data for the quantitative determination of the amounts of decarbonylation products present were obtained from prepared solutions of known composition. The relative amounts of the compounds in the prepared solutions approximated those occurring in the decarbonylation reaction mixtures. The vapor phase chromatographic analysis operational procedure for these determinations was identical with that of the actual decarbonylation analysis operational procedure for each series.

Aldehydes. With the exception of 1-methylcyclopropanecarboxaldehyde, all of the aldehydes used in this work were prepared by the reduction of the corresponding 1-acylaziridines (from the acids via acid chlorides) with lithium aluminum hydride following the general procedure of Brown and Tsukamoto.³⁴ All of the aldehydes had sat-

isfactory NMR and infrared spectra³³ and all gave 2,4-dinitrophenylhydrazones whose melting points agreed with literature values, except in the case of 1-methylcyclobutanecarboxaldehyde, where no literature melting point was found. The boiling points of the aldehydes and yields from acid chlorides were as follows: cyclohexanecarboxaldehyde, bp 57.5–58.5 °C (10 mm) [lit.³⁵ bp 159–160 °C], 47%; cyclopentanecarboxaldehyde, bp 42–44 °C (20 mm) [lit.³⁶ bp 41–43 °C (18 mm)], 49%; cyclobutanecarboxaldehyde, bp 114.0–115.5 °C (753 mm) [lit. bp 116–118³⁷ and 113–115 °C³⁸], 54%; cyclopropanecarboxaldehyde, bp 39–41 °C (12 mm) [lit. bp 98–101³⁹ and 42–44 °C⁴⁰ (14 mm)], 52%; 1-methylcyclohexanecarboxaldehyde, bp 55–56 °C (6 mm) [lit. bp 166.5–167.0³⁵ and 120 °C⁴¹ (54 mm)], 56%; 1-methylcyclopentanecarboxaldehyde, bp 47.3–48.4 °C (25 mm) [lit. bp 142.0–142.5³⁵ and 31–33 °C³⁶ (10 mm)], 43%.

1-Methylcyclobutanecarboxaldehyde was isolated in 56% yield by preparative VPC on Carbowax. The NMR spectrum (CCl₄) showed a singlet at δ 9.52 (1.0 H) assigned to the aldehydic proton, a multiplet in the region δ 1.40–2.65 (6.0 H) assigned to the cyclobutyl methylene protons, and a singlet at δ 1.27 (3.0 H) assigned to the 1-methyl protons. The infrared spectrum (film) showed bands at 3425 (vw), 2967 (m), 2874 (m), 2793 (m), 2710 (m), 1721 (s), 1456 (m), 1439 (m), 1393 (w), 1379 (w), 1312 (w), 1287 (vw), 1255 (w), 1247 (w), 1212 (w), 1195 (w), 1151 (w), 1053 (vw), 982 (vw), 929 (m), 889 (w), 858 (w), and 722 (w) cm⁻¹.

The 2,4-dinitrophenylhydrazone of 1-methylcyclobutanecarboxaldehyde, recrystallized from ethyl acetate–ethanol–water, melted at 176.4–177.3 °C.

Anal. Calcd for C₁₂H₁₄N₄O₄: C, 51.80; H, 5.07; N, 20.13. Found: C, 51.90; H, 5.03; N, 20.38.

When they were not commercially available, the carboxylic acids used for the above preparations were prepared by standard literature methods. An exception was 1-methylcyclobutanecarboxylic acid, which was prepared in 72% yield, bp 56.5–59.5 °C (0.3–0.4 mm) [lit.⁴² bp 98 °C (13 mm)], by the α -methylation of cyclobutanecarboxylic acid following the technique of Pfeffer and Silbert⁴³ and Creger.⁴⁴

1-Methylcyclopropanecarboxaldehyde, bp 102.5–104.5 °C (750 mm) [lit.⁴⁵ bp 103–104 °C], was prepared in 44% yield by the lithium aluminum hydride reduction of 1-methylcyclopropanecarbonitrile⁴⁶ using the procedure of Smith and Rogier⁴⁷ as modified by Schuster and Roberts.⁴⁵

Ethyl 1-Methylcyclobutanecarboxylate. To a 50-mL flask containing 3.0 g (0.023 mol) of 1-methylcyclobutanecarbonyl chloride at 0 °C was slowly added 8.0 g (0.173 mol) of ethanol, and the solution was stirred for 36 h. The crude ester was washed with portions of a saturated sodium bicarbonate solution until carbon dioxide evolution ceased. Distillation afforded 2.95 g (92%) of ethyl 1-methylcyclobutanecarboxylate, bp 154.3–155.2 °C (735 mm). The NMR spectrum (CCl₄) showed a quartet centered at δ 4.08 ($J = 7.0$ Hz, 2.0 H) assigned to the ethyl methylene protons, a multiplet in the region δ 1.62–2.65 (6.0 H) assigned to the ring methylene protons, a triplet centered at δ 1.23 ($J = 7.0$ Hz) assigned to the methyl protons of the ethyl group, and a singlet at δ 1.36 assigned to the 1-methyl protons. The infrared spectrum (film) showed absorption at 3448 (vw), 2976 (s), 2933 (m), 2907 (m), 2874 (m), 1724 (vs), 1460 (m), 1391 (m sh), 1374 (m), 1348 (w), 1304 (s), 1252 (m), 1220 (m), 1208 (m), 1174 (m), 1126 (vs), 1098 (m), 1044 (m), 1026 (m), 922 (w), and 864 (m) cm⁻¹.

Anal. Calcd for C₈H₁₄O₂: C, 67.57; H, 9.92. Found: C, 67.57; H, 9.89.

Decarbonylation of Aldehydes. The general procedure has been described earlier¹ and has been modified only in minor ways.³³ The reaction products were all identified by comparison with authentic samples, to which literature references are given where appropriate. The products and analytical conditions used were as follows.

Cyclohexanecarboxaldehyde: The products were chlorocyclohexane and ethyl cyclohexanecarboxylate⁴⁸ (from ethanolysis of the acid chloride during the analytical procedure¹). The analysis was done on column A, programmed between 50 and 230 °C. A control showed that a mixture of chlorocyclohexane and cyclohexanecarbonyl chloride did not change composition when included in a decarbonylation run of cyclobutanecarboxaldehyde.

Cyclopentanecarboxaldehyde: The products were chlorocyclopentane and ethyl cyclopentanecarboxylate.⁴⁸ The analysis was done on column B, programmed between 50 and 230 °C. A control showed that a mixture of chlorocyclopentane and cyclopentanecarbonyl chloride did not change composition when included in a decarbonylation run of cyclobutanecarboxaldehyde. The cyclopentanecarboxaldehyde case was unique among those studied here in giving also a nonvolatile product in about 25% yield. This material decomposed at 275 °C in the injection port of the gas chromatograph to give 93–95% of the original aldehyde. A polymerization of the aldehyde evi-

dently competes with the reactions of interest but should not substantially affect the determination of k_1/k_2 .

Cyclobutanecarboxaldehyde: The products were chlorocyclobutane²⁹ and ethyl cyclobutanecarboxylate.⁴⁹ The analysis was done on column A, programmed between 25 and 230 °C. A careful search for cyclobutane⁵⁰ product at the highest instrument sensitivity (column C) revealed none. A control showed that a mixture of chlorocyclobutane and cyclobutanecarbonyl chloride did not change composition when included in a decarbonylation run of cyclohexanecarboxaldehyde.

Cyclopropanecarboxaldehyde: The products were cyclopropyl chloride⁵¹ and ethyl cyclopropanecarboxylate.⁵² The cyclopropyl chloride was formed in amounts too small for collection and spectroscopic identification, so it was identified by its retention time on column C at 25 °C in comparison with that of an authentic sample. The analysis of the rest of the mixture was done on column A using the same conditions as for cyclobutanecarboxaldehyde. No cyclopropane or allyl chloride could be detected. A control showed that a mixture of cyclopropyl chloride and cyclopropanecarbonyl chloride did not change composition when included in a decarbonylation run of cyclohexanecarboxaldehyde.

1-Methylcyclohexanecarboxaldehyde: The products were methylenecyclohexane,⁵³ 1-methylcyclohexene, 1-chloro-1-methylcyclohexane,⁵⁴ and ethyl 1-methylcyclohexanecarboxylate.⁵⁵ It was shown that the first two were formed from the third in the injection port (205 °C) of the gas chromatograph. The analysis was done on column A, programmed between 50 and 233 °C. A control showed that a mixture of 1-chloro-1-methylcyclohexane and 1-methylcyclohexanecarbonyl chloride did not change composition when included in a decarbonylation run of 1-methylcyclopropanecarboxaldehyde.

1-Methylcyclopentanecarboxaldehyde: The products were methylenecyclopentane,⁵⁶ 1-methylcyclopentene,⁵⁷ 1-chloro-1-methylcyclopentane,⁵⁴ and ethyl 1-methylcyclopentanecarboxylate.⁴⁸ The first two products were shown to arise from the third in the injection port of the gas chromatograph. The analysis was done on column A, programmed between 50 and 233 °C. A control showed that a mixture of 1-chloro-1-methylcyclopentane and 1-methylcyclopentanecarbonyl chloride did not change composition when included in a decarbonylation run of 1-methylcyclopropanecarboxaldehyde.

1-Methylcyclobutanecarboxaldehyde: The products were 1-chloro-1-methylcyclobutane⁵⁴ and ethyl 1-methylcyclobutanecarboxylate. The analysis was done on column A, programmed between 50 and 233 °C. Analysis on column D at 25 °C demonstrated the absence of methylenecyclobutane, 1-methylcyclobutene, and methylcyclobutane. A control showed that a mixture of 1-chloro-1-methylcyclobutane and 1-methylcyclobutanecarbonyl chloride did not change composition when included in a decarbonylation run of 1-methylcyclopropanecarboxaldehyde.

1-Methylcyclopropanecarboxaldehyde: The products were 1-chloro-1-methylcyclopropane and methyl 1-methylcyclopropanecarboxylate.^{58,59} Analyses were done on columns A, C, and D, each programmed between 50 and 230 °C. A control showed that a mixture of 1-chloro-1-methylcyclopropane and 1-methylcyclopropanecarbonyl chloride did not change composition when included in a decarbonylation run of 1-methylcyclobutanecarboxaldehyde.

1-Chloro-1-methylcyclopropane. The procedure of Kirmse, Kapps, and Hager for the addition of diazomethane to allylic chlorides was used here.⁶⁰ A 250-mL distillation flask was equipped with a short stem addition funnel, a magnetic stirring bar, and a condenser set downward for distillation. A 500-mL receiving flask was equipped with a reflux condenser with an attached drying tube and a magnetic stirring bar. To the distilling flask was added a solution of 10.6 g (0.189 mol) of potassium hydroxide dissolved in 18 mL of water followed by 62 mL of 2-(2-ethoxyethoxy)ethanol and 35 mL of ether. The stirred solution was heated to 65–70 °C, and as soon as the ether began to distill a solution of 38.1 g (0.178 mol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 350 mL of ether was added over a period of 140 min.⁶¹ The ethereal diazomethane distilled into a vigorously stirred solution of 34.9 g (0.456 mol) of 2-chloropropene⁶² and 0.6 g of cupric chloride dihydrate at 8–15 °C. After all of the diazomethane had been added, the solution was stirred for an additional 10 h at room temperature. The catalyst was then filtered off, and the ether was removed by fractionation through a 1.7 m modified Podbielniak column with a total reflux head. The reflux to take-off ratio was kept at greater than 5:1. After the major part of the ether had been removed, the residue was flash distilled to afford approximately 4 g of a clear mobile liquid, bp 50–72 °C. Vapor phase chromatographic analysis (column A) of the distillate showed the presence of ether and one minor and two major products.

The crude distillate was separated by preparative vapor phase

chromatography (column 1). One of the two major components proved to be 1-chloro-1-methylcyclopropane, isolated as a clear mobile liquid in 8.4% yield. The NMR spectrum (CCl_4) showed a singlet at δ 1.60 (3.0 H) assigned to the 1-methyl protons and a typical A_2B_2 pattern in the region δ 0.55–1.15 (4.0 H) assigned to the cyclopropyl methylene protons. The infrared spectrum (film) showed absorption at 3086 (m), 3003 (m), 2967 (m), 2924 (m), 2882 (m), 2747 (vw), 1451 (m), 1429 (m), 1408 (m), 1387 (m), 1311 (w), 1198 (m), 1151 (w), 1103 (m), 1053 (w sh), 1026 (m), 1017 (m), 929 (m), 861 (m), and 807 (cm^{-1}).

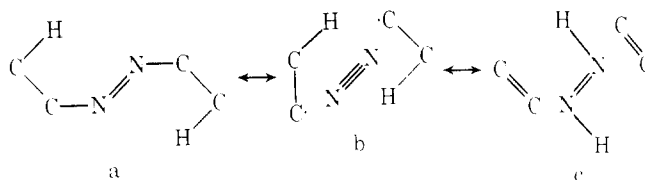
Anal. Calcd for $\text{C}_4\text{H}_7\text{Cl}$: C, 53.06; H, 7.79; Cl, 39.15. Found: C, 53.25; H, 7.79; Cl, 38.89.

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Registry No.—1-Methylcyclobutanecarboxaldehyde, 65338-30-9; 1-methylcyclobutanecarboxaldehyde 2,4-DNP, 65338-29-6; 1-methylcyclobutanecarbonyl chloride, 21890-82-4; ethanol, 64-17-5; ethyl 1-methylcyclobutanecarboxylate, 65338-28-5; cyclohexanecarboxaldehyde, 2043-61-0; cyclopentanecarboxaldehyde, 872-53-7; cyclobutanecarboxaldehyde, 2987-17-9; cyclopropanecarboxaldehyde, 1489-69-6; 1-methylcyclohexanecarboxaldehyde, 6140-64-3; 1-methylcyclopentanecarboxaldehyde, 6140-63-2; 1-methylcyclopropanecarboxaldehyde, 4515-89-3; 1-chloro-1-methylcyclopropane, 50915-28-1; diazomethane, 334-88-3; 2-chloropropene, 557-98-2.

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- One possibility is that the transition state for azo decomposition is stabilized by a contribution of a hyperconjugative resonance structure (c):



Contribution of c to the bridgehead cases is prohibited by Bredt's rule.

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