A Free-Radical 1,2-Vinyl Migration

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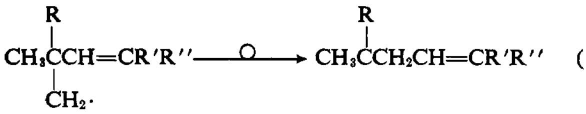
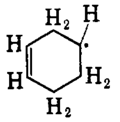
Δ^2-Cyclopentenylmethyl radicals (II), formed in solution by the thermal decomposition of t-butyl Δ^2-cyclopentenylperoxyacetate, rearrange to 4-cyclohexenyl radicals (I) via a 1,2-vinyl group migration. Under similar conditions, the reverse rearrangement of I to II does not occur.

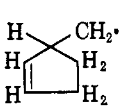
Rearrangements of hydrocarbon free radicals involving 1,2-migrations of alkyl groups or hydrogen atoms usually do not occur.[1,2] On the other hand, 1,2-phenyl migrations are facile under a variety of conditions.[1a,b] Previously, we reported that vinyl groups also will undergo 1,2-migration.[2] These radical rearrangements (eq. 1) occurred during the high temperature (~450°), gas phase reaction of iodine with hydrocarbons.


$$\mathrm{CH_3\overset{R}{\underset{CH_2\cdot}{C}}CH{=}CR'R''} \xrightarrow{\circ} \mathrm{CH_3\overset{R}{C}CH_2CH{=}CR'R''} \qquad (1)$$

Only recently have rearrangements of this type been observed to occur under more moderate conditions, although several radicals having the necessary structural requirements have been formed in solution at 25 to 175°.[3-7] Montgomery, Matt, and Webster have found that the acyclic radicals resulting from decarbonylation of 3-methyl-4-pentenal and *trans*-3-methyl-4-hexenal in diphenyl ether rearrange *via* 1,2-vinyl migrations[7] (*vide infra*).

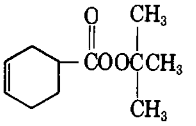
Other appropriate radicals should be formed under moderate conditions in order to understand better the scope and mechanism of these reactions. We have generated in solution 4-cyclohexenyl (I) and Δ^2-cyclopentenylmethyl (II) radicals which, in principle, may undergo ring contraction or ring enlargement, respectively, *via* 1,2-vinyl migrations. The propensities of these radicals to rearrange and a consideration of the reaction mechanism are the subjects of this communication.

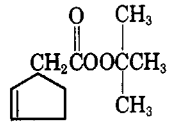

I


II

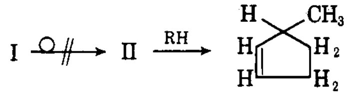
Results and Discussion

Wilt and Levin[5] experienced considerable difficulty in their attempts to decarbonylate unsaturated aldehydes, such as cyclohexene-4-carboxaldehyde. Consequently, radicals I and II were generated by heating (140°) dilute solutions of *t*-butyl cyclohexene-4-peroxycarboxylate (III) and *t*-butyl Δ^2-cyclopentenylperoxyacetate (IV), respectively. In general, the experimental procedures for preparing[8,9] and decomposing[10] the peroxy esters were similar to those previously established.


III


IV

Decomposition of III in *p*-cymene at 140° produced cyclohexene and cyclohexadienes in 57 and <3% yields, respectively. The yields are based upon the amount of CO_2 evolved which was 80% theory, assuming the peroxyester to be of 100% purity. If rearrangement of the intermediate radical I had occurred *via* a 1,2-vinyl migration, 3-methylcyclopentene would have been formed (eq. 2). However, careful g.l.c. analyses demonstrated that no one of the methylcyclopentenes was present. Although the yields of monomeric hydrocarbons were lower, the same general results were obtained with *o*-dichlorobenzene as the solvent.


(2)

When III was heated to generate I in α,α,α-trichlorotoluene, an efficient chlorine atom donor solvent,[11] the only chlorinated monomeric product formed was 4-chlorocyclohexene (57% yield). The anticipated product of rearrangement, Δ^2-cyclopentenylmethyl chloride, could not be detected. Treatment of the chloride product with lithium aluminum hydride produced only cyclohexene and no methylcyclopentene.

These results agree with those obtained by Wilt and Levin who found that I did not rearrange when generated by the radical-catalyzed decomposition of cyclohexene-4-carboxaldehyde.

Very different results were obtained when IV was decomposed to produce II in either *p*-cymene or α,α,α-trichlorotoluene. In the former solvent, 12.2% 3-

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(1) (a) R. Kh. Freidlina, V. N. Kost, and M. Ya. Khorlina, *Russ. Chem. Rev.*, **31**, 1 (1962); (b) C. Walling, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 7; (c) L. H. Slaugh, E. F. Magoon, and V. P. Guinn, *J. Org. Chem.*, **28**, 2643 (1963).

(2) L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *J. Am. Chem. Soc.*, **85**, 3180 (1963).

(3) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *ibid.*, **80**, 635 (1958).

(4) D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963).

(5) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

(6) J. D. Roberts, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p. 8-O; M. E. H. Howden, Ph. D. Thesis, California Institute of Technology, 1962.

(7) L. K. Montgomery, J. Matt, and J. R. Webster, Abstracts, 147th National Meeting, of the American Chemical Society, Philadelphia, Pa., April 1964, p. 29N.

(8) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(9) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1760 (1960).

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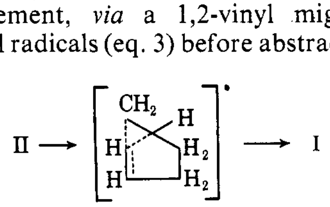
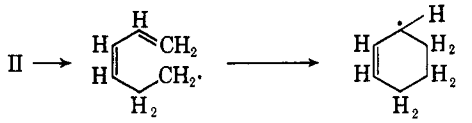
methylcyclopentene and 47.3% cyclohexene were produced. Assuming that the relative yields of the monomeric products are proportional to the respective populations of intermediate radicals, 79.5% of the Δ^2-cyclopentenylmethyl radicals must have undergone ring enlargement, *via* a 1,2-vinyl migration, to 4-cyclohexenyl radicals (eq. 3) before abstracting hydrogen


(3)

atoms from the solvent.

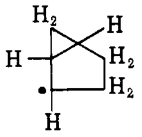
However, there are alternate mechanisms to be considered. Either β-cleavage followed by ring closure (eq. 4) or a concerted 1,2-alkyl migration within II

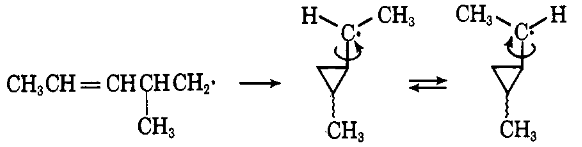

(4)

also would ultimately produce cyclohexene. These latter reaction paths are excluded as major contributors by virtue of the particular cyclohexyl chloride formed when IV is decomposed in α,α,α-trichlorotoluene. In addition to the unrearranged product, Δ^2-cyclopentenylmethyl chloride (29.4% yield) and 4-chlorocyclohexene (25.9% yield) was formed. The formation of the latter chloride is consistent only with a 1,2-vinyl migration to produce the intermediate 4-cyclohexyl radical (eq. 3) which then abstracts a chlorine atom from the solvent. Had cleavage–ring closure (eq. 4) or 1,2-alkyl migration occurred, the 3-cyclohexenyl radical would have resulted and 3-chlorocyclohexene would have been the product. Unfortunately, 3-chlorocyclohexene is rather unstable and difficult to analyze quantitatively by g.l.c. techniques. Also some decomposition occurs under the reaction conditions. However, the analytical data indicate that little if any 3-chlorocyclohexene was formed (see Experimental for details).[12]

The relative amounts of 4-chlorocyclohexene and Δ^2-cyclopentenylmethyl chloride formed by the decomposition of IV in α,α,α-trichlorotoluene is indicative of 46.8% rearrangement of II to I. This is considerably less than the 79.5% rearrangement that resulted in *p*-cymene. α,α,α-Trichlorotoluene has a high chain-transfer constant,[11] probably much higher than that of *p*-cymene under comparable conditions.[11,13] Since rearrangement was more extensive in the solvent with the lower chain-transfer constant, the decomposition of the peroxy ester and rearrangement must be successive steps and II must have an independent existence. II should have a longer life time in *p*-cymene than in α,α,α-trichlorotoluene and consequently would be expected to rearrange to a greater extent. In these respects, the present 1,2-vinyl migration is similar to the 1,2-phenyl migration which occurs within the neophyl radical when the latter is generated by the decarbonylation of β-phenylisovaleraldehyde.[16]

The 1,2-migration of a vinyl group might proceed either smoothly through a transition state, as depicted by eq. 3, or form an intermediate cyclopropylcarbinyl radical, such as V. Although sufficient data are not available to allow general conclusions to be made regarding the mechanistic details of this type of rearrangement, it seems appropriate to mention a few pertinent observations. Several cyclopropylcarbinyl radicals have been generated independently and found to undergo β-cleavage rather easily with opening of the cyclopropyl ring.[17-20] Therefore, V, if formed, could readily revert to II or give the rearranged radical I. The formation of either bicyclo[3.1.0]hexane or 2-chlorobicyclo[3.1.0]hexane would have indicated the intermediacy of V. These compounds were not prepared independently to aid in the product analyses; however, several g.l.c. analyses did not show extraneous peaks which might be attributed to these materials. Montgomery, Matt, and Webster were unable to find 1,2-dimethylcyclopropane which would have indicated the intermediacy of the 2-methylcyclopropylcarbinyl radical during the 1,2-vinyl migration within the 2-methyl-3-butenyl radical. On the other hand, stereochemical integrity was not maintained during a similar rearrangement of the *trans*-2-methyl-3-pentenyl radical.[7] Apparently, a bridged intermediate was formed with sufficient life time for rotation to occur as shown in eq. 5. Howden and Roberts have generated the 4,4-diphenyl-3-butenyl radical by decomposing the appropriate peroxy ester in hydrogen atom donor solvents and have isolated cyclopropyldiphenylmethane in addition to 1,1-diphenylbutene.[6] Although 1,2-migration of the $(C_6H_5)_2C{=}CH-$ group may have occurred, it would not have been detected since 1,1-diphenylbutene can be formed from either the initial or rear-


V


(5)

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(12) As part of an identification scheme, we hydrogenated the product resulting from the decomposition of IV in *p*-cymene. G.l.c. analyses showed that methylcyclopentane and cyclohexane were produced from the 3-methylcyclopentene and cyclohexene, respectively. Incidentally, we noted that *n*-hexane was not produced by the hydrogenation, which indicates the absence of *n*-hexadienes in the unhydrogenated material. If the cleavage–ring closure mechanism (eq. 4) were operative even to a small extent for the rearrangement of II to I, one might have anticipated the formation of some *n*-hexadiene since the intermediate *n*-hexadienyl radicals should have abstracted hydrogens from the solvent. However, this evidence against the cleavage–ring closure mechanism is considered to be strictly ancillary to the conclusive evidence provided above.

(13) The chain-transfer constant for *p*-cymene apparently has not been measured; however, it probably does not differ greatly from that of cumene[14] or diethylbenzene.[15]

(14) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947).

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(16) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

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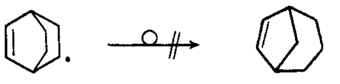
ranged radicals. Nevertheless, an intermediate cyclopropyldiphenylcarbinyl radical is indicated.

Even though II and I are primary and secondary radicals, respectively, and may differ in strain energy, it is somewhat surprising that the rearrangement of II to I is facile whereas the reverse reaction is undetectable under the present conditions. This shows that 1,2-vinyl migrations are not general. Several other examples have been reported which further illustrate this point. Wilt and Levin[5] generated, *via* aldehyde decarbonylations, radicals which might have rearranged as shown by eq. 6 and 7. However, products which would result from these 1,2-vinyl migrations were not reported. Several persons have studied the free-radical addition of a variety of reagents (X–Y) to norbornadiene without products resulting from 1,2-vinyl migrations being formed (eq. 8).[3,4] The only observed rearranged products from norbornadiene were nortricyclene compounds. It should be noted that the nortricyclene products are formed by a quenching reaction (eq. 9) on nortricyclyl radicals which also are possible intermediates of 1,2-vinyl migrations (eq. 10). It is surprising, therefore, that some rearrangement of the latter type does not occur.



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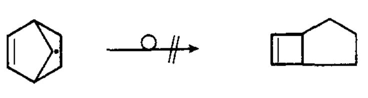

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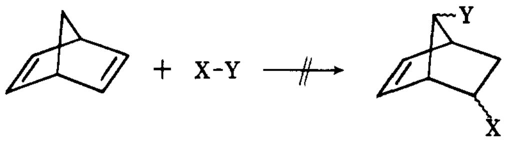

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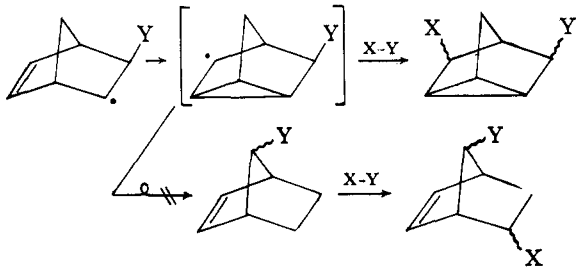

(9)

(10)

Experimental

Δ²-Cyclopentenylacetyl Chloride. Two hundred grams (1.59 moles) of Δ²-cyclopentenylacetic acid (Aldrich Chemical Co.) in 400 ml. of benzene was treated with 1.8 moles of thionyl chloride. Work-up of the liquid product gave 1.0 mole (62.9% yield) of Δ²-cyclopentenylacetyl chloride, $n^{20}D$ 1.4747, b.p. 122° at 145 mm.

Anal. Calcd. for C_7H_9ClO: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 58.4; H, 6.3; Cl, 24.6.

In one preparation, 4-methyl-2-pentene was added at the beginning of the experiment and recovered unchanged (g.l.c. analysis) upon distillation of the product. Since 2-methyl-2-pentene was not formed, double bond isomerization probably did not occur during the preparation of Δ²-cyclopentenylacetyl chloride. N.m.r. analyses were in agreement with the proposed structure.

Cyclohexene-4-carboxoyl Chloride. This compound was synthesized from cyclohexene-4-carboxylic acid (Shell Chemical Co.) by the same procedure as above, $n^{20}D$ 1.4868, b.p. 133–134° at 187 mm.

Anal. Calcd. for C_7H_9ClO: C, 58.14; H, 6.27. Found: C, 58.14; H, 6.28.

t-Butyl Δ²-Cyclopentenylperoxyacetate (IV). The topic compound was prepared from 0.2 mole of Δ²-cyclopentenylacetyl chloride and 0.3 mole of *t*-butyl hydroperoxide in *n*-pentane according to published procedures.[8,9] The *t*-butyl hydroperoxide (Lucidol Chem. Co.) was purified by vacuum distillation through a 2-ft. glass spiral column, $n^{24}D$ 1.3983, b.p. 24° at ~6 mm. (lit.[8] $n^{25}D$ 1.3986, b.p. 20–20.5 at 5 mm.).

The *n*-pentane solvent was removed at ≤20° from the final, dried product with a rotating evaporator. To avoid contamination, teflon sleeves rather than lubricants were used for the glass joints throughout this experiment. Twenty-six grams of a colorless oil was obtained which analyzed correctly for IV.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.5; H, 9.2.

An n.m.r. analysis (Varian Associates Model A-60) of the peroxy ester indicated the sample to be somewhat impure; however, the spectrum was in agreement with the proposed structure, IV. Absorptions were centered at $\delta = \sim 5.7$ from tetramethylsilane for two vinylic (olefinic) protons, at ~3.0 for one proton which is probably allylic and tertiary, and at ~1.3 p.p.m. (singlet) for the nine equivalent protons of the *t*-butyl group. Absorption for the remaining four protons extended from $\delta = 2.6$ to ~1.3 p.p.m. which is indicative of two kinds of protons as in IV rather than four of the same type as would be the case for the allylic protons if the structure were *t*-butyl Δ³-cyclopentenylperoxyacetate.

t-Butyl Cyclohexene-4-peroxycarboxylate (III). This compound was prepared in good yields from cyclohexene-4-carboxoyl chloride *via* the same procedure described above for *t*-butyl Δ²-cyclopentenylperoxyacetate.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.6; H, 9.1.

Decomposition of III in p-Cymene and o-Dichlorobenzene. The three ports of a flask were fitted, respectively, with a nitrogen gas inlet, a serum cap, and an exit tube leading through two Dry Ice–acetone traps and a weighed ascarite tube. The flask containing 50 ml. of purified *p*-cymene was placed into an oil bath set at 140°. After the temperature of the system had equilibrated, 10 mmoles (assuming the peroxyester to be of 100% purity) of *t*-butyl cyclohexene-4-peroxycarboxylate was rapidly injected and the flask agitated. For the next 1.5 hr., nitrogen was slowly passed through the system. The weight increase of the ascarite tube indicated that ~8 mmoles (~80% of theory) of CO_2 had been liberated.

The product solution was combined with *p*-cymene washings from the cold traps, washed several times with cold water, and then dried over magnesium sulfate. A g.l.c. analysis of the product at 100° on a 20-ft. column packed with *m*-polyphenyl ether (five rings) on Chromosorb W (Wilkins instrument and Research, Inc.) showed that methylcyclopentenes were not formed. API samples of 1-, 2-, and 3-methylcyclo-

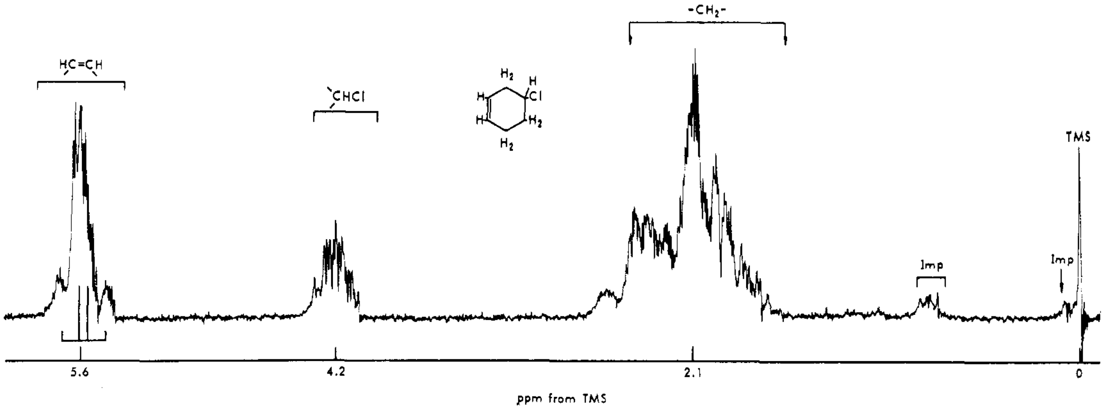

Figure 1. HR-100 spectrum of 4-chlorocyclohexene.

pentenes were used as standards for these analyses. Three compounds in 4.6-mmoles, 0.1-mmole, and 0.1-mmole quantities with emergence times identical with those of cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene, respectively, were indicated. The first compound was trapped at the exit of the g.l.c. and identified as cyclohexene by the detailed coincidence of its mass spectrometric fragmentation pattern with authentic cyclohexene. The combined yield of the cyclohexyl products was ~60% of the CO_2 liberated. Dimeric products were not analyzed.

A repeat of the above experiment with *o*-dichlorobenzene as the solvent produced cyclohexene in a 20% yield based upon the CO_2 liberated which was 53% of theory. Once again products of rearrangement, methylcyclopentenes, were not formed.

Decomposition of III in α,α,α-Trichlorotoluene. Forty-six mmoles (assuming the peroxyester to be of 100% purity) of *t*-butyl cyclohexene-4-peroxycarboxylate dissolved in 85 ml. of pure α,α,α-trichlorotoluene was decomposed at 140° in the apparatus described above. The peroxy ester was injected in 15 equal portions over a period of 90 min. Nitrogen was continually passed through the system during the entire experiment. CO_2 liberated was ~30 mmoles or ~65% of theory. The product solution was washed with cold water and dried over magnesium sulfate. G.l.c. analyses with several columns, including one packed with DC-710 on firebrick, indicated that only one compound (17 mmoles or 56.7% yield based on the CO_2 liberated) was formed which emerged at the time estimated for 4-chlorocyclohexene.

This chloride was isolated from the solvent by preparative g.l.c. techniques with an Aerograph Autoprep instrument. A portion of this material was reduced in a capillary tube with $LiAlH_4$ in diethyl ether. G.l.c. analyses showed that only cyclohexene was produced. The absence of methylcyclopentenes indicates that rearrangement did not occur. The identity of the cyclohexene was confirmed by comparing in detail its mass spectrometric fragmentation pattern with that of authentic cyclohexene. The formation of cyclohexene from the above reduction shows that the product is a cyclohexyl chloride. In further support of this, mass spectrometric analysis showed that the chloride had the correct molecular weight for C_6H_9Cl and that it likely was not a cyclopentenylmethyl chloride since the large m/e 67^+ fragmentation peak, which is characteristic of this type of compound, was absent in the fragmentation pattern. The mass spectra indicated the compound to be either 3- or 4-chlorocyclohexene but not 1-chlorocyclohexene.

The 60- and 100-Mc./sec. (Figure 1) n.m.r. spectra of the cyclohexyl chloride showed absorptions centered at $\delta = \sim 5.6$ p.p.m. from tetramethylsilane for two vinylic hydrogens, at $\delta = \sim 4.2$ p.p.m. for one hydrogen vicinal to the chlorine, and at $\delta = \sim 2.1$ p.p.m. for the remaining six hydrogens. 1-Chlorocyclohexene can easily be excluded as a possibility since it has only one vinylic hydrogen. A comparison of the spectrum with one of authentic 3-chlorocyclohexene showed that the latter is not a possibility either since the absorption for its hydrogen located vicinal to the chlorine is centered at $\delta = 4.6$ p.p.m.

The detailed interpretation of the 100 Mc./sec. spectrum (Figure 1) in the region near $\delta = 2.1$ p.p.m. from tetramethylsilane is not very clear. However, assuming that the compound is 4-chlorocyclohexene, one would expect the downfield portion of this spectral region to be produced by the four allylic protons, the part most downfield being produced by the two allylic protons which also are adjacent to the CHCl group. Furthermore, one would also expect that the portion most upfield would arise from the third CH_2 group which is not allylic. These suppositions were confirmed by spin-decoupling experiments.

The above data confirm that 4-chlorocyclohexene is the product obtained from the decomposition of III in α,α,α-trichlorotoluene.

Decomposition of IV in p-Cymene. Ninety-six mmoles (assuming the peroxy ester to be of 100% purity) of *t*-butyl Δ^2-cyclopentenylperoxyacetate (IV) was decomposed in 160 ml. of purified *p*-cymene at ~140° as described above for the decomposition of III in α,α,α-trichlorotoluene. The yield of CO_2 was 58.5 mmoles or 61% of theory. G.l.c. analyses of the washed and dried product indicated the presence of 7.13 mmoles (12.2% yield based on CO_2 evolved) of 3-methylcyclopentene, 27.6 mmoles (47.3% yield) of cyclohexene, and 2.3 mmoles (7.9% yield) of what are believed to be dimeric products. The structures of the latter were not further investigated. The amount of cyclohexene formed indicates that 79.5% of the Δ^2-cyclopentenylmethyl radicals resulting from the decomposition of IV underwent rearrangement.

Part of the product was hydrogenated at room temperature over Pd–carbon. Methylcyclopentane and cyclohexane were produced and identified by the coincidence of their g.l.c. emergence times and mass spectrometric fragmentation patterns with those of authentic materials. *n*-Hexane, which would have resulted from the hydrogenation of any *n*-hexadiene present, could not be detected by g.l.c. techniques.

The remaining unhydrogenated product from the decomposition of IV was distilled and the fraction boiling 20–100° collected. The two product hydrocarbons were isolated in a pure form by preparative g.l.c. techniques. The detailed identity of their infrared, n.m.r., and mass spectra with those of authentic compounds (API samples) proved conclusively that the two monomeric products formed were 3-methylcyclopentene and cyclohexene.

Decomposition of IV in α,α,α-Trichlorotoluene. Eighty-five mmoles (assuming the peroxyester to be of 100% purity) of *t*-butyl Δ^2-cyclopentenylperoxyacetate was decomposed in 170 ml. of α,α,α-trichlorotoluene according to the procedure described above. Thirty-four mmoles or 40.3% of theory of CO_2 was evolved. G.l.c. analysis on a 5-ft. DC-710 column at 100° indicated the presence of two compounds believed to be Δ^2-cyclopentenylmethyl chloride and 4-chlorocyclohexene. From the amounts formed, 10 mmoles (29.4% yield based on CO_2) and 8.8 mmoles (25.9% yield), respectively, it appears that 46.8% of the 3-methylcyclopentenyl radicals rearranged to 4-cyclohexenyl radicals. G.l.c. analyses indicated that 3-methylcyclopentene and cyclohexene were not present.

The two chlorides were isolated in a pure state by preparative g.l.c. One of the compounds, proposed to be Δ^2-cyclopentenylmethyl chloride, has a shorter g.l.c. emergence time (DC-710 column) than either 1-, 3-, or 4-chlorocyclohexene. The mass spectrometric fragmentation pattern of this C_6H_9Cl compound supports the above structure proposal. For example, the fragmentation ion peak at m/e 67^+, which is characteristic of the cyclopentenyl structure, is very intense and accounts for $\sim$41% of the total ion current. The 60-Mc./sec. n.m.r. spectrum of this compound showed absorptions centered at $\delta = \sim 5.6$ p.p.m. from tetramethylsilane for two vinylic hydrogens, $\sim$3.5 for two hydrogens vicinal to the chlorine, and at 3.0 p.p.m. for one hydrogen which is probably allylic and tertiary. Absorption for the remaining four hydrogens extended from $\delta = 2.6$ to $\sim$1.2 p.p.m. which might be expected for two kinds of protons such as the two allylic and two secondary protons of Δ^2-cyclopentenylmethyl chloride. We conclude that the latter is the correct structure for one of the products from the decomposition of IV in α,α,α-trichlorotoluene.

The second product from the decomposition of IV was shown to be the anticipated product of rearrangement, 4-chlorocyclohexene. The infrared, n.m.r., and mass spectra of this compound were all identical in detail with those of 4-chlorocyclohexene which was obtained by the decomposition of III in α,α,α-trichlorotoluene (*vide supra*).

Although 3-chlorocyclohexene has a g.l.c. emergence time (5-ft. DC-710 column) which is greater than that of 4-chlorocyclohexene, it was difficult to exclude it as an additional product from the decomposition of IV by this analysis alone. That is, 3-chlorocyclohexene was shown to undergo some decomposition under the above reaction conditions. However, when a small amount of 3-chlorocyclohexene was heated at 140° in α,α,α-trichlorotoluene in a control experiment, cyclohexadienes were found in the product in $\sim$70% yields. Cyclohexadienes were not produced during the decomposition of IV in α,α,α-trichlorotoluene, which indicates that 3-chlorocyclohexene was not a significant product.

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Mechanisms of Deboronobromination

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Deboronobromination is a stereospecific trans elimination, dibutyl erythro-2,3-dibromobutane-2-boronate yielding cis-2-bromo-2-butene on treatment with water or base. Rates of ethylene evolution from dibutyl 2-bromoethaneboronate in aqueous ethanol are pseudo-first-order. The Grunwald–Winstein equation is followed in 70–90% ethanol with a slope of 0.40, but the observed rate in 100% ethanol is much slower than predicted. The rate is much slower in aqueous formic acid than in ethanol of similar ionizing power. Second-order kinetics were obtained with several substituted anilines in 100% ethanol, and a plot of log k vs. pK_b *for* $ArNH_2$ *was linear. Dimethylaniline reacted much too slowly to fit the Brønsted correlation and its reaction was not appreciably slowed in O-deuterioethanol,* $K_H/K_D = 1.06 \pm 0.03$. *We conclude that the general mechanism of deboronobromination is* $BrCH_2CH_2B(OR)_2 + X: \rightarrow BrCH_2CH_2B^-X^+(OR)_2 \rightarrow Br^- + C_2H_4 + (RO)_2BX^+$, *where X: is a Lewis base such as water or an amine.*

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