Zwitter Annihilation in the Halogenation of Allylic Alkoxides. II. The 1-Phenyl-2-methyl-2-cyclohexen-1-ol System[1]

HUGH W. THOMPSON,* RICHARD R. MUCCINO,[2] AND MARIANNE T. TRUBELHORN

Department of Chemistry, Rutgers University, Newark, New Jersey 07102

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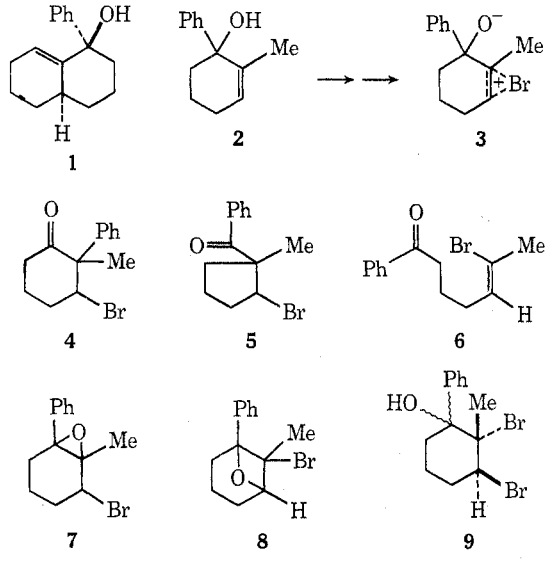
Study of the fate of bromonium alkoxides derived from allylic alcohols has been extended to the title system **2**. The products isolated from bromination of the salt of **2** result from alkyl migration (**5**), epoxide closure (**7t** and **7c**), and bromide attack (**9**) and account for 55% of starting material. Evidence for the stereochemistry of these products is presented and the mechanisms of their formation are discussed. It is argued that **5** and **7t** arise by straightforward zwitter annihilation mechanisms, while **7c** and **9** arise by interrelated routes resulting from the use of $BrMg^+$ as the alkoxide counterion, which also is responsible for the failure to observe phenyl migration.

Our initial investigation of the reactions of bromonium alkoxides derived from allylic alcohols involved the system represented by **1**.[3] We have now extended our study to **2**, which incorporates similar critical elements into a system which is less rigid and which has no predetermined stereochemistry. We hoped thereby to eliminate the influence of these factors in order to discover the reaction's outcome in the more general case. In addition the vinylic methyl group in **2** was expected to provide a readily observable nmr singlet in all of the foreseeable simple products of the reaction (**4**–**9**). These could arise from the bromonium alkoxide **3** by, respectively, bond migration away from the alkoxide carbon (**4**–**6**), direct alkoxide attack on the bromonium ion (**7**, **8**), and attack of external bromide (**9**).

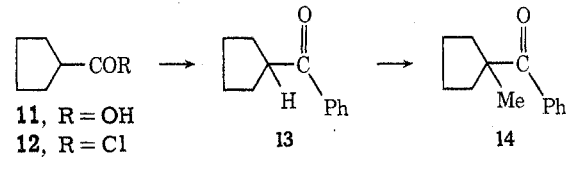


Results

Our allylic alcohol **2** was prepared by addition of phenylmagnesium bromide to 2-methylcyclohexenone, chromatographic separation of the alcohol from ketonic conjugate addition product, and distillation. Regeneration of the bromomagnesium alkoxide with Grignard reagent and bromination, both at 0°, proceeded as previously described[3] to give an isolated product mixture which nmr indicated to contain appreciable quantities of at least four components having unsplit methyl absorptions. The similar reaction of **1** had resulted in isolation of only two products, corresponding in type to **4** and **5**, and arising apparently from attachment of Br^+ on, respectively, the top and bottom sides of **1**. In the present instance no phenyl-migration product (**4**) was detected but the components of the reaction mixture were isolated chromatographically as pure materials whose spectral and other properties are consistent with structures **5**, **7** (two epimers), and **9**. In addition a very small amount of 1-phenyl-1,6-heptanedione (**10**) was isolated. The evidence concerning the structure and stereochemistry of these materials is as follows.

While the analytical data and the position of the infrared carbonyl absorption for compound **5** (6.8% yield) are consistent with either structure **5** or **6**, nmr evidence excludes the latter. Synthetic proof of the carbon skeleton of this material was established by carrying out the sequence in Scheme I, whose product

SCHEME I



(**14**) is identical in all respects with material obtained from catalytic hydrogenolysis of **5**.

Two of the materials isolated from bromination of the bromomagnesium alkoxide of **2** are isomeric with **5** but exhibit neither carbonyl nor hydroxyl absorption (ir). They both exhibit 1-H nmr absorptions in the δ 4.2–4.7 region, possibly consistent with tertiary hydrogens geminal to either bromine (**7**) or oxygen (**8**). However the latter structure also contains a methyl geminal to bromine, requiring a singlet at about δ 1.7.[4] The positions of the methyl singlets (δ 1.21 and 1.13) in the two isolated materials are consistent only with structures having methyl geminal to epoxide oxygen,[4,5] thus excluding an oxetane structure. The low multiplicity of the midfield nmr absorptions clearly indicates that the bromine is in the expected position in both isomers.

The stereochemical assignments for this pair of epimers can be made on the basis of the nmr spectra.

(1) Abstracted in part from the Ph.D. thesis of R. R. M.

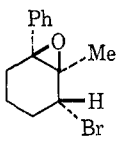
(2) National Institutes of Health Predoctoral Fellow, 1970–1971.

(3) H. W. Thompson and R. R. Muccino, *J. Amer. Chem. Soc.*, **94**, 1183 (1972).

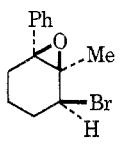
(4) (a) "NMR Spectra Catalog," Vol. 1 and 2, N. S. Bhacca, L. F. Johnston, and J. N. Shoolery, Ed., Varian Associates, Palo Alto, Calif., 1962; (b) "Nuclear Magnetic Resonance Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1970.

(5) P. M. McCurry, Jr., *Tetrahedron Lett.*, 1841 (1971).

In the isomer **7t** the trans arrangement of bromine and epoxide results in deshielding through space of the methinyl proton by the adjacent epoxide and of the methyl protons by bromine. In **7c**, where this reciprocal deshielding is absent, these absorptions are shifted to higher field by 0.18 and 0.08 ppm, respectively. These arrangements would also result in a partial cancellation of dipoles in **7t** *vs.* a reinforcement in **7c**, which is consistent with the more rapid elution of **7t** in column chromatography (Al_2O_3) and vpc.[6] The constants for splitting of the hydrogen geminal to bromine by adjacent methylene have been analyzed in both **7t** and **7c** with respect to the vicinal dihedral CH–CH_2 angles.[7] In each case the result indicated a conformation which models showed to be the one allowing greatest opposition of dipoles.



7t



7c

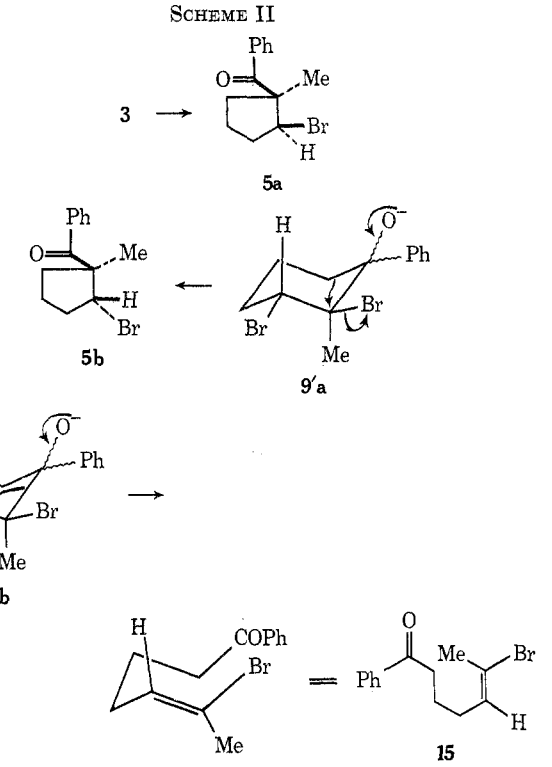
The fourth material isolated from the bromination gave analytical data consistent with addition of two bromine atoms. Its spectral properties indicate that it is an alcohol whose stereochemistry, we have found (see below), arises from trans addition of bromine (**9**).

Discussion

The amount by which the methyl group in **5** is deshielded relative to that in **14** (0.19 ppm) must be attributed to the effect of a vicinal bromine in **5**. While the exact magnitude of this shift should depend on the angular relationship between bromine and methyl, we have not been able to find sufficiently extensive analogies in the literature to allow us to make a firm stereochemical assignment to **5** on this basis. However, the 30% reduction in π–π^* ultraviolet intensity on loss of bromine from **5** seems more easily reconciled with the epimer of **5** having bromine cis to the benzoyl group. This stereochemistry (**5a**) is that to be expected from a zwitter annihilation mechanism. The most obvious source of the alternate isomer **5b** would be rearrangement of the halomagnesium salt of either isomer of **9** which has trans bromines[8] by internal displacement of an equatorial tertiary bromine. Several kinds of evidence suggest that the latter is not the method by which **5** is formed. Halomagnesium salts of vicinal halohydrins normally do not rearrange spontaneously at ice-bath temperature but must be heated to induce rearrangement.[9] Consistent with that, when **9** (obtained in 9.2% yield), which is known to have trans bromines (see below), was reconverted to its bromomagnesium salt and subjected to the original reaction conditions, it was recovered unchanged in 89% yield. Thus **9′** (denoting the anion of **9**) is not a precursor of **5** or of any of the other major products isolated. The possibility remains that **5** arose from the other trans-bromo isomer of **9′**, which we did not find because it was entirely consumed. We have not been able completely to eliminate this possibility. However, if **5** (**5b**) had arisen by this route it would mean that little or no **5a** could have arisen by zwitter annihilation, as only one epimer was detected. We therefore consider **5a** the more probable stereochemistry and zwitter annihilation the likely method of formation.

If **5** did arise from rearrangement of another isomer of **9′** it would presumably mean that that isomer could offer an equatorial tertiary bromine (*cf.* **9′a**, Scheme II),

SCHEME II



while ours could not; hence information about such conformational factors is of some interest. When **9** was converted to its sodium salt at room temperature in dimethoxyethane, rearrangement to compound **15** proceeded in 85% yield. The configuration shown for **15**, which is very clearly supported vis à vis structure **6** by the nmr spectrum,[10] is one which obviously requires two equatorial bromines in **9′** if elimination is to occur by a trans process through a chair form of the molecule. This not only supports our general assumption of trans addition of bromide to **3**,[8] but makes it clear that the sodium alkoxide, at least, has no difficulty attaining a conformation in which both bromines are equatorial.

The failure of **9′** to rearrange to **15** when its counterion is bromomagnesium may be interpreted in several ways. Similar conformations of the alkoxide may be involved for Na^+ and $BrMg^+$, with the difference in

(6) A. 0.125 in. × 6 ft stainless steel column packed with 10% UC-W98 silicone on 80–100 mesh firebrick was used for this analysis.

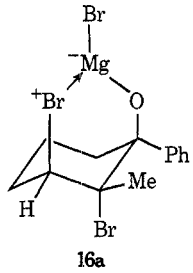
(7) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965, pp 116–117.

(8) We have assumed that bromine will be added trans in **9**; see H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 422 ff.

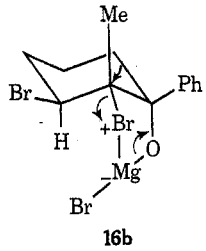
(9) (a) P. D. Bartlett and R. H. Rosenwald, *J. Amer. Chem. Soc.*, **56**, 1990 (1934); (b) M. Tiffeneau and B. Tchoubar, *C. R. Acad. Sci.*, **198**, 941 (1934); (c) M. Tiffeneau and B. Tchoubar, *ibid.*, **207**, 918 (1938); (d) B. Tchoubar, *ibid.*, **208**, 355 (1939); (e) M. Tiffeneau, B. Tchoubar, and S. LeTellier, *ibid.*, **216**, 856 (1943); (f) M. Tiffeneau, B. Tchoubar, and S. LeTellier, *ibid.*, **217**, 588 (1943); (g) T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.*, **73**, 1993 (1951); (h) A. S. Hussey and R. R. Herr, *J. Org. Chem.*, **24**, 843 (1959); (i) A. J. Sisti, *ibid.*, **33**, 453 (1968); (j) A. J. Sisti and A. C. Vitale, *Tetrahedron Lett.*, 2269 (1969).

(10) (a) J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961); (b) S. W. Tobey, *ibid.*, **34**, 1281 (1969).

reactivity solely the result of lower negative charge density on oxygen because of the greater covalency of the O–Mg bond.[11,12] This implies that such lack of electron density would probably also prevent rearrangement to **5**, regardless of which isomer of **9** was involved (and that **5** must have arisen therefore from zwitter annihilation). An alternate explanation is that the rearrangement **9′** → **15** does not proceed when the cation is $BrMg^+$ because the secondary bromine to be eliminated cannot occupy an equatorial bond, but can when the cation is Na^+. This requires for the bromomagnesium alkoxide some way of overcoming its 1,3-diaxial crowding interactions which will not operate for the sodium alkoxide, and implies that our isomer is **16a**. A third alternative incorporates both ideas, to the effect that **16a** fails to rearrange through a combination of low electron density on oxygen and lack of facilitating coordination with a bromine in the correct configuration, and that modification of either one of these conditions would suffice to cause rearrangement. Thus the sodium salt of **9′** rearranges to **15** while even the bromomagnesium salt of the other isomer of **9′** (**16b**) should rearrange (to **5b**) because of effective Br coordination. While any of these is a plausible explanation for the difference in behavior of the sodium and bromomagnesium alkoxides, the corollary idea in the last two, that the bromomagnesium salt of opposite alkoxide stereochemistry (**16b**) would rearrange by eliminating bromide, remains speculative.



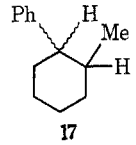
16a



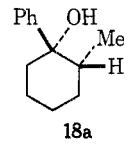
16b

Of the two bromoepoxides isolated, **7t** (21.3% yield) is the one which would be expected to arise in zwitter annihilation by back-side attack of alkoxide on a (trans) bromonium ion. The unexpected stereochemistry of **7c** (18% yield) might arise by several mechanisms. That it does not result from isomerization of the anticipated bromoepoxide was shown by demonstrating the stability of **7t** to the original reaction conditions. Bromoepoxide **7c** might also arise through halohydrin closure in a dibromoalkoxide (**9′**); several lines of evidence operate against this. First, halohydrin salts which involve tertiary (and secondary) halides normally undergo migratory rearrangements rather than epoxide closure[9g,9i,13] (but will not do either at ice-bath temperature[9]). Secondly, because of the requirement for a trans diaxial arrangement in epoxide closure,[14] if **7c** were to arise from **9′**, the required isomer would be that corresponding to **16a**. However there is, as indicated, some reason for believing that this structure represents the isomer of **9** which we have isolated, and yet this material does not produce **7c** on subjection to the original reaction conditions.

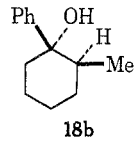
Several attempts were made at proving the epimeric relationship of **7t** and **7c** by conversion to a common debrominated derivative. Subjection of **7c** to catalytic hydrogenolysis (5% Pd/C, H_2, MeOH, $NaHCO_3$) led to rapid debromination. Under minimal conditions (5 min, 1 atm, 25°) loss of halogen proceeded to the extent of 90–95%, the nearly exclusive product being the allylic alcohol **2**. Over longer periods of time additional products appeared, evidently the result of further reduction of **2**. These were separable by vpc[6] and column chromatography and distinguishable by their vpc retention times and their nmr methyl doublets in the region δ 0.5–0.7. Hydrogenation of pure **2** produced the same three materials, which are assigned structures **17**, **18a**, and **18b**. These assignments were based in part on their order of elution from Al_2O_3 columns and vpc[6] (numerical order), the higher degree of crowding about hydroxyl in **18a** allowing more rapid elution. This assignment of stereochemistry to these epimeric alcohols was confirmed by the observations that hydrogenation of **2** produced more **18b** than **18a**, consistent with the often observed haptophilicity of hydroxyl,[15] that **18b** was hydrogenolyzed more rapidly than **18a**, and that **18a** was the preponderant isomer produced by addition of phenylmagnesium bromide to 2-methylcyclohexanone.[16]



17



18a



18b

Under the same minimal hydrogenolysis conditions, loss of bromine from **7t** was only *ca.* 30% complete. Over periods of time long enough to ensure complete loss of bromine, complex mixtures were produced which contained **17**, **18a**, and **18b** as well as two new materials with unsplit nmr methyl absorptions, thought to be isomers of **19**.

Thus the hydrogenolysis of **7c** is appreciably faster than that of **7t**. While a trans process might be thought to be more favorable if loss of bromine from **7** were accompanied by epoxide cleavage,[17] it must be remembered that this reaction may be greatly facilitated by simultaneous transfer of hydrogen to bromine and to oxygen. Since both such transfers would take place from the face of the catalyst, the success of this process for the trans isomer would require a very exact and hence improbable juxtaposition of surfaces. The reaction might be expected therefore to proceed more readily and cleanly in **7c**, as was found to be the case.

Conclusions

Only one of the products (**5**) observed from this bromonium alkoxide reaction is of a type observed in the similar reaction of system **1**. Therefore the fol-

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 97–102.

(12) The evidence concerning rearrangeability of Na *vs.* BrMg salts of halohydrins is not readily interpretable; see, *e.g.*, ref 9h, and P. D. Bartlett and R. V. White, *J. Amer. Chem. Soc.*, **56**, 2785 (1934).

(13) (a) A. J. Sisti, *J. Org. Chem.*, **33**, 3953 (1968); (b) *ibid.*, **35**, 2670 (1970).

(14) J. G. Phillips and V. D. Parker in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, San Francisco, Calif., 1963, Chapter 14.

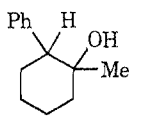
(15) (a) H. W. Thompson, *J. Org. Chem.*, **36**, 2577 (1971); (b) H. W. Thompson and R. E. Naipawer, unpublished results.

(16) J. R. Luderer, J. E. Woodall, and J. L. Pyle, *J. Org. Chem.*, **36**, 2909 (1971).

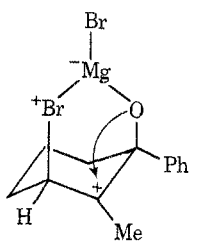
(17) (a) S. Winstein, D. Pressman, and W. G. Young, *J. Amer. Chem. Soc.*, **61**, 1645 (1939); (b) H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958); (c) C. L. Stevens and J. A. Valicenti, *ibid.*, **87**, 838 (1965).

lowing points require some explanation: (1) the appearance of **7t** and **9**, representing products which are predictable but of types not observed before; (2) the appearance of **7c**, whose stereochemistry is anomalous, at least with respect to simple zwitter annihilation mechanisms; (3) the failure to observe any phenyl-migration product (**4**) of the type isolated from reaction of **1**.

We believe that the following explanation accounts for the observed facts. Formation of a bromonium ion trans to the alkoxide function leads, "normally," to **7t** and possibly to **5** (it should be noted that **5** could arise from either the cis or the trans bromonium alkoxide). Formation of the cis bromonium alkoxide, however, leads to an internally complexed species **20** with most of its positive charge at the tertiary carbon but whose phenyl group is held equatorial by the complexation. The latter effectively prevents the phenyl migration which might be expected from an uncomplexed cis bromonium alkoxide and the former allows closure of the epoxide, which would require trans stereochemistry if a symmetrical bromonium ion were involved.[8] This species is also attacked by bromide ion from below, since the magnesium side of this [3.3.1] ring system would be more hindered by solvation and should bear enough negative charge to repel bromide ion. In **1**[3], however, the entire bromonium ion is rendered immune to involvement with alkoxide oxygen, either in terms of complexation or direct attack, because the C–O bond is approximately in the plane of the olefin (and aimed away from it).



19



20

These explanations imply that direct attack of alkoxide at the bromonium ion is a normal process, not observed in **1** simply because it is atypical stereochemically, and they imply that bromomagnesium as a counterion may, because of Lewis acidity,[18] produce results quite different from those to be found with alkali metal cations.

Experimental Section[19]

1-Phenyl-2-methyl-2-cyclohexen-1-ol (2).—A cooled solution of 23.7 g (215 mmol) of 2-methylcyclohex-2-en-1-one[20] in 60 ml of dry ether was treated under N_2 with 100 ml (242 mmol) of ethereal 2.42 *M* phenylmagnesium bromide by dropwise addition. The resulting solution was stirred for 2 hr at room temperature and hydrolyzed with basic saturated aqueous NH_4Cl; this mixture was extracted and the combined organic portions yielded 48.2 g of yellow oil. Chromatography of a 10-g portion of this on 400 g of neutral Al_2O_3 (2% H_2O added) and elution with ether–hexane mixtures allowed the separation of biphenyl, followed by 2-methyl-3-phenylcyclohexanone, isolated as a colorless oil: bp *ca.* 140–145° (5 mm) (675 mg, corresponding to 8%); ir 1710 cm^{-1}; nmr δ 0.95 (3 H d, J = 7 Hz), 1.3–2.6 (7 H complex), 3.15–3.55 (1 H m), 7.0–7.5 (5 H complex).

This ketone (157 mg, 0.828 mmol) was converted to its 2,4-DNP by treatment with 178 mg (0.896 mmol) of 2,4-dinitrophenylhydrazine in 20 ml of refluxing acidic EtOH,[21] providing 306 mg (63%) of the derivative, mp 206–207°. Recrystallization from EtOAc–EtOH gave material melting at 216.5–217°.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47. Found: C, 62.02; H, 5.73.

Concentration of later chromatographic fractions provided, after distillation at 72–73° (0.03 mm), 4.40 g (representing 52%) of **2**: ir 3615 cm^{-1}; nmr δ 1.48 (3 H d, J = 1.5 Hz), 1.55–2.2 (7 H, complex), 5.65 (1 H, broad), 7.65 (5 H, complex).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.87; H, 8.84.

Bromination of the Magnesium Salt of 2.—Ethereal 1.87 *M* phenylmagnesium bromide (13.8 ml, 25.7 mmol) was slowly added with stirring to a cooled solution of 2.49 g (12.7 mmol) of **2** in 25 ml of dry ether under N_2. The clear solution was stirred for 20 min at room temperature and then recooled and a solution of 1.32 ml (24.2 mmol) of Br_2 in 15 ml of dry CH_2Cl_2 was slowly added with stirring until an orange color persisted. An aqueous solution of $NaHCO_3$ and Na_2SO_3 was added until the color was discharged and the mixture was then washed with aqueous $NaHCO_3$, water, and brine. The dried, concentrated oil, which displayed ir and nmr absorptions corresponding to all the subsequently isolated compounds and a vpc[6] pattern of at least four discernible major peaks, was chromatographed on 150 g of neutral Al_2O_3 (2% H_2O added) and eluted with ether–hexane mixtures.

***trans*-3-Bromo-1,2-epoxy-1-phenyl-2-methylcyclohexane (7t).**—Concentration of early chromatographic fractions eluted with 1% ether in hexane provided 726 mg (21.3%) of **7t**, mp 47–50°. Sublimation at 60–70° (0.04 mm) and recrystallizations from pentane gave needles melting at 54–54.5°; ir 855 cm^{-1}, no absorption in C=O or OH regions; uv 242 nm (ϵ 124), 247 (138), 252 (172), 262 (200), 264 (143); nmr δ 1.2 (3 H, s), 1.3–2.5 (6 H, complex), 4.55 (1 H, $W_{1/2}$ = 6 Hz), 7.3 (5 H, s).

Anal. Calcd for $C_{13}H_{15}OBr$: C, 58.44; H, 5.66. Found: C, 58.28; H, 5.57.

***cis*-3-Bromo-1,2-epoxy-1-phenyl-2-methylcyclohexane (7c).**—Concentration of later 1% ether fractions gave 613 mg (18.0%) of **7c**, mp 68–71°. Sublimation at 70–80° (0.04 mm) and recrystallizations from pentane provided needles melting at 73–73.5°; ir 855 cm^{-1}, no absorption in C=O or OH regions; uv 246 nm (ϵ 212), 253 (206), 259 (224), 265 (155); nmr δ 1.12 (3 H, s), 1.4–2.4 (6 H, complex), 4.4 (1 H, t, J = 7 Hz), 7.3 (5 H, s).

Anal. Calcd for $C_{13}H_{15}OBr$: C, 58.44; H, 5.66. Found: C, 58.72; H, 5.92.

1-Benzoyl-1-methyl-2-bromocyclopentane (5).—Concentration of chromatographic fractions eluted with 10% ether in hexane afforded 230 mg (6.8%) of **5**, mp 39–43°. Sublimation at 50–60° (0.03 mm) and recrystallizations from pentane yielded material melting at 50–50.5°; ir 1680 cm^{-1}; uv 242 nm (ϵ 10,000), 278 (804); nmr δ 1.6 (3 H, s), 1.8–2.6 (6 H, complex), 5.0 (1 H, t, J = 6 Hz), 7.3–7.65 (3 H, complex), 7.83 (2 H, q, J = 2, 7 Hz).

Anal. Calcd for $C_{13}H_{15}OBr$: C, 58.44; H, 5.66. Found: C, 58.50; H, 5.66.

1-Phenyl-1,6-heptanedione (10).—Concentration of fractions eluted with 1:1 ether–hexane yielded 35 mg (1.4%) of dione melting at 39–42.5° (lit.[22] mp 43°), identified by its spectra: ir 1725, 1695 cm^{-1}; nmr δ 1.4–1.95 (4 H, complex), 2.05 (3 H, s), 2.4 (2 H, t, J = 7 Hz), 2.9 (2 H, t, J = 7 Hz), 7.1–7.6 (3 H, complex), 7.9 (2 H, q, J = 2, 7.5 Hz).

2,3-Dibromo-1-phenyl-2-methylcyclohexanol (9).—Concentration of chromatographic fractions eluted with ether furnished 409

(18) (a) G. A. Olah in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience, New York, N. Y., 1963, pp 220–221; (b) H. O. House, *J. Amer. Chem. Soc.*, **77**, 3070, 5083 (1955).

(19) Melting points were determined with a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken using a Beckman IR-10 spectrometer, with CCl_4 as solvent. Ultraviolet spectra were determined in 95% EtOH solution with a Cary Model 14 spectrophotometer; nmr spectra were taken with a Varian A-60 spectrometer (CH_2Cl_2 and/or TMS internal standard) and using CCl_4 or $CDCl_3$ as solvent. Mass spectra were determined with a Perkin-Elmer Model 270 mass spectrometer through the kindness of Dr. R. E. Naipawer and Givaudan Corp. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

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mg (9.2%) of **9**, mp 89–97°. Sublimation at 90–95° (0.03 mm) and recrystallizations from pentane gave material melting at 101–102°; ir 3610, 3555 cm^{-1}; uv 253 nm (ϵ 199), 258 (278), 262 (278), 264 (247), 268 (208); nmr δ 1.95 (3 H, s), 2.1–2.5 (6 H, complex), 3.12 (1 H, broad s), 4.9–5.3 (1 H, m), 7.15–7.6 (5 H, complex).

Anal. Calcd for $C_{13}H_{16}OBr_2$: C, 44.86; H, 4.63. Found: C, 44.76; H, 4.54.

1-Benzoyl-1-methylcyclopentane (14) by Hydrogenolysis of 5.—A solution of 300 mg (1.12 mmol) of **5** in 8 ml of MeOH was injected into a stirred suspension of 150 mg of 5% Pd/C catalyst and 75 mg of $NaHCO_3$ in 8 ml of MeOH which had been presaturated with H_2. Analysis of material isolated after 30 min indicated substantial carbonyl reduction, which, from other analyses, appeared to occur faster than C–Br hydrogenolysis. Reoxidation with Jones reagent[23] afforded, after isolation, 143 mg (67.5%) of **14**, identical with subsequently described synthetic material.

Benzoylcyclopentane (13).—Cyclopentanecarboxylic acid (4.8 ml, 44 mmol) was cooled with an ice bath and treated with 3.8 ml (53 mmol) of $SOCl_2$ by dropwise addition over 15 min.[24] The solution was refluxed for 45 min and, after removal of excess $SOCl_2$, distilled at 98–100° (102 mm) to give 4.0 g (30 mmol, 69%) of **12**, which was then slowly added in 36 ml of dry benzene to a stirred suspension of 4.1 g (31 mmol) of anhydrous $AlCl_3$ in 73 ml of dry benzene.[25] The sclution of bright yellow complex was refluxed for 1 hr and decomposed with cold dilute aqueous HCl. Separation and extraction of the organic solution with aqueous base provided, on concentration, a residue which was distilled at 88–90° (*ca.* 0.25 mm) to give 4.8 g (92%) of **13** [lit.[25] bp 156–160° (15 mm)]: ir 1690 cm^{-1}; nmr δ 1.3–1.9 (8 H, complex), 3.55 (1 H, quintet, J = 7 Hz), 7.3 (3 H, complex), 7.9 (2 H, q, J = 2, 7 Hz).

1-Benzoyl-1-methylcyclopentane (14).—A solution of DMSO anion was prepared from 40 ml of dry DMSO and 1.0 g (41 mmol) of NaH.[26] Benzoylcyclopentane (3.5 g, 21 mmol) in 5 ml of dry DMSO was converted to its anion by titration with this solution under N_2 until the small amount of Ph_3CH present as indicator with the ketone gave a red color. After another 20 min of stirring, 6.2 ml (100 mmol) of MeI was added and the colorless solution was diluted with pentane, washed with water, dried, and concentrated. The residue was chromatographed on 150 g of neutral Al_2O_3 (2% H_2O added) and pure fractions (tlc) were combined and distilled at 83–84° (*ca.* 0.25 mm) to give 2.8 g (74%) of **14** as a colorless oil: ir 1680 cm^{-1}; uv 240 nm (ϵ 6980), 277 (695); nmr δ 1.4 (3 H, s), 1.5–1.8 (6 H, complex), 2.3–2.5 (2 H, m), 7.6 (3 H, complex), 7.9 (2 H, q, J = 2, 7 Hz), no absorption at 3.0–4.0 (*cf.* **13**).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.98; H, 8.63.

Synthetic **14** and hydrogenolysis product **14** had identical ir and nmr spectra, identical vpc retention times,[6] and only negligible differences in their mass spectra. Parent ion (*m/e* 188) intensity, expressed as percentage of total intensity for all ions with $m/e \geq 50$, was 1.44% for synthetic **14** and 1.49% for hydrogenolysis product **14**.

Stability of 9 to Reaction Conditions.—A solution of 150 mg (0.43 mmol) of dibromo alcohol **9** in 4.5 ml of dry ether was injected with stirring into 0.50 ml (1.0 mmol) of cold ethereal 2.0 *M* phenylmagnesium bromide under N_2. A solution of 0.27 ml (0.50 mmol) of Br_2 in 0.3 ml of dry CH_2Cl_2 was slowly added and the resultant solution was stirred for 1 hr at ice-bath temperature. Work-up as described and chromatography gave 134 mg (89.3%) of unchanged **9**, mp 97–99°.

Reaction of 9 with Sodium Hydride.—Dry dimethoxyethane (5 ml) was injected into a flask containing 210 mg (0.605 mmol) of dibromo alcohol **9** and 0.75 mmol of NaH (from 32 mg of 56% oil dispersion, washed with pentane) under N_2. Gas was evolved and the resulting gray suspension was stirred for 1 hr. Removal of solvent under vacuum and extraction of the residue with pentane gave material which was chromatographed and sublimed at *ca.* 60° (0.03 mm) to yield 141 mg (85.2%) of compound, mp 47–48°. Recrystallizations from pentane afforded pure **15**: mp 48–49° ir 1690, 1652 cm^{-1}; uv 235 nm (ϵ 12,700), 268 (984); nmr δ 1.5–2.1 (4 H, complex), 2.18 (3 H, s), 2.90 (2, H, t, J = 7 Hz), 5.83 (1 H, t, J = 6 Hz), 7.3–7.55 (3 H, complex), 7.9 (2 H, q, J = 2, 7 Hz).

Anal. Calcd for $C_{13}H_{15}OBr$: C, 58.44. H, 5.66. Found: C, 58.47; H, 5.73.

Stability of 7t to Reaction Conditions.—Ethereal 2.17 *M* phenylmagnesium bromide (0.03 ml, 0.075 mmol) was added to a cold solution of 10 mg (0.038 mmol) of bromoepoxide **7t** in 0.25 ml of dry ether under N_2. The mixture was stirred at ice-bath temperature for 30 min and 0.032 ml (0.075 mmol) of Br_2 in 0.04 ml of dry CH_2Cl_2 was added. After an additional 1 hr of stirring at ice-bath temperature, the mixture was worked up as described and analyzed by vpc[6] under conditions that were capable of separating and allowing identification of **5**, **7t**, **7c**, and **9**. Only unchanged **7t** was detected.

Catalytic Hydrogenolysis of 7c.—A solution of 100 mg (0.37 mmol) of bromoepoxide **7c** in 2 ml of MeOH was injected into a suspension of 50 mg (0.60 mmol) of $NaHCO_3$ and 50 mg of 5% Pd/C catalyst in 2 ml of MeOH which had been presaturated with H_2. The mixture was stirred vigorously for 5 min under 1 atm of H_2 at room temperature, then rapidly filtered. Analysis by nmr and vpc[6] of the isolated organic product indicated about 90% of **2** and about 5% each of **17** and of remaining **7c**.

When bromoepoxide **7c** was similarly treated under more drastic conditions, with its own weight of catalyst for 15 min, and the product was analyzed by nmr and vpc,[6] the components present and their amounts were similar to those found in the subsequently described hydrogenation of **2**.

Catalytic Hydrogenation of 2.—A solution of 300 mg (1.60 mmol) of allylic alcohol **2** in 5 ml of MeOH was injected into a slurry of 150 mg of 5% Pd/C catalyst in 10 ml of MeOH which had been presaturated with H_2, and stirred under 1 atm of H_2 at room temperature for 110 min Filtration and concentration gave material shown by nmr to be essentially free of starting material. Analysis by vpc[6] at 180° showed three components, with retention times of 3.0 (**17**, *ca.* 50%), 4.5 (**18a**, *ca.* 25%), and 5.1 min (**18b**, *ca.* 25%). Subsequent experiments indicated that **18b** was actually formed more rapidly than **18a** but was also hydrogenolyzed more rapidly to **17**. The above mixture was chromatographed on 12 g of neutral Al_2O_3 (2% H_2O added) as follows.

Elution with hexane gave 129 mg (46.5%) of **17** as an oil whose vpc retention time at 180° was 3.0 min; ir no OH absorption; nmr δ 0.66 (3 H, d, J = 7 Hz), 1.1–2.3 (9 H, complex), 2.75 (1 H, m), 7.1 (5 H, s).

Early fractions eluted with 25% ether in hexane provided 26 mg (14%) of **18a** as an oil whose vpc retention time at 180° was 4.5 min; ir 3620 cm^{-1}; nmr δ 0.56 (3 H, d, J = 6 Hz), 1.1–2.3 (10 H, complex), 7.0–7.8 (5 H, complex). This material was identical with a sample prepared as described below by addition of phenylmagnesium bromide to 2-methylcyclohexanone.

Later fractions eluted with 25% ether in hexane afforded 32 mg (17%) of **18b** as an oil whose vpc retention time at 180° was 5.1 min; ir 3620 cm^{-1}; nmr δ 0.62 (3 H, d, J = 7 Hz), 1.0–2.3 (10 H, complex), 7.0–7.45 (5 H, complex.)

2-Methyl-1-phenylcyclohexanol (18a).[16]—Ethereal 2.0 *M* phenylmagnesium bromide (27 ml, 54 mmol) was added dropwise to a stirred solution of 5.0 g (45 mmol) of 2-methylcyclohexanone in 15 ml of anhydrous ether at ice-bath temperature. The solution was stirred for 1 hr at room temperature and hydrolyzed with basic saturated aqueous NH_4Cl. Fractional distillation of the isolated organic material at 95–96° (*ca.* 0.20 mm) gave 8.5 g (61%) of colorless liquid. One of the distillation fractions, shown by vpc[6] to consist of **18a** with less than 5% of **18b** present, gave ir and nmr spectra identical with those of **18a** produced by hydrogenation of **2**.

Catalytic Hydrogenolysis of 7t.—Hydrogenolytic treatment of **7t** for 5 min under the milder conditions described for **7c** gave material which nmr and vpc analysis indicated to consist of *ca.* 70% **7t** and 30% **17**. Under the more drastic treatment described for **7c**, **7t** yielded material whose nmr spectrum indicated complete loss of **7t**, with conversion principally to **17**, accompanied by smaller amounts of **18a** and **18b** and two materials believed to be epimers of **19** (singlets at δ 0.91 and 1.07).

Registry No.—**2**, 35639-05-5; **5**, 35639-06-6; **7c**, 35639-07-7; **7t**, 35639-08-8; **9**, 35639-09-9; **14**, 17206-

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29-0; **15**, 35639-11-3; 2-methyl-3-phenylcyclohexanone, 18018-02-5; 2-methyl-3-phenylcyclohexanone (DNP), 18018-03-6.

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Decarboxylation of Halogenated 2-Oxetanones

WILLIAM T. BRADY* AND ARVIND D. PATEL

Department of Chemistry, North Texas State University, Denton, Texas 76201

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Halogenated 2-oxetanones are less susceptible to decarboxylation than other 2-oxetanones. A trichloromethyl substituent in the 4 position of the 2-oxetanone ring severely inhibits decarboxylation. The decarboxylation of 2-oxetanones derived from the cycloaddition of halogenated ketenes and chloral over an electrically heated wire produces halogenated allenes. This method provides a useful synthesis for trichloromethylallenes.

It is well known that 2-oxetanones are quite susceptible to thermal decarboxylations to yield olefinic compounds.[1,2] However, the effect of substituents such as a halogen on the rate of thermal decarboxylations is relatively unknown. In our investigations concerning the cycloaddition of halogenated ketenes and carbonyl compounds to produce 2-oxetanones we have prepared a number of halogenated 2-oxetanones. It was of interest to study the decarboxylation of these compounds and determine the effect of halogen and other electronegative substituents on the thermal stability of the 2-oxetanones. Consequently, the purpose of this paper is to relate the results of our study on the decarboxylation of halogenated 2-oxetanones. A preliminary report describing a novel method for the preparation of some trichloromethylallenes has appeared.[3]

Preparation of Halogenated 2-Oxetanones.—We have recently reported the cycloaddition of dichloroketene with several simple ketones to produce 3,3-dichloro-2-oxetanones.[4] The generation of dichloroketene by the triethylamine dehydrochlorination of dichloroacetyl chloride in the presence of activated carbonyl compounds also yields 2-oxetanones.[5] This method has been applied to the cycloaddition of bromochloroketene with certain aldehydes to produce 3-bromo-3-chloro-2-oxetanones.

The 3,3-dichloro-2-oxetanones may be selectively reduced with tri-*n*-butyltin hydride to the corresponding monochloro-2-oxetanones. The reduction may also be effected to produce the nonhalogenated-2-oxetanones.

Alkylchloroketenes also undergo *in situ* cycloadditions but only with activated carbonyl compounds such as chloral to yield the expected 2-oxetanones. We have also previously described the cycloaddition of chloroketene with chloral at room temperature to yield both *cis*- and *trans*-2-oxetanones.[6] We have since found that conducting this reaction at −78° and allowing warming to room temperature produces only the trans isomer.

Decarboxylations.—The effect of halogen in the 3 position upon the rate of decarboxylation was easily determined by comparing the rates of decarboxylation of the compounds in Table I. The relative rates represent the time required for 50% decarboxylation. The decarboxylation was measured by observing the disappearance of the carbonyl band in the infrared using the carbonyl band of the solvent, 2-heptanone, as an internal standard.

TABLE I

EFFECT OF CHLORO SUBSTITUENT IN 3 POSITION ON RATE OF DECARBOXYLATION

Compd	R	R′	Relative rate
I	H	H	>100
II	H	Cl	6
III	Cl	Cl	1

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