Samples Co.): bp 160–161° (lit.[16] bp 161°); ir ($CHCl_3$) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) 1.05 (s, 9 H), 1.10 (s, 9 H), 2.40 ppm (2 H); mass spectrum *m/e* (rel abundance) 156 (M^+, 40), 57 (100).

4-Bromo-2,2,5,5-tetramethyl-3-hexanone was prepared from the above ketone on the 50-mmol scale. The reaction was notably slower than the other reactions, with addition requiring 8 hr. Work-up as usual gave 10.9 g (93%) of the bromo ketone as clear, colorless oil: bp 31° (0.10 mm); ir ($CHCl_3$) 1709 cm^{-1}; ^1H NMR ($CDCl_3$) 1.16 (s, 9 H), 1.25 (s, 9 H), 4.53 ppm (s, 1 H); mass spectrum *m/e* (rel abundance) 236/234 (M^+, 60/60), 151/149 (M − C_4H_9CO, 70/70), 57 (100).

Anal. Calcd for $C_{10}H_{19}BrO$: C, 51.07; H, 8.14; Br, 33.98. Found: C, 51.04; H, 8.11; Br, 34.04.

Attempted Preparation of 2,2,5,5-Tetramethyl-3,4-hexanedione via Iodide-Catalyzed Oxidation. When the usual reaction was attempted on the above bromo ketone, even after reaction times of up to 25 hr at 150°, no diketone could be isolated, although there was development of some yellow color. The liquid reisolated from the reaction (105% based on mass of starting bromo ketone), which had an NMR identical with that of starting material, was shown by GLC (12% Carbowax 20M) to be a 55:45 mixture of α-bromo and α-iodo ketone: mass spectrum *m/e* 282 (RI), 236/234 (RBr), 197 (RI − C_4H_9CO), 151/149 (RBr − C_4H_9CO).

2,2,5,5-Tetramethyl-3,4-hexanedione was prepared by Kornblum's method;[12] 4-bromo-2,2,5,5-tetramethyl-3-hexanone (2.35 g, 10 mmol) was dissolved in 15 ml of acetonitrile, and a solution of silver nitrate (1.87 g, 11 mmol) in 15 ml of acetonitrile was added. After stirring for 60 hr at ambient temperature the mixture was filtered, the silver bromide was washed with diethyl ether, and the combined filtrate and washing were rotary evaporated (water aspirator, 30°). The residue was taken up in ether, washed with water, and dried, and the solvent was removed. The crude nitrate ester was dissolved in 70 ml of DMSO and then a suspension of sodium acetate trihydrate (0.20 g) in 20 ml of DMSO was added. After stirring for 5–10 min at room temperature, the reaction mixture was worked up in a similar manner to the previously mentioned DMSO oxidation reactions: yield 0.80 g (47%); bp 38–40° (5 mm) [lit.[1] bp 59–62° (14 mm)]; ir (neat) 1700 cm^{-1}; NMR (CCl_4) 1.18 ppm (s); mass spectrum *m/e* (rel abundance) 170 (M^+, 6), 57 (100).

Acknowledgment. We wish to thank PHS, NIH, for their generous support of this work (Grant 5 R01 AI 11690-02 MCHB).

Registry No.—2-Bromocyclododecanone, 31236-94-9; 2-bromocyclooctanone, 39261-18-2; 2-bromo-2-phenylacetophenone, 1484-50-0; α-bromopropiophenone, 2114-00-3; 2,2,5,5-tetramethyl-3-hexanol, 55073-86-4; 4-bromo-2,2,5,5-tetramethyl-3-hexanone, 55073-87-5; 4-iodo-2,2,5,5-tetramethyl-3-hexanone, 55073-88-6; 2,2,5,5-tetramethyl-3,4-hexanedione, 4388-88-9.

References and Notes

(1) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950).

(2) J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, *J. Am. Chem. Soc.*, **96**, 4385 (1974).

(3) T. R. Evans and P. A. Leermakers, *J. Am. Chem. Soc.*, **89**, 4380 (1967).

(4) S. Selman and J. F. Eastham, *Q. Rev., Chem. Soc.*, **14**, 221 (1960).

(5) F. Ramirez et al., *J. Am. Chem. soc.*, **85**, 3056 (1963).

(6) V. Prelog and M. Speck, *Helv. Chim. Acta*, **38**, 1786 (1955).

(7) C. W. N. Cumper, G. B. Leton, and A. T. Vogel, *J. Chem. Soc.*, 2067 (1965).

(8) Several examples of the selenium dioxide oxidation of ketones to give cyclic and acyclic α diketones can be found in L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 992 ff.

(9) (a) N. Kornblum et al., *J. Am. Chem. Soc.*, **79**, 6562 (1957); (b) A. P. Johnson and A. Pelter, *J. Chem. Soc.*, 520 (1964); (c) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

(10) R. Iacona, A. Rowland, and H. Nace, *J. Org. Chem.*, **29**, 3495 (1964); H. Nace and R. Iacona, *ibid.*, 3498 (1964).

(11) W. W. Epstein and J. Ollinger, *J. Chem. Soc. D*, **20**, 1338 (1970).

(12) N. Kornblum and H. Frazier, *J. Am. Chem. Soc.*, **88**, 865 (1966).

(13) W. S. Trahanovsky, Ed., "Oxidation in Organic Chemistry", Academic Press, New York, N.Y., 1973, Part B, p 67; ref 8, p 161.

(14) N. Bosworth and P. D. Magnus, *J. Chem. Soc., Chem. Commun.*, 257 (1972).

(15) While iodide has, to the best of our knowledge, never been used to catalyze a DMSO oxidation, it has been used as a nucleophilic catalyst; see, for example, S. Kawai, T. Nakamura, and N. Sugiyama, *Ber.*, **72**, 1146 (1939).

(16) In support of this argument, it was observed that formation of the 2,4-dinitrophenylhydrazone of 2,2,5,5-tetramethyl-3-hexanone was extremely difficult: W. J. Hickinbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, 2533 (1954); F. C. Whitmore and J. W. Heyd, *J. Am. Chem. Soc.*, **60**, 2030 (1938).

(17) L. T. Zakharkin and V. V. Korneva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1817 (1962).

(18) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6039 (1958).

(19) A. C. Cope and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 3889 (1957).

(20) A. Lespagnol, F. Mercier, J. Bertrand, and J. Mercier, *Ann. Pharm. Fr.*, **8**, 241 (1950).

(21) C. Liebermann and J. Homeyer, *Ber.*, **12**, 1971 (1879).

(22) A. V. Dombrovskii, M. I. Shevchuk, and V. P. Kravets, *Zh. Obshch. Khim.*, **32**, 2278 (1962).

(23) von J. Wegmann and H. Dahn, *Helv. Chim. Acta.*, **29**, 1247 (1946).

(24) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

Oxidation of Alcohols with Acetyl Hypoiodite

Thomas R. Beebe* Beverly A. Barnes, Keith A. Bender,
Allan D. Halbert, Robert D. Miller, Martin L. Ramsay,
and Michael W. Ridenour

Department of Chemistry, Berea College, Berea, Kentucky 40403

Received December 13, 1974

This report covers the reaction of a variety of alcohols with acetyl hypoiodite and the subsequent decomposition of the alkyl hypoiodite that was formed. The formation and decomposition of the alkyl hypoiodite product was done in the absence of metal salts. Previous reported reactions of steroid alcohols with acetyl hypoiodite involved the preparation and decomposition of the products in the presence of mercury, silver, or lead salts.[1] These salts very likely have a direct effect on the product composition.

To determine the generality of preparing alkyl hypoiodites from acetyl hypoiodite and alcohols, we have treated several alcohols with acetic acid solutions of acetyl hypoiodite. Solutions of acetyl hypoiodite were prepared by treating silver acetate with a 5% molar excess of iodine in glacial acetic acid.[2] The molar amount of precipitated silver iodide accounted for more than 99% of the starting silver acetate.

The alcohols to be oxidized were selected so that the proposed alkyl hypoiodite intermediates would break down to products in a variety of ways. Good yields of products were obtained by irradiating the cooled (20–25°) reaction mixtures immediately after the alcohols were mixed with the acetyl hypoiodite solutions. The product yields were cut approximately in half when the reaction mixtures were irradiated and heated (90–100°), and yields were very low (10–20%) when the reaction mixtures were run in the dark at ambient temperatures.

A general sequence for the reaction between acetyl hypoiodite and an alcohol is suggested below. The acetyl hypoiodite reacts with the alcohol to give an equilibrium with the alkyl hypoiodite and acetic acid. The O–I bond of the alkyl hypoiodite then is cleaved homolytically by visible light to produce alkoxy radicals. The alkoxy radicals have several decomposition pathways available to them.

$$CH_3COOI + ROH \rightleftharpoons CH_3COOH + ROI$$

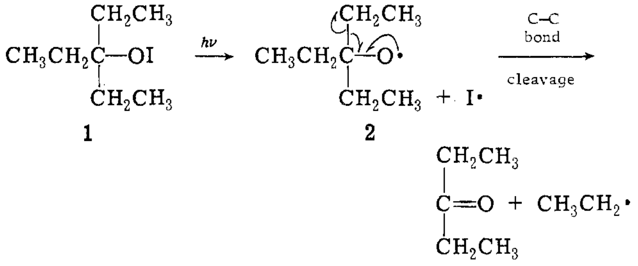
$$ROI \xrightarrow{h\nu} I\cdot + RO\cdot \longrightarrow \text{products}$$

The oxidations of 3-ethyl-3-pentanol, 1-pentanol, and benzyl alcohol with acetyl hypoiodite will be discussed in some detail. The only detectable products from the reaction of 3-ethyl-3-pentanol with acetyl hypoiodite were 3-pentanone and iodoethane. The 3-pentanone is formed from β-scission[3] of the intermediate alkoxy radical **2**, while the iodoethane is produced when the ethyl radical and the hypoiodite **1** collide.

Table I
Oxidations[a] of Alcohols with Acetyl Hypoiodite

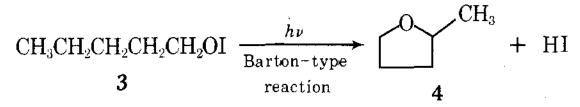
Registry no.	Alcohol	Products (% yield[b])	Irradiation time, hr
597-49-9	3-Ethyl-3-pentanol	3-Pentanone (90) Ethyl iodide (84)	1
6032-29-7	2-Pentanol	2-Methyltetrahydrofuran (30) 2-Pentanone (60[c])	24
71-41-0	1-Pentanol	2-Methyltetrahydrofuran (80)	24
100-51-6	Benzyl alcohol	Benzaldehyde (85[c]) Iodobenzene (0)	4
611-69-8	2-Methyl-1-phenyl-1-propanol	Benzaldehyde (61[c]) 2-Iodopropane (>15[d]) 2-Methyl-1-phenyl-1-propanone (40[c])	17

[a] The oxidations were performed at 20-25° with irradiation. [b] The percent yields were an average of three runs. [c] The yield was based on a 50% maximum because of a presumed disproportionation reaction of the alkoxy radical. [d] The 2-iodopropane was not stable under our GLC conditions and more than 15% was probably formed.



$$1 + CH_3CH_2\bullet \longrightarrow CH_3CH_2I + 2$$

Reaction of 1-pentanol with acetyl hypoiodite produces 80% yields of 2-methyltetrahydrofuran (**4**). The furan product gives evidence that a Barton-type[4] decomposition is the preferred pathway for the intermediate hypoiodite **3**.



Benzaldehyde is the major product when benzyl alcohol and acetyl hypoiodite are mixed and irradiated. The benzoxy radical **6** forms benzaldehyde and presumably benzyl alcohol, by a radical disproportionation reaction.

$$\underset{6}{2C_6H_5CH_2O\bullet} \xrightarrow[\text{disproportionation}]{\text{radical}} C_6H_5CHO + C_6H_5CH_2OH$$

Two products, 2-pentanone (60%) and 2-methyltetrahydrofuran (30%), were formed when 2-pentanol and acetyl hypoiodite were mixed together with irradiation. The 2-pentanone was probably formed by a disproportionation reaction of the 2-pentoxy radical while the 2-methyltetrahydrofuran was produced by a Barton-type reaction.

The decomposition of the hypoiodite obtained from 2-methyl-1-phenyl-1-propanol gave benzaldehyde (61%) and 2-iodopropane (>15%) from a β-scission of the alkoxy radical and produced 2-methyl-1-phenyl-1-propanone (40%) by radical disproportionation of the alkoxy radical.

A list of alcohols oxidized with acetyl hypoiodite, the percentage yields of the products, and the reaction times are given in Table I.

The reactions of some alcohols with acetyl hypoiodite other than those listed in Table I were tried. 1-Phenyl-1-ethanol and *tert*-butyl alcohol dehydrated too rapidly in the acetic acid solution before any substantial hypoiodite formation could take place. Diphenylcarbinol and triphenylcarbinol acetylated before an oxidation could occur.

In summary, the acetyl hypoiodite converted several alcohols to their corresponding alkyl hypoiodites in good yields. The reaction of acetyl hypoiodite with alcohols provides an excellent source of the not easily accessible primary and secondary alkoxy radicals. With no metal ions present the alkyl hypoiodites gave products that indicated light-induced homolytic decomposition. We are presently looking for an inert solvent in which the acetyl hypoiodite is stable so that the reaction of alcohols with acetyl hypoiodite would be more general.

Experimental Section

Analyses were performed on a Perkin-Elmer 810 GLC and a Varian Aerograph Model 700 GLC. Irradiation of the reaction mixtures was effected with a G. E. projector spot 150-W, 130-V tungsten lamp. Liquid chemicals used in reaction mixtures and standard GLC mixtures all had greater than 99.5% purity as determined on the gas chromatograph. The silver acetate was dried under vacuum in the dark at 64°. The iodine was sublimed. The acetic acid was refluxed for 24 hr with 2% acetic anhydride and was fractionally distilled. GLC analyses of the acetic acid solutions were performed using a 6 ft × 0.25-in. copper column of 20% FFAP (modified Carbowax 20M from Varian) adsorbed on 60–80 mesh base-washed Chromosorb P. All oxidations were run between 20 and 25° with irradiation. The oxidations were monitored frequently and the time for maximum yields of products ranged from 1 to 24 hr. Descriptions of the preparation of acetyl hypoiodite and of the oxidation of 3-ethyl-3-pentanol with acetyl hypoiodite are given in detail. The other oxidations were performed in a similar manner.

Preparation of Acetyl Hypoiodite. Dry silver acetate (4.09 mmol) was placed in an aluminum foil covered 100-ml round-bottomed flask containing a small magnetic stirrer. Forty milliliters of acetic acid containing iodine (4.3 mmol) was added dropwise into the flask with stirring. The mixture was stirred for 1 hr at room temperature and was filtered through a fine sintered-glass funnel. The precipitate contained 4.08 mmol of silver iodide. The liquid filtrate contained 2.5 mmol of acetyl hypoiodite. Analysis was done by adding aliquot portions of the acetyl hypoiodite to aqueous potassium iodide solutions. The liberated iodine was titrated with standard thiosulfate solutions.

Oxidation of 3-Ethyl-3-pentanol with Acetyl Hypoiodite. Five milliliters of an acetic acid solution containing 3-ethyl-3-pentanol (1.0 mmol) and chlorobenzene (0.25 mmol) was added to a 25-ml round-bottomed flask. To this solution was added 5 ml of acetic acid solution containing acetyl hypoiodite (0.25 mmol). The combined solutions were placed in a cooling bath (20–25°) and irradiated. GLC analysis showed 50% iodoethane and 53% 3-pentanone within 19 min and a maximum of 84% iodoethane and 90% 3-pentanone in 1 hr.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—Acetyl hypoiodite, 6540-76-7.

References and Notes

(1) C. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, *Experienta,* **17,** 475 (1961); K. Heusler, J. Kalvoda, C. Meystre, G. Anner, and A. Wettstein, *Helv. Chim. Acta,* **45,** 2162 (1962); K. Heusler and J. Kalvoda, *Angew. Chem.,* **76,** 518 (1964).

(2) J. R. Barnett, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.,* **94,** 6129 (1972).

(3) C. Walling and A. Padwa, *J. Am. Chem. Soc.,* **85,** 1593 (1963).

(4) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.,* 181 (1965).

Vinyl Cations. 19.[1] Preparation and Solvolysis of (1-Bromo-1-arylmethylene)cyclopropanes. Effect of *p*-Aryl Substituents on the Generation of Stabilized Vinyl Cations

J. Salaun and M. Hanack*

Fachbereich 14, Organische Chemie,
Universität des Saarlandes,
D 6600 Saarbrücken, Germany

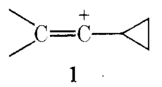
Received September 10, 1974

Vinyl cation intermediates are now readily available in solvolysis reactions either through heterolysis of vinyl substrates or triple bond participations.[2] Although vinyl cations are generally less stable than the corresponding saturated carbenium ions,[3] recent studies have given evidence for their formation.

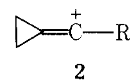
Thus, in the solvolysis of simple alkyl vinyl derivatives the choice of a more reactive leaving group (e.g., arylsulfonates[4] or, even better, the "super leaving groups" triflate[5] and nonaflate[6]), or the stabilization of the positive charge by electron-releasing neighboring groups (e.g., vinyl,[7] aryl,[7,8] cyclopropane[9]) have favored the generation of this challenging intermediate.

In the particular case of a cyclopropane ring, it appears possible to stabilize a positive charge in two ways.

In the vinyl cation 1 the cyclopropane ring is directly attached to the positive center. In the vinyl cation 2, the β carbon atom of the vinyl double bond is in the cyclopropyl ring.



1

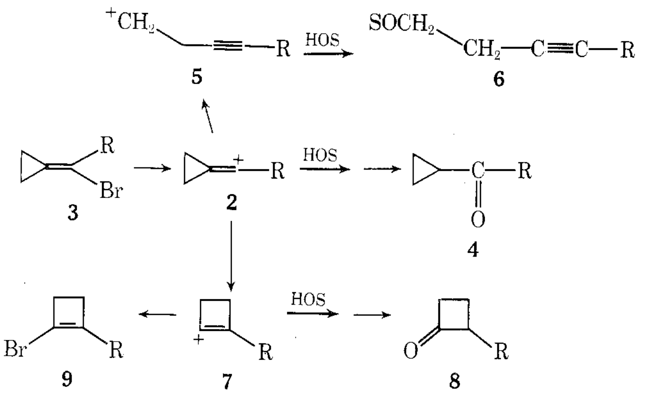


2

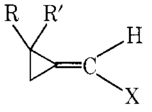
Vinyl cation 1 appears analogous to the cyclopropyl carbinyl cation, where the stabilizing effect of the cyclopropyl group is well established.[10] Vinyl cation 2 was first proposed by us as an intermediate in the homopropargyl rearrangement;[11] its high stability, arising from its special geometry (favorable overlapping of the vacant p orbital with the cyclopropane bonds and short C–C distance of the double bond), was confirmed by MO calculations.[12] If we consider now the generation of the vinyl cation 2 by the solvolysis of (halomethylene)cyclopropanes 3, the reaction products given in Scheme I are possible.

Besides direct substitution by solvent leading to the cyclopropyl ketone 4, the cyclopropylidenemethyl cation 2 is able to undergo either a homopropargylic rearrangement to give the homopropargyl cation 5 and then 6, or a ring enlargement to the cyclobutenyl cation 7 and formation of the cyclobutanone 8.

Scheme I

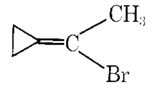


We have previously reported the generation of primary cyclopropylidene methyl cations 2 (R = H) through the solvolysis reactions of vinyl halides 10. If the cyclopropane ring is substituted by one or two methyl groups (10a, 10b) the corresponding primary vinyl cations undergo partial rearrangement to the corresponding homopropargyl cations (secondary and tertiary derivative of ion 5).[13,14] The (1-bromomethylene)cyclopropane 10c solvolyzes to cyclobutanone as the only solvolysis product,[15] involving a rearrangement of the labile primary vinyl cation 2 into a nonclassical stabilized cyclobutenyl cation 7.[12]

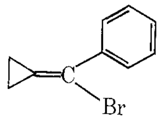


10a, R = R′ = CH$_3$; X = Cl
b, R = CH$_3$; R′ = H; X = Br
c, R = R′ = H; X = Br

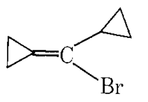
Further work has led to the generation of secondary vinyl cations 2 (R $\neq$ H) through the solvolysis of the (bromomethylene)cyclopropanes 11, 12, and 13 in order to obtain additional stabilization of the positive charge by electron-releasing substituents.[16,17] As expected, the kinetic data and product analysis have evidenced the formation of stabilized cyclopropylidenemethyl cation intermediates such as 2.[17]



11

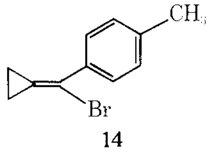


12

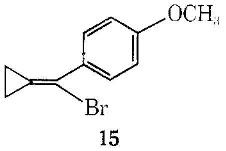


13

We report here the syntheses and the solvolysis reactions of the (1-bromo-1-arylmethylene)cyclopropanes 14 and 15 in which the phenyl ring is substituted by a *p*-methyl and a *p*-methoxy group, respectively, in order to study the increase in the stabilization of the intermediate vinyl cations induced by the increased electron-releasing effect of such para substituents.



14



15

Syntheses. The syntheses of the vinyl bromides 14 and 15 were carried out via the methylenecyclopropanes 16 and 20.

(1-*p*-Tolylmethylene)cyclopropane (16) was prepared in 70% yield by the Wittig reaction of *p*-methylbenzaldehyde with cyclopropyltriphenylphosphonium bromide (from 1,3 dibromopropane and triphenylphosphine), as recently reported for the synthesis of benzylidenecyclopropane.[16,18]