Pinacolone and acetone were identified by comparison of respective vpc retention times with authentic samples and co-injections on the vpc column.

2,4,4-Trimethylpentanal had bp 37.8–38.8° (10 mm); $n^{20}\mathrm{D}$ 1.4131 [lit.[18] bp 39° (9 mm), $n^{20}\mathrm{D}$ 1.4155]; 2,4-DNP, mp 145–146° (lit.[19] mp 145°).

4,4-Dimethyl-2-pentanone had bp 34–35° (15 mm) [lit.[20] bp 79–80° (75 mm)]; semicarbazone, mp 175–176.5° (lit.[14] mp 176°).

4,4-Dimethyl-2-neopentylpentanal had bp 68–72° (11 mm) [lit.[19] 85–90 (15 mm)]; 2,4-DNP, mp 188.3–189.3°. *Anal.* Calcd for $C_{18}H_{28}N_4O_4$: C, 58.84; H, 7.69; N, 15.25. Found: C, 58.93; H, 7.60; N, 15.29. Air oxidation[19] of the aldehyde gave **4,4-dimethyl-2-neopentylpentanoic acid**: mp 86.5–87.5° (lit.[19] mp 87–88°); amide, mp 141.5–142.5° (lit.[19] mp 139–140°).

2,4,4-Trimethyl-1,2-epoxypentane.—To a solution of 25.6 g (0.25 mol) of 2,4,4-trimethyl-1-pentene in 75 ml of methylene chloride (Matheson) was added dropwise with rapid stirring a solution of 49.3 g (0.25 mol) of 85% *m*-chloroperbenzoic acid (FMC) in 200 ml of methylene chloride over a period of 30 min. The rate of addition was adjusted to keep the reaction mixture below 40°. After addition, the reaction mixture was stirred for 1 hr, refluxed for 3 hr, allowed to stand at room temperature for 2 days, and filtered. The solid *m*-chlorobenzoic acid was washed with methylene chloride. The combined filtrate and wash solution gave a negative test with starch–iodide paper. The solution was transferred to a separatory funnel, washed with 5% sodium bicarbonate solution followed by saturated sodium chloride solution, dried ($MgSO_4$), filtered and concentrated. The residue was distilled under reduced pressure to yield 16.1 g (55%) of the epoxide, bp 61–62° (50 mm) [lit.[16] bp 140.5–141.5° (760 mm)]. The epoxide isomerizes to **2,4,4-trimethylpentanal** on standing or on treatment with dilute acid.

Registry No.—Chromyl chloride, 7791-14-2; 2,3,3-trimethylbutanol, 17408-48-9; 2,4,4-trimethylpentanol, 17414-46-9; 4,4-dimethyl-2-pentanone, 590-50-1; 4,4-dimethyl-2-neopentylpentanol, 17414-47-0; 4,4-dimethyl-2-neopentylpentanol 2,4-DNP derivative, 17408-49-0.

Acknowledgments.—We express our deep appreciation for support of this work to Long Beach California State College Foundation, the Research Corporation, and the Petroleum Research Fund administered by the American Chemical Society.

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(18) A. Byers and W. J. Hickinbottom, *J. Chem. Soc.*, 1416 (1954).

(19) See footnote *c*, Table I.

(20) J. Colonge and A. Perrot, *Bull. Soc. Chim. Fr.*, 658 (1957).

Concerning the Nature of the Polar Effect in Hydrogen Atom Abstractions from Alcohols, Ethers, and Esters[1]

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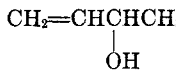
Received April 15, 1968

Earlier work by one of us showed that abstractions of benzylic hydrogens from substituted toluenes by trichloromethyl radicals are influenced by a polar effect.[3] A similar polar effect was postulated to explain the difference in reactivities of primary, secondary and tertiary allylic hydrogens toward abstraction by trichloromethyl radicals.[4] The polar effect postulated for these reactions was one in which the trichloromethyl radical displayed electron accepting qualities in the transition state of the hydrogen abstraction reaction and the reactivities of hydrogens toward abstraction by this radical depended on the ability of the substrate to act as an electron donor in the transition state of the reaction. The donor qualities of the substrate appear to be directly related to the stabilities of carbonium ions that might be obtained by loss of an electron from the radical produced in the reaction. This was evidenced by the reactivities of substituted toluenes paralleling stabilities of the corresponding benzylic carbonium ions[3] and reactivities of allylic hydrogens paralleling the corresponding carbonium ion stabilities[4] rather than radical stabilities.[5]

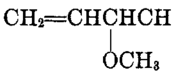
$$\mathrm{Cl_3C\cdot + HR \longrightarrow [\overset{\delta-}{Cl_3C}\cdots H\cdots \overset{\delta+}{R}] \longrightarrow Cl_3CH + R\cdot} \qquad (1)$$

The present work is concerned with the abstractions of allylic hydrogens from carbon atoms bonded to an oxygen function. The compounds used in this study were 1-buten-3-ol (I), 1-buten-3-yl methyl ether (II), and 1-buten-3-yl acetate (III). Each of these compounds has a terminal double bond and a single allylic hydrogen. They differ only in the nature of the group bonded to the oxygen.



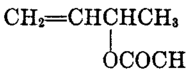
$$\mathrm{CH_2{=}CH\underset{OH}{\underset{|}{C}}HCH_3}$$

I



$$\mathrm{CH_2{=}CH\underset{OCH_3}{\underset{|}{C}}HCH_3}$$

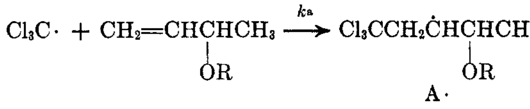
II



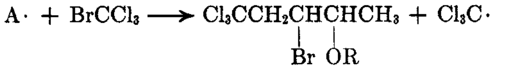
$$\mathrm{CH_2{=}CH\underset{OCOCH_3}{\underset{|}{C}}HCH_3}$$

III

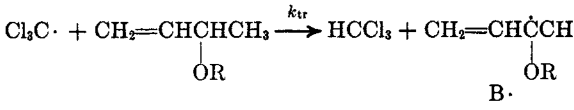
Reaction of each of these compounds with bromotrichloromethane results in addition of this reagent to the unsaturated linkage by the chain reaction 2 and 3 and substitution of the allylic hydrogen for bromine[6]



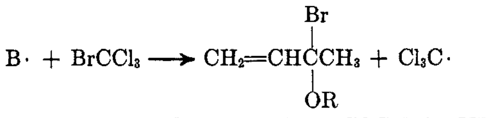
$$\mathrm{Cl_3C\cdot + CH_2{=}CH\underset{OR}{\underset{|}{C}}HCH_3 \xrightarrow{k_a} \underset{A\cdot}{Cl_3CCH_2\dot{C}H\underset{OR}{\underset{|}{C}}HCH_3}} \qquad (2)$$



$$\mathrm{A\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2\underset{Br}{\underset{|}{C}}H\underset{OR}{\underset{|}{C}}HCH_3 + Cl_3C\cdot} \qquad (3)$$



$$\mathrm{Cl_3C\cdot + CH_2{=}CH\underset{OR}{\underset{|}{C}}HCH_3 \xrightarrow{k_{tr}} HCCl_3 + \underset{B\cdot}{CH_2{=}CH\underset{OR}{\underset{|}{\dot{C}}}CH_3}} \qquad (4)$$



$$\mathrm{B\cdot + BrCCl_3 \longrightarrow CH_2{=}CH\overset{Br}{\underset{OR}{C}}CH_3 + Cl_3C\cdot} \qquad (5)$$

($R = H$ for I, $R = CH_3$ for II, $R = COCH_3$ for III)

by the chain reaction 4 and 5. The relative reactivity ratio k_a/k_{tr} for each compound can be determined from the amounts of bromotrichloromethane consumed in the reaction and chloroform produced[4] using eq 6.

$$k_a/k_{tr} = (\mathrm{BrCCl_3\ reacted - HCCl_3\ produced})/\mathrm{HCCl_3\ produced} \qquad (6)$$

Table I lists the data for reactions of each compound and the calculated values for k_a/k_{tr} and shows that the nature of the R group markedly affects the re-

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[1] This work was supported by a grant from the National Institutes of Health (AM-08517-02).

[2] Taken from the Ph.D. Thesis submitted by K. L. J. to the University of Kansas, 1968.

[3] E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960).

[4] E. S. Huyser, *J. Org. Chem.*, **27**, 3261 (1961).

[5] E. S. Huyser and D. T. Wang, *ibid.*, **29**, 2720 (1964).

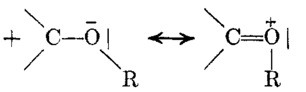
[6] In the case of I (R = H), reaction 5 leads to formation of the ketone and HBr. Cyclohexene oxide was employed as a trap for HBr to avoid any complications arising from the presence of this acid in these reactions.

TABLE I

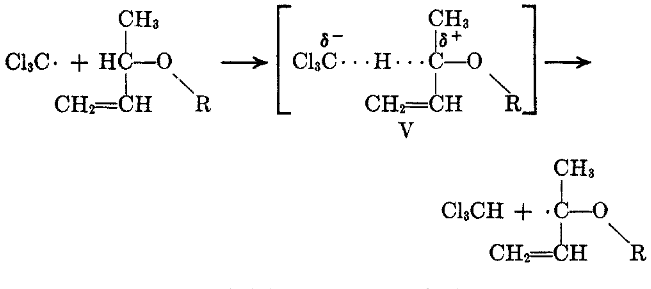
RELATIVE REACTIVITY RATIOS

Substrate (mmol)	$BrCCl_3$ Before	$BrCCl_3$ After	$HCCl_3$ produced	k_a/k_{tr}	Av
I (1.71)	0.904	0.072	0.107	7.53	
I (3.75)	2.253	0.044	0.229	8.65	8.34 ± 0.53
I (3.75)	2.253	0.050	0.224	8.84	
II (2.084)	0.917	0.093	0.043	18.2	
II (1.556)	1.065	0.048	0.047	16.4	16.9 ± 0.7
II (2.409)	0.939	0.108	0.046	17.0	
II (1.662)	0.766	0.140	0.037	15.9	
III (2.157)	1.532	0.0269	0.0030	505	530 ± 25
III (2.425)	2.144	0.0468	0.0038	555	

activity ratio. Since there is no apparent mode of interaction of the saturated linkage with the R groups on the oxygen bonded to the allylic carbon atom, the differences in k_a/k_{tr} must reflect mainly the effects of the R groups on the reactivities of the allylic hydrogens. For that matter, direct interaction of the R groups imparting either radical stability or polar characteristics to the allylic carbon is not possible. However, it is possible that the character of the R groups could have an effect on the oxygen and its interaction with the carbon in the transition state. Generally one expects an oxygen bonded to a carbon to stabilize a positive charge on that carbon because of the contribution of structures such as IV to the resonance hybrid. If the R group should increase or decrease the availability of the nonbonding electrons for such resonance contributions, the R groups might be expected to enhance or retard the rate of reaction in which the carbon atom is a donor species in the transition state of a free-radical reaction. In the case of hydrogen abstraction from the carbon by a trichloromethyl radical, a good electron acceptor radical, the transition state of the hydrogen abstraction resembles that shown in V and effects of the R group on stabilizing such a transition state should be expected.



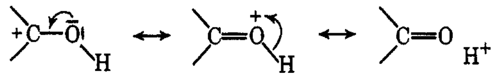
IV

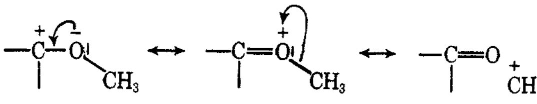


V

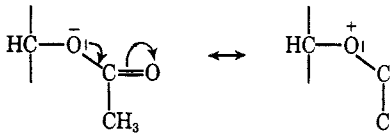
When the reactivities of the allylic hydrogens of I, II, and III are compared with that of 1-octene (k_a/k_{tr} = ∼50 at 80°),[4] it is obvious that the hydroxy group of I and the alkoxy group of II enhance the reactivity of the hydrogen markedly. The acetate group, on the other hand, does not enhance the reactivity of the allylic hydrogens toward hydrogen abstraction and possibly even retards the reaction relative to that observed for 1-octene.

In the case of I, the hydrogen bonded to oxygen may increase the stability of the donor species because the hydrogen is capable of accommodating the positive charge in the transition state of the hydrogen abstraction reaction. Similarly, the methoxy group in II may enhance the donor qualities, although somewhat less pronounced than in I, of the allylic carbon in the transition state of the allylic hydrogen abstraction from II. In this case, the charge may reside partially on the alkyl group.



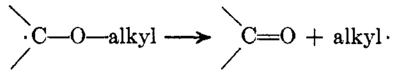


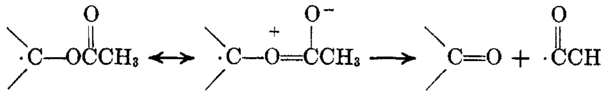
The comparatively low reactivity of the allylic hydrogen in III reflects not only the inability of the acetyl group to accomodate the charge as effectively as either hydrogen or methyl, but also the possibility of a deactivation of the oxygen in exercising its ability to influence the donor qualities of the transition state of the allylic hydrogen abstraction. Quite likely this may be caused by strong resonance interactions of the nonbonding electrons on the ether oxygen with the carbonyl function as shown in VI. This would render the nonbonding electrons less available for the stabilizing influence they might have on the transition state of the hydrogen abstraction reaction.



VI

The importance of resonance contributions of the kind suggested for the acetate group may be reflected by some differences in the free-radical chemistry of α-hydroxyalkyl radicals and α-alkoxyalkyl radicals compared with α-acetoxyalkyl radicals. When a suitable hydrogen acceptor is available (a carbonyl function[7] or a peroxide[8]) α-hydroxyalkyl radicals transfer their hydrogens with ease. Fragmentations of α-alkoxyalkyl radicals resulting in β-elimination reactions are also known. On the other hand, α-acetoxyalkyl radicals are quite stable and do not fragment readily at temperatures at which the α-alkoxyalkyl radicals decompose. Their inability to do so may possibly be caused by interaction of the oxygen with the acetyl group thereby strengthening the bond that would need to be broken if fragmentation occurred.





Experimental Section

Materials.—Bromotrichloromethane (Dow Chemical Co.) was redistilled under reduced pressure until it gave a single peak on gas chromatographic analysis. 1-Buten-3-ol (Aldrich Chemical

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(7) E. S. Huyser and D. C. Neckers, *J. Amer. Chem. Soc.*, **85**, 3641 (1963).

(8) E. S. Huyser and C. J. Bredeweg, *ibid.*, **86**, 4148 (1964).

Co.) was redistilled before using. 1-Buten-3-yl methyl ether (bp 49–50°) was prepared by reaction of α-methallyl chloride[9] with sodium methoxide in methanol.[10] 1-Buten-3-yl acetate, bp 112° (lit.[11] bp 110°), was prepared by reaction of the alcohol with acetic acid in the presence of pyridine. The infrared and nmr spectra of the three compounds were consistent with their assigned structures.

Determination of k_a/k_{tr} Ratios.—Solutions consisting of compounds I, II, and III and bromotrichloromethane in the amounts shown in Table I were sealed in Pyrex (6 mm by 120 mm) tubes. In the reactions of I, cyclohexene oxide in an amount slightly in excess of the bromotrichloromethane was added. The tubes were wrapped in aluminum foil to protect the contents from light and placed in a constant temperature water bath (40 ± 0.1°). After being allowed to warm to the temperature of the bath, the foil was removed and the tubes were illuminated with a 275-W G.E. sunlamp positioned about 5 in. from the tubes. Illumination was allowed to take place until most of the polyhalomethane had reacted (2–5 hr). The amounts of bromotrichloromethane that had reacted and amounts of chloroform produced were determined by gas chromatographic analysis of a weighed portion of reaction mixtures along with a weighed amount of 3-pentanol which served as an internal standard. The analyses were performed on an F & M Model 5750 Research chromatograph equipped with a Mosely Model 17503A recorder with a disc integrator and employing a thermal conductivity detector. The separations were accomplished on a 0.125-in. by 10-ft column packed with 15% E-600 on 60–80 mesh Chromosorb W.

Registry No.—I, 598-32-3; II, 17351-24-5; III, 6737-11-7; bromotrichloromethane, 75-62-7.

(9) W. G. Young, S. H. Sharman, and S. Winstein, *ibid.*, **82**, 1376 (1960).

(10) A. G. Catchpole and E. O. Huges, *ibid.*, 4 (1948).

(11) D. Semenow, C. H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958).

Diphenylketene. Triphenylphosphine Dehalogenation of α-Bromodiphenylacetyl Bromide[1]

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Received November 17, 1967

The reactions of triphenylphosphine with halogen derivatives of carbonyl compounds have been the subject of intensive study.[3] In view of the proposed mechanisms for the reactions of triphenylphosphine with these compounds, an α-haloacyl halide should offer attack by the nucleophilic phosphine at the α-carbon, carbonyl carbon, or at either halogen. While phosphonium salts at carbon would not be unusual, displacements at halogen might yield a new enol phosphonium salt or a ketene. Attack at the α halogen appears favorable considering that the acyl halide would stabilize a carbanion. Such a reaction might be considered similar to the zinc dehalogenation of α-haloacyl halides.[4] Additional stabilization could be achieved by phenyl substitution on the α carbon.

We wish to report a convenient synthesis of diphenylketene 2 from α-bromodiphenylacetyl bromide 1.

$$\underset{\mathbf{1}}{Ph_2CBrCOBr} + Ph_3P \longrightarrow \underset{\mathbf{2}}{Ph_2C{=}C{=}O} + Ph_2PBr_2$$

The acetyl bromide 1 was first prepared by Staudinger[5] from the addition of bromine to diphenylketene. A subsequent preparation of the dibromide from benzylic acid by the action of phosphorus pentabromide was reported.[6] Its preparation from diphenylacetic acid does not appear to have been reported. This source of the acyl bromide proved to furnish easily purified product. The usual bromination procedure was modified to use phosphorus pentabromide prepared *in situ*, followed by additional bromine to complete the reaction. In contrast the dihalide obtained from the benzylic acid bromination, in our hands, was difficult to purify, resulting in a considerable loss of product.

To obtain diphenylketene from the dibromide **1**, the solutions of acyl halide and triphenylphosphine were mixed. A mildly exothermic reaction occurred which was accompanied by the formation of a precipitate and an intense yellow color. The precipitate when removed under nitrogen was found to fume in moist air. Complete hydrolysis of the solids produced triphenylphosphine oxide.

The reaction of triethylphosphite with chloroacetyl chloride is presumed to be initiated at the carbonyl carbon.[7] A similar reaction path for triphenylphosphine does not seem likely at first. The recent report of reaction between triphenylphosphine and chloroacetyl chloride indicates that at least some reaction is initiated at the α halogen.[8] When α-bromoisobutyryl bromide was added to a triphenylphosphine solution, the formation of a precipitate was very slow, and no evidence for dimethylketene was obtained. This suggests that stabilization of the displaced enolate anion is necessary. The fact that acyl halides do not appear to form phosphonium salts readily with triphenylphosphine might also be taken as evidence for a halogen displacement reaction. However, it is still possible that the type of reaction observed here occurs only when acyl phosphonium salts are formed first. While acetyl chloride or the bromide are unreactive, the presence of electron-withdrawing groups on the α carbon have been shown to enhance markedly the reactivity of acyl halides toward water and amines.[9] Trichloroacetyl chloride will react with 1 equiv of triphenylphosphine to give an ether insoluble solid. Methanolysis of this solid gave methyltrichloro acetate, thus indicating that an acyl phosphonium salt has been formed.

As would be expected for nucleophilic attack on the α halogen or the reaction of a less reactive acyl halide, α-chlorodiphenylacetyl chloride undergoes dehalogenation at a much slower rate than the dibromo compound.

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(1) Acknowledgment is made to the Petroleum Research Fund administered by the American Chemical Society, for partial support of this research.

(2) (a) Taken from a dissertation submitted by R. L. Kidwell to the University of Southern California in partial fulfillment of the requirements for the Ph.D. degree. (b) Du Pont Teaching Fellow, 1963–1964; Stauffer Fellow, 1964–1965; National Science Foundation Summer Fellowship, 1965; Petroleum Research Fund Fellow, 1965–1966.

(3) For recent reviews, see (a) H. Hoffman and H. S. Diehr, *Angew. Chem. Intern. Ed. Engl.*, **3**, 737 (1964); (b) B. Miller in "Topics in Phosporus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., John Wiley & Sons, Inc., New York, N. Y., 1965, pp 133–195.

(4) W. E. Hanford and John C. Sauer, *Org. Reactions*, **3**, 120 (1946).

(5) H. Staudinger, *Ann.*, **356**, 121 (1907).

(6) H. K. Kinger and G. Nickell, *ibid.*, **390**, 365, 371 (1912).

(7) Reference 3b, p 179.

(8) P. A. Chapared, *J. Org. Chem.*, **31**, 107 (1916).

(9) J. Ugi and F. Beck, *Ber.*, **94**, 1839 (1961).