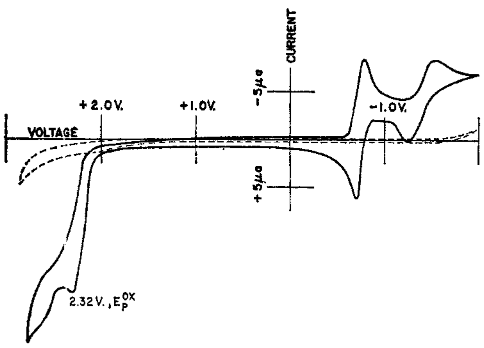

Figure 1.—Cyclic polarogram of 12.5 mM DEQ in acetonitrile with 0.1 M tetrabutylammonium perchlorate (scan rate 40 mV/sec). The dashed line is the residual current.

an acid. Electrode coating problems prevented meaningful study of the oxidation of BAQ at its first wave. Quantitative oxidation at the second wave required 4.0 electrons/molecule and also produced an acid among the products. The electrochemical oxidation of aromatic amines[12] and aliphatic amides[13] in aprotic solvents produces strong acid *via* initial cation–radical formation followed by coupling with elimination of a proton or proton abstraction from the solvent.

Experimental Section

DEQ[14] and BAQ[15] were prepared as described in the literature and purified by column chromatography and vacuum sublimation. The long wavelength absorption maxima of DEQ and BAQ in methylene chloride appeared at 372 mμ (ϵ 3.13 × 10^2) and 478 mμ (ϵ 2.44 × 10^2), respectively. DDQ and benzidine were sublimed. The preparation and purification of the other materials have been described.[2,9]

The quinone–quinone complexes were obtained by concentration and cooling of equimolar mixtures of DDQ with either DEQ or BAQ in methylene chloride causing the solid complexes to precipitate. The DEQ complex was obtained as brilliant orange plates, mp 193–194°.

Anal. Calcd for $C_{26}H_{12}N_4Cl_4O_8$ (2:1 DDQ–DEQ): C, 48.0; H, 1.9; N, 8.6. Found: C, 47.8; H, 1.9; N, 8.5.

The BAQ complex was a black crystalline solid which turned brick red abruptly and irreversibly at 123° and melted with decomposition at about 200°.

Anal. Calcd for $C_{24}H_{20}N_6N_6Cl_2O_6$ (2:1 BAQ–DDQ): C, 51.5; H, 3.6; N, 15.0. Found: C, 51.6; H, 3.7; N, 15.0.

The procedures used for the spectroscopic study of CT complexes and treatment of the data have been described.[2] A special technique was required to observe the DMT–DDQ complex because it had a half-life of only a few seconds. Briefly, the CT absorption band which had a maximum at 900 ± 20 mμ was reconstructed from data obtained at several wavelengths. A hypodermic syringe was used to rapidly add a DMT solution to the DDQ solution in an absorption cell in the spectrophotometer. The spectrophotometer recorded the rapid increase and decay of the absorbance at a fixed wavelength as a function of time.

Polarographic measurements were made on deoxygenated solutions containing 1–15 mM quinone together with 0.1–0.5 M tetrabutylammonium perchlorate in methylene chloride or acetonitrile. Polarograms were obtained at both dropping mercury and stationary platinum electrodes *vs.* an aqueous sce. Three-electrode electronics was employed. Quantitative reductions were done at a mercury pool; the oxidations were done at a rotating platinum mesh anode. The i/t curves were recorded and intergrated with a planimeter. The semiquinone anion-radicals generated for epr spectra were the final products from quantitative reductions of the quinones at their first waves. Aliquots were transferred under nitrogen to a flat quartz cell and spectra were recorded with equipment described earlier.[16] In the case of diethoxysemiquinone anion the epr spectrum at $g = 2.0050$ was analyzed in terms of two-proton hfsc; $a_H = 0.89 \pm 0.01$ G for the methylene protons of the ethoxy groups and 0.76 ± 0.01 G for the ring protons. The spectrum of the bis-N-methylaminosemiquinone at $g = 2.0042$ contained 91 resolved lines and was fitted with a septet, $a_H = 2.27 \pm 0.04$ G, due to splitting by the protons of the methyl groups; a pentet, $a_N = 2.03 \pm 0.06$ G arising from the nitrogen nuclei; and two sets of unassigned triplets, $a_H = 1.36 \pm 0.04$ G and 0.91 ± 0.04 G due to the amino and ring protons. The solids were examined in evacuated quartz tubes. A Varian temperature control unit was emoypled.

Registry No.—DEQ complex, 17299-14-8; BAQ complex, 17299-15-9.

Acknowledgment.—Thanks are due Dr. Byron Gorres who did the X-ray work and to Dr. Paul Toren and Professors Stanley Bruckenstein and James Bolton for helpful discussions.

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Chromyl Chloride Oxidations. I. Preparation of Carbonyl Compounds from Alkenes

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Recently several reports have described the preparation of aldehydes and ketones from alkenes.[2] We wish to report a simple, convenient, and one-step, high yield synthesis of aliphatic carbonyl compounds *via* the chromyl chloride oxidation of readily accessible alkenes. The formation of aldehydes and ketones in good yields is unique since the chromyl chloride oxidation of alkenes has been reported to give a mixture of products in low yields.[3-5] This procedure differs from previous methods primarily in the reductive hydrolysis step. In some of the past reports,[3,5] the alkene–chromyl chloride adduct was isolated and reductive hydrolysis was carried out on the adduct, while in other reports,[4,6] the entire reaction mixture was subjected to reductive hydrolysis with sulfur dioxide. We have found that zinc dust is a more effective reducing agent than sulfur dioxide.[7-11] Also, it appears that sul-

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(1) Petroleum Research Fund Scholar, 1967–1968.

(2) (a) H. Hart and L. R. Lerner, *J. Org. Chem.*, **32**, 2669 (1967). (b) H. C. Brown and M. W. Ratkke, *J. Amer. Chem. Soc.*, **89**, 2738, 4528 (1967). (c) H. C. Brown, M. W. Ratkke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967).

(3) R. A. Stairs, D. G. M. Diaper, and A. L. Gatzke, *Can. J. Chem.*, **41**, 1059 (1963).

(4) S. J. Cristol and K. R. Eilar, *J. Amer. Chem. Soc.*, **72**, 4353 (1950).

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(6) I. Necesoui, A. T. Balaban, I. Pascaru, E. Sliam, M. Elizan, and C. D. Nenitzescu, *Tetrahedron*, **19**, 1133 (1963).

(7) During hydrolysis, chromium(IV), -(V), and -(VI) are produced. It appears that zinc dust is more effective than sulfur dioxide in reducing the chromium species to chromium(III), since it is known that chromium(VI) cleaves alkenes to carbonyl compounds[8,9] and that chromium(IV) and -(V) are more powerful oxidizing agents than chromium(VI).[10,11]

(8) J. H. Garvin, *J. Chem. Soc.*, 678 (1959).

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TABLE I

CHROMYL CHLORIDE OXIDATION OF ALKENES

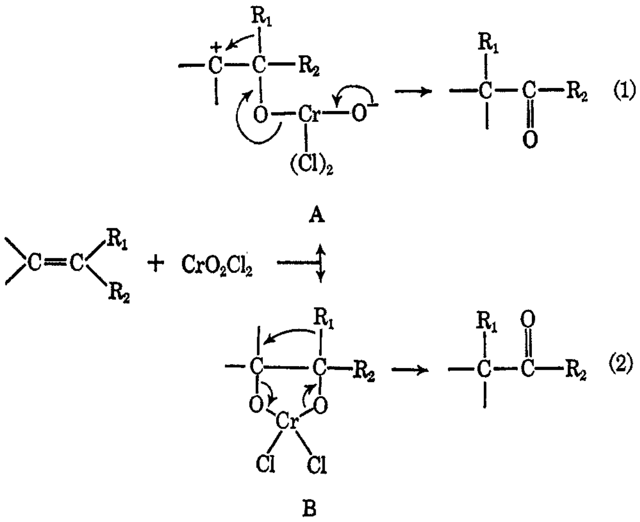
Alkene	Method	Cleavage product	Yield, %	Rearranged product	Yield, %	Lit. yield, %
2,3,3-Trimethyl-1-butene	A	Pinacolone	10.8	2,3,3-Trimethylbutanal	28.7	24[b]
	B		<1.0		34.9	
2,4,4-Trimethyl-1-pentene	A	3,3-Dimethyl-2-2-pentanone	4.8	2,4,4-Trimethylpentanal	38.3	
	C		0		75.8	
4,4-Dimethyl-2-neopentyl-1-pentene	A	Dineopentyl ketone[a]	<1 trace	4,4-Dimethyl-2-neopentylpentanal	54.8	25[c]
	C				80.8	
2,3-Dimethyl-2-butene	A	Acetone	6.2	Pinacolone	50	

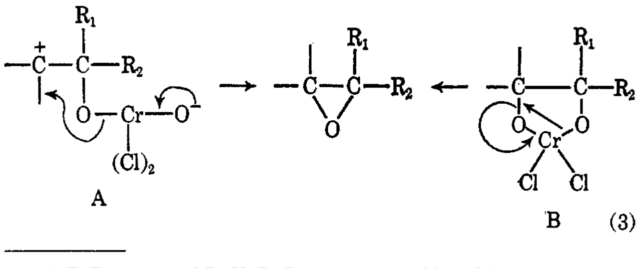
[a] Not obtained in sufficient amount for characterization. [b] See ref 15. [c] P. D. Bartlett, G. L. Frazer, and R. B. Woodward, *J. Amer. Chem. Soc.*, **63**, 495 (1941); W. J. Hickinbottom and D. G. M. Wood, *J. Chem. Soc.*, 1600 (1951).

fur dioxide catalyzes the polymerization of aliphatic aldehydes.[12]

Table I shows the yields and the improvement of this procedure over previous multistep methods which generally involved intermediate preparation of a glycol or an epoxide.[13,14] For example, 2,3,3-trimethylbutanal has been previously prepared in only 24% yield *via* a five-step reaction sequence.[15] Also, it can be seen from Table I that reductive hydrolysis with zinc dust gives better yields (method C) and less cleavage products than the sulfur dioxide procedure (method A).[3,6,7]

The reaction presumably involves an electrophilic attack of chromyl chloride at the double bond *via* eq 1 or 2 to give the intermediate A or B. Either A or B could rearrange to give the carbonyl product. Alternatively, A or B can rearrange to an epoxide intermediate which subsequently rearranges to the carbonyl product.





In order to test the possibility of an epoxide intermediate, 2,4,4-trimethyl-1,2-epoxypentane[16] was prepared and subjected to the reaction along with the olefin. The result is inconclusive since the epoxide is unstable to the hydrolytic conditions and rearranges to the corresponding aldehyde. Methyl migration in 2,3-dimethyl-2-butene could proceed *via* intermediate A or the pinacol-type intermediate B. The scope, kinetics, and mechanisms of these oxidations are under investigation.

Experimental Section

All melting points are uncorrected and were determined on a Thomas-Hoover apparatus. Ir spectra were taken on a Baird-Atomic spectrophotometer. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Starting Materials.—The alkenes were obtained commercially: 2,4,4-trimethyl-1-pentene, 2,3,3-trimethyl-1-butene, 4,4-dimethyl-2-neopentyl-1-pentene (Aldrich), and 2,3-dimethyl-2-butene (Chemicals Procurement Laboratories, Inc.).

Method A.—Freshly distilled chromyl chloride (Alfa), 0.52 mol (82.1 g), dissolved in 400 ml of methylene chloride (Matheson) was added dropwise to a stirred solution of 0.5 mol of freshly distilled alkene in 1000 ml of methylene chloride at 0–5°. The reaction mixture was allowed to stand in the cooling bath for 1 hr and then decomposed by addition of a solution of 30.0 g (0.16 mol) of sodium metabisulfite (Baker) in 400 ml of water and 200 g of ice and 0.32 mol of concentrated hydrochloric acid. After standing 1 hr, the aqueous layer was separated and washed three times with 50-ml portions of methylene chloride. The combined organic solution was dried ($MgSO_4$) and filtered, and the solvent was removed through a 58-cm vacuum-jacketed Vigreux column while maintaining the pot vapors below 44°. The product was analyzed *via* vpc on a 10-ft 20% Carbowax 4000 on Chromosorb W column with an internal standard.

Method B.—The oxidation was carried out as described above except twice the concentration of reactants was used; the complex was stirred for 15 min, treated with 92 g (1.25 mol) of 90% zinc dust (Allied), and stirred an additional 5 min. A mixture of 500 ml of water and 200 g of ice was added with vigorous stirring. The mixture was stirred for 15 min and then steam distilled. The aqueous layer in the distillate was separated and washed three times with 50-ml portions of methylene chloride. The solvent was removed from the combined organic solution described above, and the product was analyzed *via* vpc.

Method C.—Same as method B except the product was isolated by fractional distillation under vacuum.

2,3,3-Trimethylbutanal[17] had bp 45–47° (30 mm) [lit.[15] bp 66–68° (69 mm)]; 2,4-DNP, mp 132–133° (lit.[15] mp 126–127°). *Anal.* Calcd for $C_{13}H_{18}N_4O_4$: C, 52.52; H, 6.10; N, 18.85. Found: C, 52.64; H, 6.09; N, 18.93.

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[12] F. Freeman and R. H. DuBois, 1967, unpublished data.

[13] W. J. Hickinbottom and M. B. Green, *J. Chem. Soc.*, 3262 (1957).

[14] A. Byers and W. J. Hickinbottom, *ibid.*, 1328 (1948).

[15] W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964).

[16] A. Byers and W. J. Hickenbottom, *J. Chem. Soc.*, 1328 (1948).

[17] Although 2,3,3-trimethylbutanal, which possesses a strong camphoraceous odor, has been reported[15] as a liquid, it solidified in the distillation apparatus during distillation and liquified during attempted purification. Since aldehydes are notoriously unstable and are difficult to obtain in the pure state,[2c] this aldehyde was characterized *via* the 2,4-dinitrophenylhydrazone.

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); $n^{20}D$ 1.4131 [lit.[18] bp 39° (9 mm), $n^{20}D$ 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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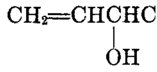
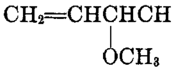
Earlier work by one of us showed that abstractions of benzylic hydrogens from substituted toluenes by trichloromethyl radicals are influenced by a polar effect.[3] A similar polar effect was postulated to explain the difference in reactivities of primary, secondary and tertiary allylic hydrogens toward 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]

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

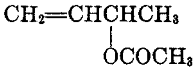
The present work is concerned with the abstractions of allylic hydrogens from carbon atoms bonded to an oxygen function. The compounds used in this study were 1-buten-3-ol (I), 1-buten-3-yl methyl ether (II), and 1-buten-3-yl acetate (III). Each of these compounds has a terminal double bond and a single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


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

I

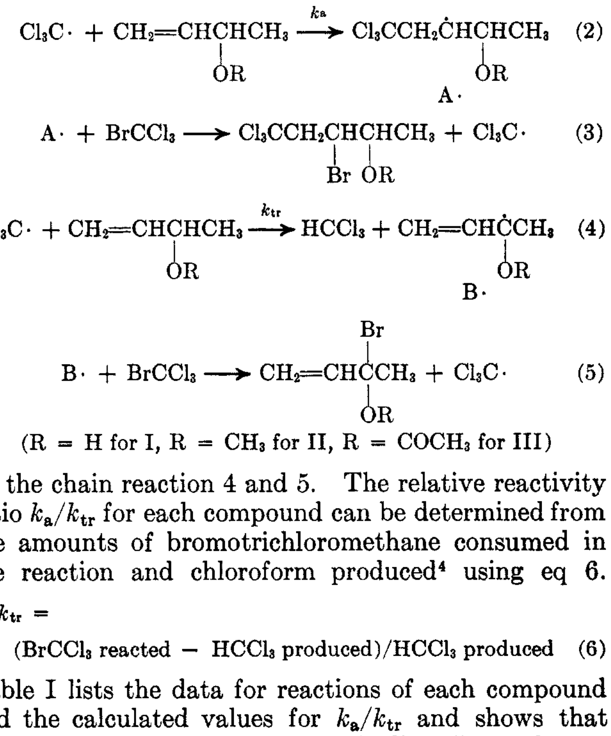

$CH_2{=}CH\underset{OCH_3}{\underset{|}{C}}HCH_3$

II


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

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] by the chain reaction 4 and 5.


$$Cl_3C\cdot + CH_2{=}CH\underset{OR}{\underset{|}{C}}HCH_3 \xrightarrow{k_a} Cl_3CCH_2\dot{C}H\underset{OR}{\underset{|}{C}}HCH_3 \qquad (2)$$
$$\text{A}\cdot$$
$$\text{A}\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2\underset{Br}{\underset{|}{C}}H\underset{OR}{\underset{|}{C}}HCH_3 + Cl_3C\cdot \qquad (3)$$
$$Cl_3C\cdot + CH_2{=}CH\underset{OR}{\underset{|}{C}}HCH_3 \xrightarrow{k_{tr}} HCCl_3 + CH_2{=}CH\underset{OR}{\underset{|}{\dot{C}}}CH_3 \qquad (4)$$
$$\text{B}\cdot$$
$$\text{B}\cdot + BrCCl_3 \longrightarrow CH_2{=}CH\overset{Br}{\overset{|}{\underset{OR}{\underset{|}{C}}}}CH_3 + Cl_3C\cdot \qquad (5)$$

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

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.

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

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.