Reactions of Organic Peroxides with Chromium(II). Reduction of Free Radicals by Metal Ions[1]
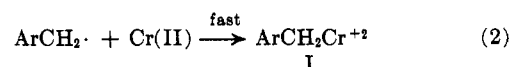
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Tertiary alkyl hydroperoxides are reduced instantaneously by 2 equiv. of chromium(II) salts in aqueous solution to a mixture of alcohols, ketones, and alkanes; the latter are formed in equimolar amounts. The relative yields of tertiary alcohol and ketone (or alkane) vary with the structure of the alkyl hydroperoxide and slightly on the mode of addition. The yields of alcohol are highest with *t*-butyl, nil with α,α-dimethyl-β-phenethyl, and intermediate with *t*-amyl hydroperoxides. Tertiary alkoxy radicals are postulated as direct intermediates which are formed by the one-electron transfer between chromium(II) and the hydroperoxide. Alkyl radicals formed simultaneously with ketone by the fragmentation of *t*-alkoxy radical are subsequently reduced by chromium(II) to alkane. Little or no products of dimerization of these radicals is evident. Aliphatic diacyl peroxides are also readily reduced (but more slowly than alkyl hydroperoxides) by 2 equiv. of chromium(II) to alkane, carbon dioxide, and carboxylatochromium(III) salts. The effect of solvent, solvent composition, buffer, and pH are examined, and the reaction can be made stoichiometric. The mechanism of these reductions by chromium(II) and other metal ions is described in terms of a transition state involving ligand transfer. The formation of organochromium(II) complexes, RCr^{+2}, between free radicals and Cr(II), similar to the isolable benzylchromium ion, and their role as intermediates in the reduction by chromium(II) of free radicals from peroxides as well as alkyl halides is discussed. Reductive elimination of 1,2-dihalides and halo esters to alkenes and 1,3-dihalides to cyclopropanes can be considered as an intramolecular ligand transfer from such a complex.

Chromium(II) salts are effective reducing agents for a multitude of organic compounds, including halides,[2] alkynes,[3] nitriles,[4] unsaturated compounds,[5] epoxides,[6] aldehydes,[7] and esters.[8] The reduction generally involves addition to or replacement of the functional group with hydrogen, although coupling and elimination products are not uncommon. The high reduction potential (0.41 v.) of chromium(II) makes it the last readily available species which can be employed in aqueous solutions. Heterogeneous reactions with chromous chloride have also been described.

Aralkyl halides, like benzyl chloride, react with chromium(II) to yield a mixture of toluene (simple reduction) and bibenzyl (coupling).[9] Benzylchromium ion I, $C_6H_5CH_2Cr^{+2}$, has been described and isolated as an intermediate. A mechanism has been presented for its formation,[10] and its mode of decomposition[11] to toluene and bibenzyl. The formation of I occurs by a two-step mechanism involving successive one-electron changes[12] as given in eq. 1 and 2, the first step being rate determining.[13]

$$ArCH_2\text{—}Cl + Cr(II) \longrightarrow ArCH_2\cdot + Cr(III)Cl^{+2} \quad (1)$$

$$ArCH_2\cdot + Cr(II) \xrightarrow{\text{fast}} ArCH_2Cr^{+2} \quad (2)$$
$$I$$

The kinetics of the protonolysis of benzylchromium ion to toluene have been investigated under a variety of conditions. The mechanism of the acid-catalyzed reaction has been formulated as follows.[11]

$$C_6H_5CH_2Cr^{+2} + X^- \rightleftarrows C_6H_5CH_2CrX^+ \quad (3)$$

$$C_6H_5CH_2CrX^+ + H^+ \longrightarrow C_6H_5CH_3 + CrX^{+2} \quad (4)$$
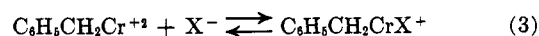
Organometallic complexes analogous to I have not yet been detected with other simple alkyl moieties. However, species formulated as such can be readily incorporated (*vide infra*) into a consistent mechanism for the reduction and elimination reactions of alkyl halides and polyhalides by chromium(II). The absence, by and large, of dimeric products from simple alkyl halides[14] can be attributed to the rapid reduction (eq. 5) of alkyl radicals by chromium(II) (*vide infra*).

$$R\cdot + Cr(II)_{solv} \longrightarrow R\text{—}H + Cr(III)_{solv} \quad (5)$$
$$solv = \text{protic solvent}$$
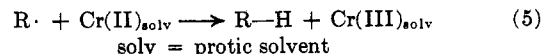
Peroxides are reliable sources[15] of free radicals. The reaction of peroxides with chromium(II) was investigated in order to delineate further the interaction of free radicals with reducing metal ions. In addition, the chromium system is of particular interest since chromium(III) complexes, unlike many other inorganic systems, are stable to substitution reactions.[16] This inertness of chromium(III) compounds is a valuable tool[17] for tracing the course of oxidation–reduction reactions.

(1) Part III. Reductions with Chromium(II).

(2) (a) P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *J. Am. Chem. Soc.*, **67**, 1728 (1945); (b) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *ibid.*, **72**, 4077 (1950); (c) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959); (d) J. F. Neumer and S. Aktipis, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 98; (e) L. H. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964); (f) C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2769 (1963).

(3) M. Berthelot, *Ann. chim.*, **49**, 401 (1866); W. Traube and W. Passarge, *Ber.*, **49**, 1692 (1916).

(4) R. Graf, *J. prakt. Chem.*, **140**, 34 (1934); **146**, 90 (1936).

(5) J. B. Conant and H. B. Cutter, *J. Am. Chem. Soc.*, **48**, 1023 (1926).

(6) W. Cole and P. L. Julian, *J. Org. Chem.*, **19**, 131 (1954); C. W. L. Bevan, T. Halsall, M. N. Nwaji, and D. A. H. Taylor, *J. Chem. Soc.*, 768 (1962); O. Jeger, *et al.*, *Experientia*, **16**, 41 (1960).

(7) K. O. Kopple, *J. Am. Chem. Soc.*, **84**, 1586 (1962).

(8) P. L. Julian, W. Cole, E. W. Meyer, and B. M. Regan, *ibid.*, **77**, 4601 (1955); D. H. R. Barton and J. T. Pinhey, *Proc. Chem. Soc.*, 279 (1960); 280 (1962); G. Büchi and H. J. E. Loewenthal, *ibid.*, 280 (1962).

(9) F. A. L. Anet and E. LeBlanc, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

(10) J. K. Kochi and D. D. Davis, *ibid.*, **86**, 5264 (1964).

(11) J. K. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965).

(12) The terms one-electron and two-electron change refer to the change in the formal oxidation state of the metal ion. Nothing is implied here of the mechanism of the transformation.

(13) In the subsequent discussion, solvation of the chromium and other metal ions by water and alcohol [J. Baltisberger and E. L. King, *J. Am. Chem. Soc.*, **86**, 795, 3989 (1964)] is implied; though not explicitly written, a coordination number of six is indicated.

(14) Biallyl under certain conditions can be obtained from allyl bromide.[2e]

(15) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Inc., New York, N. Y., 1961; A. G. Davies, "Organic Peroxides," Butterworths and Co. (Publishers) Ltd., London, 1961.

(16) H. Taube, *Chem. Rev.*, **50**, 72 (1952); *J. Am. Chem. Soc.*, **75**, 1463 (1953).

(17) H. Taube, "Advances in Inorganic and Nuclear Chemistry," Vol. 1, Academic Press Inc., New York, N. Y., 1959, p. 1.

Results and Discussion

t-Alkyl Hydroperoxides and Chromium(II).—Alkyl hydroperoxides are rapidly reduced in aqueous solutions by chromium(II) salts. *t*-Butyl hydroperoxide is reduced principally to *t*-butyl alcohol with smaller amounts of acetone, methane, and ethane (trace) occurring as side products. At room temperature the reaction is instantaneous, and the peroxide can be titrated in the absence of air with chromous perchlorate potentiometrically. The stoichiometry observed is somewhat dependent on the order of addition of reagents. When *t*-butyl hydroperoxide is added to a solution of chromous perchlorate, *t*-butyl alcohol is formed in 93% yield accompanied by acetone (6%) and methane (7%). A trace of ethane is also detected. If a reverse procedure is followed, and chromous perchlorate is added to *t*-butyl hydroperoxide in solution, the rela-

$$(CH_3)_3CO_2H + 2Cr(II) + H_2O \longrightarrow$$
$$(CH_3)_3COH + 2OH^- + 2Cr(III) \quad (6)$$
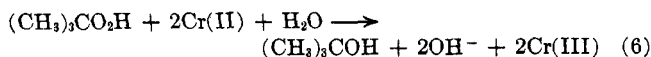
tive amount of acetone (18%) is increased at the expense of *t*-butyl alcohol (80%). The amount of ethane ($\sim$0.3%) also increases with methane (18%) yields. The relative amounts of *t*-butyl alcohol and acetone are also dependent to a degree on the concentrations and rate of addition, but at low temperatures these are less critical factors and the stoichiometry given in eq. 6 is faithfully followed. Substantially the same results are obtained with chromous sulfate and chloride in aqueous solutions. With the latter reagent, if it is prepared from chromic chloride and titanous chloride, a small but significant amount of methyl chloride ($\sim$0.3%) is found.

t-Amyl hydroperoxide reacts with chromium(II) in aqueous ethanol solutions with a similarly rapid rate. However, the amount of *t*-amyl alcohol (50–60%) is diminished relative to *t*-butyl alcohol from the lower homolog and a correspondingly higher yield of acetone (40–50%) is found. The ethyl moiety is found mainly as ethane (40–50%) with minor amounts of *n*-butane ($\sim$3%).

Acetone and methane or ethane, as principal side products from *t*-butyl or *t*-amyl hydroperoxide, are formed from a common intermediate. It is most likely a *t*-alkoxy radical (*t*-butoxy or *t*-amyloxy), which

$$R(CH_3)_2CO\cdot \longrightarrow R\cdot + CH_3\overset{\overset{\textstyle O}{\|}}{C}-CH_3 \quad (7)$$
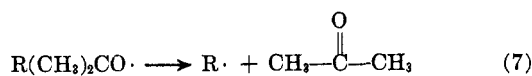
is known to fragment unimolecularly to acetone and an alkyl (methyl or ethyl, respectively) radical.[18] The *t*-butoxy radical from *t*-butyl hydroperoxide and chromous chloride in aqueous ethanol solutions at 0° can be trapped with butadiene as a mixture of butenyl *t*-butyl ethers. The increase in yield of cleavage products, acetone and alkane, from alkyl hydroperoxide and chromous salt by inverse addition of reagents is consistent with this postulate. Moreover, it is known that the fragmentation of the *t*-amyloxy radical is faster than the *t*-butoxy radical. The absolute rate constant of the latter in the gas phase at 51° is estimated to be 10⁴

sec.$^{-1}$,[19] and the best value for the activation energy is 12 kcal./mole.[19,20] There is no information regarding the fragmentation of the *t*-amyloxy radical in the gas phase. On the basis of enthalpy change,[18] it can be estimated[21] as 4–5 kcal./mole. The pre-exponential term for both should be approximately the same, and the relative rates of cleavage of *t*-butoxy and *t*-amyloxy radicals are ascribable mainly to the difference in activation energy. This large difference in rates of cleavage is considerably modified in solution owing to solvation,[22] but the large predominance of the *t*-amyloxy cleavage is undoubtedly maintained.

α,α-Dimethyl-β-phenethyl hydroperoxide reacts instantaneously at 0° with chromium(II) to afford acetone in quantitative yield. The weak benzyl bond in the radical intermediate, α,α-dimethylphenethoxy radical, has been shown to cleave rapidly, although no assistance was evident in the thermolysis[23,24] of the hydroperoxide.

The tertiary alcohols are formed from the hydroperoxide by further one-electron reduction of *t*-alkoxy radicals with chromium(II), followed by neutraliza-

$$R(CH_3)_2CO\cdot + Cr(II) \longrightarrow R(CH_3)_2COCr(III) \quad (8)$$
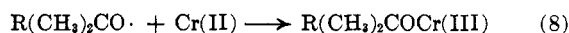
tion. The high yields of *t*-butyl butenyl ethers obtainable under appropriate conditions is evidence against a two-electron reduction (*vide infra*) of the hydroperoxide by chromium(II). The yields of acetone obtainable from the hydroperoxides, compared to tertiary alcohols (together they comprise the major material balance), fall in the order, dimethylphenethyl $\gg$ *t*-amyl $>$ *t*-butyl, which is also the order of increasing stability of the *t*-alkoxy radical. The alkyl moiety would not be expected to influence the two-electron reduction of the hydroperoxide so markedly.[25]

α,α-Dimethylphenethyl hydroperoxide also yields acetone quantitatively when it is reduced by iron(II). The yields of acetone from *t*-butyl hydroperoxide (45–55%) and *t*-amyl hydroperoxide (80–90%) are significantly higher when ferrous is compared to chromous salt. These differences reflect the abilities of the metal ions to reduce *t*-alkoxy radicals.[26] A similar difference is apparent in the composition of the alkane fraction when ferrous[27] and chromous are employed as reductants.

Other simple metal ions, when employed as reducing agents, yield different amounts of acetone and *t*-butyl alcohol from *t*-butyl hydroperoxide (Table I).[27] In some of the cases investigated, high yields of *t*-butyl butenyl ethers[28] can be obtained, using butadiene as a radical trap.

The formation of *t*-alkoxy radicals from *t*-alkyl hydroperoxides and these reducing metal ions can be formu-

(18) P. Gray, *Trans. Faraday Soc.*, **55**, 760 (1956); P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); R. Brinton and D. Volman, *J. Chem. Phys.*, **20**, 25 (1952); A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956).

(19) G. R. McMillan, *ibid.*, **82**, 2422 (1960).

(20) D. H. Volman and W. M. Graven, *ibid.*, **75**, 3111 (1953).

(21) Private communication, Dr. G. R. McMillan.

(22) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

(23) R. Hiatt and W. M. J. Strachan, *J. Org. Chem.*, **28**, 1893 (1963).

(24) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(25) The possibility of two concurrent one-electron and two-electron processes is not favored, though it cannot be entirely discounted.

(26) M. S. Kharasch, A. Fono, W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950); **17**, 207 (1952).

(27) J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(28) M. S. Kharasch, F. S. Arimoto, and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951); J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 2785 (1962).

TABLE I

PRODUCTS FROM *t*-BUTYL HYDROPEROXIDE AND REDUCING
AGENTS AT 25°[a]

Reducing agent	*t*-Butyl alcohol, %	Acetone, %
TiCl₃	37	63
FeSO₄	52–45	48–55
CrCl₂	81	19
Cr(ClO₄)₂	84	16
VSO₄	~50	50
V₂(SO₄)₃	42	58
VO(SO₄)	70	30
K₄Fe(CN)₆	90–95	10–5
Na₂S₄O₆	95	5

[a] See ref. 27.

lated as in eq. 9.[29] There is abundant evidence for such a step with the ferrous systems,[26,28,30] and it has been discussed with respect to copper(I).[31] From these

$$RO_2H + M^{+n} \longrightarrow RO\cdot + M(OH)^{+n} \qquad (9)$$
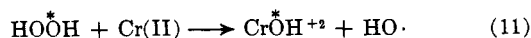$$M^{+n} = Fe(II), Cu(I), Cr(II), etc.$$
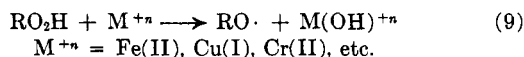
results it also appears to be applicable to chromium(II). The chromium(III) species obtainable by such a transformation would contain in its hydration sphere an oxygen derived from the hydroperoxide, and unlike iron(II) and copper(II) it would be stable toward exchange.[32a]

$$(CH_3)_3CO\overset{*}{O}H + Cr(II) \longrightarrow (CH_3)_3CO H + Cr\overset{*}{O}H^{+2} \qquad (10)$$
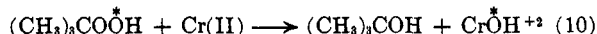
The reaction of *t*-alkyl hydroperoxides with chromium(II) is analogous to the facile reduction of hydrogen peroxide. Cahill and Taube[32b] examined the fractionation factors of oxygen isotopes in the reduction of hydrogen peroxide by chromium(II), iron(II), copper(I), and titanium(III). They concluded that hydrogen peroxide reacts with Cr(II), Fe(II), and Cu(I) by a two-electron change to generate the unstable Cr(IV), Fe(IV), and Cu(III) species. The slight isotope fractionation obtained with titanium(III) was interpreted as involving a one-electron process. The reaction of hydrogen peroxide with Cr(II) is admittedly complex, since a series of monomeric and dimeric chromium complexes have been identified. The chromium(IV) species postulated by Cahill and Taube[32b] is labile to substitution[33] and was presumed to react further with Cr(II) to form the observed products, chromium(III) compounds.

However, Anderson and Plane[34] have recently demonstrated by oxygen tracer studies that one oxygen atom in the water bound to chromium(III) is derived from the hydrogen peroxide. They favor an initial one-electron reduction similar to reaction 8, in which a hydroxy radical is an intermediate (9). However appeal-

$$HO\overset{*}{O}H + Cr(II) \longrightarrow Cr\overset{*}{O}H^{+2} + HO\cdot \qquad (11)$$

ing, the extrapolation of this mechanism to alkyl hydroperoxides is not completely tenable at the present time.

We propose that methane from *t*-butyl hydroperoxide and ethane from *t*-amyl hydroperoxide and chromium(II) arise by reduction of methyl and ethyl radicals, respectively. The reaction conducted in deuterium oxide–isopropyl alcohol-*d* solutions yielded a mixture of methane that was largely (>90%) monodeuterated. Under these conditions there is no exchange between the acidic hydrogens and those bonded to carbon atoms in isopropyl alcohol. Alkanes are formed in yields equal to acetone and are derived from alkyl radicals which accompany the fragmentation (eq. 8) of *t*-alkoxy radicals. The reduction can be formulated as proceeding *via* an alkyl chromium complex II similar to that observed with benzyl radicals.[10,11] This reac-

$$CH_3\cdot + Cr^{+2} \longrightarrow [CH_3Cr]^{+2} \qquad (12)$$
$$\qquad\qquad\qquad\qquad II$$

$$II + H_2O \longrightarrow CH_4 + Cr(OH)^{+2} \qquad (13)$$

tive complex[35] is undoubtedly readily solvolyzed by water and other weak acids.

The number of equivalents of chromium(II) required to reduce *t*-butyl hydroperoxide to *t*-butyl alcohol or acetone and alkane is the same (*viz.*, two). The stoichiometry of these reactions yielding both types of products can be typically represented as in eq. 14.

$$10(CH_3)_3CO_2H + 20Cr(II) \longrightarrow 8.35(CH_3)_3COH +$$
$$1.65(CH_3)_2CO + 1.61CH_4 \qquad (14)$$
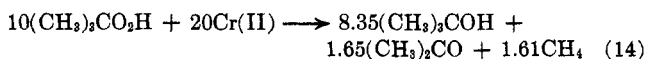
The formation of alkyl radicals as intermediates is shown by the quantitative conversion of α,α-dimethyl-β-phenethyl hydroperoxide to benzylchromium ion I by chromous perchlorate in aqueous ethanol solutions.

$$C_6H_5CH_2(CH_3)_2CO_2H + 2Cr(II) \longrightarrow$$
$$C_6H_5CH_2Cr^{+2} + CH_3COCH_3 + Cr(III) \qquad (15)$$
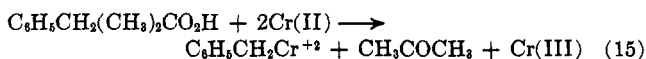
Benzylchromium ion formed in this way is identical with that formed from benzyl halide and chromium(II) or benzyl Grignard reagent with chromic chloride. The mechanism of its formation from benzyl halide (eq. 1 and 2) is quite analogous to its generation from α,α-dimethyl-β-phenethyl hydroperoxide (eq. 2, 7, and 9). With the exception of the benzyl moiety, organochromium complexes of the type RCr^{+2} appear to be unisolable. However, a series of analogous cobaltate complexes including benzyl as well as alkyl ligands have been isolated[36] as salts such as $C_6H_5CH_2Co(CN)_5^{-3}$, $CH_3Co(CN)_5^{-3}$, and $CH_3CH_2Co(CN)_5^{-3}$.

Diacyl Peroxides with Chromium(II).—Diacyl peroxides are reduced by chromium(II) in homogeneous solutions. The reduction proceeds readily at room temperature, although not so fast as the reduction of alkyl hydroperoxides. In ethanol–water solutions the reaction is first order in peroxide and in chromous ion ($k = 2.6$ l./mole sec.). The rate is somewhat dependent on the alcohol concentration, being faster at higher alcohol concentrations. The order of addition of reagents has no effect on the reaction at room temperature. On addition of a sky blue chromous per-

(29) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 95 ff.

(30) J. W. L. Fordham and H. L. Williams, *J. Am. Chem. Soc.*, **72**, 4465 (1950); **73**, 1634 (1951); R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952).

(31) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962); see, however, C. Walling and A. A. Zavitsas, *J. Am. Chem. Soc.*, **85**, 2084 (1963).
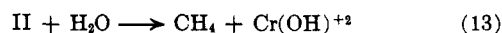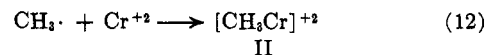
(32) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 687; (b) A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952).

(33) A. E. Ogard and H. Taube, *J. Phys. Chem.*, **62**, 357 (1958).

(34) L. B. Anderson and R. A. Plane, *Inorg. Chem.*, **3**, 1470 (1964).

(35) Alternatively, the reduction may proceed by electron transfer to form a methyl carbanion directly. Unless an alkylchromium ion II has an observable lifetime (as benzylchromium ion) there is no easy way to distinguish between these possibilities.

(36) J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **86**, 2311 (1964).

TABLE II

REDUCTION OF n-VALERYL PEROXIDE WITH CHROMIUM(II)[a]

Solvent, vol. %	Chromium(II) consumed,[b] equiv./mole	Buffer	pH[c]	Butane,[d] %	Carbon dioxide, %
EtOH–H₂O, 90	2.1	None	e	66	...
EtOH–H₂O, 75	2.2	None	e	77	...
EtOH–H₂O, 50	2.0	None	e	82	82
EtOH–H₂O,[f] 25	1.9	None	e	85	86
EtOH–H₂O,[f] 10	...	None	e	91	92
H₂O,[f] 100	2.0	None	e	94	91
EtOH–H₂O, 50	...	Acetate	5.7	100	100
EtOH–H₂O, 50	2.0	Acetate	3.8	100	100
EtOH–H₂O, 50	...	Phosphate	2.0	96	96
EtOH–H₂O, 50	2.1	Acetic acid	2.7	82	82
EtOH–H₂O, 50	...	Ammonia	12.1	34	66
Acetone–H₂O, 50	2.0	None	e	82	82
DMF–H₂O, 50	...	None	e	86	86
DMSO–H₂O, 50	...	None	e	68	68
t-BuOH–H₂O, 50	2.0	None	e	92	92

[a] In 0.06 M valeryl peroxide solutions at room temperature.   [b] Equivalents of Cr(II) consumed per mole of peroxide; theoretical is 2.   [c] Apparent pH measured by pH meter.   [d] Yields of n-butane and carbon dioxide based on 1:1 stoichiometry from peroxide.   [e] Natural pH of Cr(II) solution; no acid or base added, pH ≈ 3.5.   [f] Heterogeneous.

chlorate solution to valeryl peroxide dissolved in ethanol–water, there is an immediate change to green followed by a slower further change to the final dark blue solution. The final color change is coincident with the evolution of gas.[37] The valeryl peroxide can be accounted for as n-butane and carbon dioxide, determined by gas chromatography, and valeratochromium(III).[38] No butene or other C₄ fragment was detected. Two equivalents of chromium(II) were consumed for each mole of peroxide, and in this respect it resembled the reduction of hydroperoxides. The stoichiometry of the reaction is described by reaction 16. The rapid reduc-

$$(C_4H_9CO_2)_2 + 2Cr(II) \longrightarrow$$
$$C_4H_{10} + CO_2 + C_4H_9CO_2Cr(III) + Cr(III) \quad (16)$$

tion in 90% ethanol–water also corresponds to the lowest yields of butane obtainable. Respectable yields of butane are found in more highly aqueous solutions, as shown in Table II. The reaction in water is heterogeneous and proceeds very slowly (∼3 hr.).

Ion exchange of the crude reaction mixture on a Dowex-50 sulfonic acid resin indicated that very little free valerate ion was present. Approximately 60%[38,39] of it was eluted as the valeratochromium(III) ion with 1 M perchloric acid.[38,40] Under the reaction conditions valerate ion does not react with aquochromic ion to form this complex. The remainder of the chromium(III) species was accounted for as the aquochromic ion by elution with 4 M perchloric acid.[40]
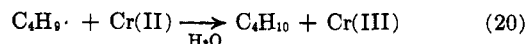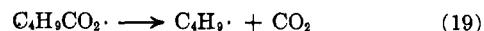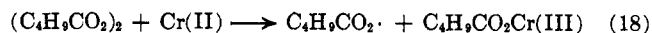
The lower yields of butane and carbon dioxide in 90 vol. % ethanol is associated with a small amount of free valerate ion, and excess valeratochromium(III) which are found generally only in those reactions which occur rapidly and give relatively poor yields of butane.

In the presence of acetate buffer, chromous ion forms an immediate brick red coloration of slightly soluble chromous acetate which reacts with valeryl peroxide slowly to form butane and carbon dioxide in excellent yields. The reaction in the absence of acetate ion
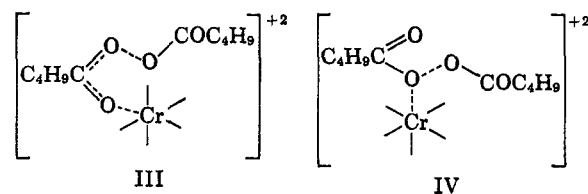
but containing acetic acid does not appear different from those conducted in ethanol–water solutions. No chromous acetate precipitates and its presence in solution is not apparent. Phosphate buffers also form a complex and there is an immediate color change to light green followed by reaction with peroxide. The best yields of butane and carbon dioxide were obtained under these conditions. A part of the lower yields of butane and carbon dioxide in 90% ethanol and other solvents may be due to the reduction of valeroxy radical by chromium(II) in a manner similar to t-alkoxy radicals discussed earlier.[41]

$$C_4H_9CO_2\cdot + Cr(II) \longrightarrow C_4H_9CO_2Cr(III) \quad (17)$$
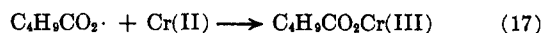
The high yields of alkanes obtained from diacyl peroxides and the stoichiometry and kinetics of the reductions allow us to postulate that diacyl peroxides, like alkyl hydroperoxides, are reduced by chromium(II) in a one-electron process (eq. 18 to 20). This mecha-

$$(C_4H_9CO_2)_2 + Cr(II) \longrightarrow C_4H_9CO_2\cdot + C_4H_9CO_2Cr(III) \quad (18)$$

$$C_4H_9CO_2\cdot \longrightarrow C_4H_9\cdot + CO_2 \quad (19)$$

$$C_4H_9\cdot + Cr(II) \xrightarrow[H_2O]{} C_4H_{10} + Cr(III) \quad (20)$$

nism is analogous to the reduction of hydroperoxides. However, unlike the latter, it is possible to trace the valerate moiety without the use of isotopic oxygen. The formation of valeratochromium(III) in equivalent amounts from valeryl peroxide indicates that it is being transferred directly from the peroxide to chromium in step 18. A transition state for such a ligand transfer step is indicated by III or IV, in which attack by chromium(II) occurs at the carbonyl oxygen or the peroxidic oxygen, respectively. The rapid initial change

III   IV

(37) These changes are being kinetically examined in detail.
(38) H. Taube, J. Am. Chem. Soc., 77, 4482 (1955); E. S. Gould and H. Taube, ibid., 86, 1318 (1964).
(39) D. K. Sebera and H. Taube, ibid., 83, 1785 (1961).
(40) E. L. King and E. B. Dismukes, ibid., 74, 1674 (1952).

(41) The excess valerate may also be formed by a two-electron reduction of the peroxide to give substitution labile Cr(IV) species (vide supra).[25]
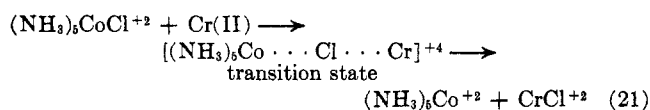
in color on mixing valeryl peroxide with chromium(II) may be due to formation of a metastable charge-transfer complex. A transition state such as IV is also probable with alkyl hydroperoxides which have no carbonyl functions[42] and they are both formally analogius to the bridged activated complex described by Taube and coworkers[17,43,44] for many oxidation–reduction reactions involving inorganic systems. Thus, chloropentamminecobalt(III) is reduced by chromium(II) through such a transition state.[43]

$$(NH_3)_5CoCl^{+2} + Cr(II) \longrightarrow$$
$$[(NH_3)_5Co \cdots Cl \cdots Cr]^{+4} \longrightarrow$$
$$\text{transition state}$$
$$(NH_3)_5Co^{+2} + CrCl^{+2} \quad (21)$$

The improvement in yields of alkanes from diacyl peroxides compared to alkyl hydroperoxides is in large part due to the instability of the aliphatic acyloxy radicals (eq. 14). Very little evidence is available for its existence during the thermolysis of diacyl peroxides[45] and the fragmentation to carbon dioxides and alkyl radicals has been estimated to be exothermic by approximately 13 to 17 kcal./mole.[46] Aside from α,α-dimethylphenethoxy and related radicals, t-alkoxy radicals are not so prone to dissociate.[18]

The stoichiometric reduction of diacyl peroxides by 2 equiv. of chromium(II) is in interesting contrast to the catalytic decomposition of these peroxides by cupric carboxylates[47] and cupric halides.[48] The latter have been shown to be chain reactions in which copper(I) species initially reduce the peroxide to acyloxy radicals and copper(II) carboxylates. The regeneration of copper(I) by subsequent re-reduction of the copper(II) carboxylates by alkyl radicals enables the reaction to be catalytic in copper species. The high reduction potential of chromium(II) prevents the subsequent re-reduction of chromium(III) in the reactions discussed here and no catalytic process is obtained. The initial reduction of diacyl peroxides by copper(I) is undoubtedly related to chromium(II) in the same way that the reduction of alkyl hydroperoxides by these reductants is similar.

Valeryl peroxide typifies the behavior of aliphatic diacyl peroxides in their reaction with chromium(II). The reaction is described by the production of alkane, carbon dioxide, and carboxylatochromium(III) salts. In

$$(R\text{—}CO_2)_2 + 2Cr(II) \longrightarrow R\text{—}H + RCO_2Cr(III) + CO_2$$
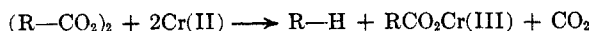
Table III is listed the structural transformation of a series of diacyl peroxides to alkanes. In all cases the yields of alkanes ranged from 70–95% and were matched by an equal amount of carbon dioxide. These transformations are singularly free of side products.

Butene-1 was the sole product obtainable from cyclopropylacetyl peroxide. Even when the chromium(II) solution was added to a solution of peroxide at −60°

(42) It is also possible that hydroperoxides are reduced via an alkylperoxychromium(II) intermediate. Such a reaction should be pH dependent.

(43) H. Taube and H. Myers, J. Am. Chem. Soc., 76, 2103 (1954).

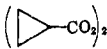(44) J. Halpern, Quart. Rev. (London), 15, 207 (1961); R. T. M. Frazer, Rev. Pure Appl. Chem., 11, 64 (1961).
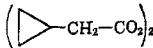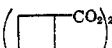
(45) H. J. Shine, J. A. Waters, and D. M. Hoffman, J. Am. Chem. Soc., 85, 3613 (1963).

(46) M. Szwarc in "Peroxide Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 153; see also, M. J. Goldstein, Tetrahedron Letters, 1601 (1964).

(47) J. K. Kochi, J. Am. Chem. Soc., 85, 1958 (1963).

(48) J. K. Kochi and R. V. Subramanian, to be published.

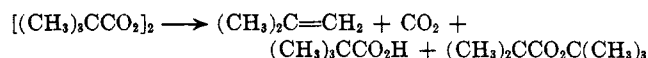## TABLE III
ALKANE FORMATION FROM DIACYL PEROXIDES AND CHROMIUM(II)[a]

Diacyl peroxide (RCO₂)₂	Alkane RH
$(CH_3CH_2CH(CH_3)CO_2)_2$	$CH_3CH_2CH_2CH_3$
$[(CH_3)_2CHCH_2CO_2]_2$	$CH_3CH(CH_3)CH_3$
$[(CH_3)_3CCH_2CO_2]_2$	$(CH_3)_4C$
$[(CH_3)_3CCO_2]_2$	$(CH_3)_3CH + (CH_3)_2C{=}CH_2$

a In 80% ethanol–water containing approximately 0.05 M peroxide.

and allowed to warm slowly, no methylcyclopropane could be found. Cyclopropylmethyl radical[49] and cyclopropylmethyl carbanion[50] are known to isomerize readily to the 3-butenyl moiety. However, its rapid interconversion under the latter conditions was not expected. Cyclobutanecarbonyl peroxide afforded only cyclobutane. No isomerized products (butene-1, methylcyclopropane, butene-2) were found under conditions in which a deficit of chromium(II) was maintained during the reaction. Similarly, butene-1 was the sole product from allylacetyl peroxide and attempts to cyclize it to the cyclobutyl moiety were unsuccessful.

Pivaloyl peroxide could not be prepared pure even at 0° since it undergoes a facile ionic decomposition to form isobutylene and esters among other products.

$$[(CH_3)_3CCO_2]_2 \longrightarrow (CH_3)_2C{=}CH_2 + CO_2 +$$
$$(CH_3)_3CCO_2H + (CH_3)_2CCO_2C(CH_3)_3$$

It is relatively stable in ether–pentane solutions at −10°, but treatment of an ethanolic solution at −10° with chromium(II) yielded a mixture of isobutane and isobutylene. The latter undoubtedly arises from a competitive ionic reaction in protic solvents, and efforts to prevent its formation under various conditions were not successful.

Bisphenylacetyl peroxide, unlike other diacyl peroxides examined, yielded benzylchromium ion as an intermediate. This complex ion was the same as that found earlier from α,α-dimethylphenethyl hydroperoxide or benzyl halide and chromium(II). The unique behavior of the benzyl group is associated with the benzyl radical which forms stable complexes with chromium(II). However transient, we believe that analogous organochromium(III) ions, RCr^{+2}, are also intermediates in related reactions. Such a radical association with chromium(II) (eq. 12) could be expected to require very little activation energy owing to the quintet character of high-spin chromium(II) ions in aqueous solutions. Such a combination has little steric requirements[51] and is probably diffusion controlled.

(49) J. D. Roberts and R. H. Mazur, J. Am. Chem. Soc., 73, 2509 (1951); C. Walling and P. S. Fredericks, ibid., 84, 3326 (1962).

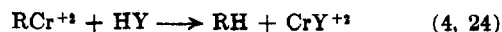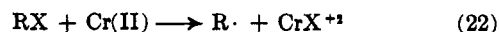(50) P. Lansbury and V. A. Pattison, ibid., 85, 1886 (1963).

(51) Solvation changes, especially in the metal ion, probably follow the association step and do not contribute to the activation process.

Reduction of Halides with Chromium(II).—Trimethylene bromide reacts slowly in aqueous ethanol with Cr(II) to afford cyclopropane. The reaction is considerably faster in aqueous dimethylformamide solutions. 1,3-Dibromobutane similarly gave good yields of methylcyclopropane in DMF solutions. 1,1-Diiodomethane and 1,1-dibromomethane were reduced[2f] with chromium(II) to methane, and neither ethane nor ethylene were present in significant amounts. Similarly, 1,1-dibromoethane afforded only ethane as a gaseous product. These results are preliminary and further work is required. It is clear, however, that these reactions are similar to the reductive elimination of 1,2-dihalides,[2] halo esters,[6] halohydrins,[52a] and haloamines.[5a] 1,2-Dihalides and halo esters can also be readily reduced with iodide, and the mechanism is commonly postulated[53] to consist of two successive nucleophilic displacements, the second being a concerted elimination from an iodo intermediate such as given in V.
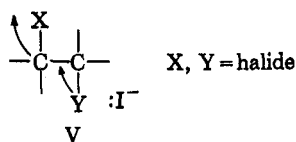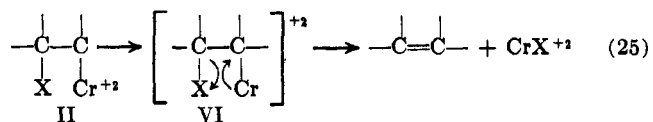

The reductive elimination of 1,2-halohydrins and haloamines, particularly the latter, is less readily accomplished, presumably owing to the difficulty of eliminating an alkoxide, hydroxide, or amide (X = OR, OH, NH₂) by a process such as given in V. Reducing metals and metal ions, however, can be employed to reduce 1,2-halohydrins and ethers. Thus, zinc[54a] and magnesium[54b] have been used extensively[53c] as a synthetic route to olefins from 1,2-halohydrins and ethers. The combination of Grignard reagents and ferric chloride, probably forms a reductant such as FeCl, which can also be effective in carrying out eliminations of such halides.[54c] Though conducted under diverse experimental conditions, these reagents resemble chromium(II) in their ability to effect vicinal elimination of halohydrins and derivatives.

These results can be reconciled, for example, if the reduction of alkyl halides by chromium(II) is considered to proceed *via* an organochromium intermediate such as II, analogous to that postulated for peroxides (*vide supra*) and shown previously to be applicable to aralkyl halides.[11] Castro and Kray[2f] have also considered such a mechanism for the reduction of alkyl halides and similar processes can be invoked for metals.[54g] The formation of a transient alkylchromium species II would facilitate removal of an adjacent hydroxy or amino

$$RX + Cr(II) \longrightarrow R\cdot + CrX^{+2} \qquad (22)$$

$$R\cdot + Cr(II) \longrightarrow RCr^{+2} (II) \qquad (23)$$

$$RCr^{+2} + HY \longrightarrow RH + CrY^{+2} \qquad (4, 24)$$

group by an intramolecular 1,4 ligand transfer without development of a formal negative charge on the leaving group X in the transition state as in VI. A pre-

liminary study has indicated the absence of free acetate ion from the reductive elimination of 2-bromo-3-acetoxybutane by chromium(II). Isolation of acetatochromium(III) is in progress. Analogous organometallic intermediates[54f] similar to II can be formulated for the reaction between an organic halide and zinc, magnesium, or iron, among others. The facilitation of an intramolecular ligand transfer of an anionic leaving group X to the metal ion is undoubtedly affected by the nature of the metal–carbon and metal–X bond; in addition, the solvent will play a major role in such transformations.[54d]

Kray and Castro[54h] have recently reported that *dl*-2,3- and *meso*-2,3-dihalobutanes afford different amounts of *cis*- and *trans*-butene-2 depending on the halogen substituent. These observations have bearing on the mechanism of the elimination from vicinal dihalides by chromium(II) and merit further investigation.

By analogy, a 1,5 intramolecular ligand transfer VII can be envisaged as a transition state in the 1,3 eliminations to form cyclopropanes.[54e] We hope further studies will aid in the development of this postulate.

$$\triangle + CrX^{+2} \qquad (26)$$
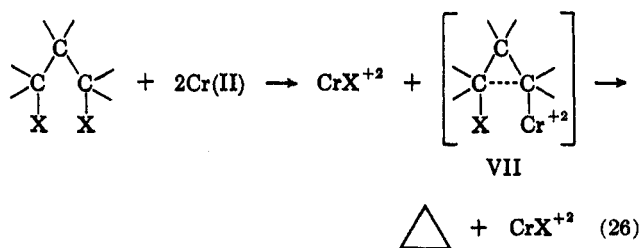
Experimental

Chromous perchlorate, Cr(ClO₄)₂, was prepared[55] in an aqueous solution by treating pure (99.995%) electrolytic chromium metal (Var-La-Coid Corp.) with perchloric acid (Mallinckrodt analytical reagent) of the desired concentration, which had previously been swept with oxygen-free nitrogen. The evolved hydrogen was released through a mercury vent and samples were removed with a hypodermic syringe which was inserted through a rubber septum cap. Chromium(II) solutions prepared in this manner were clear blue and stable for weeks at room temperature. They were assayed by adding an aliquot to an aqueous solution of excess ferric chloride (swept with nitrogen) contained in an erlenmeyer flask capped with a rubber septum. The ferrous chloride was titrated with standard ceric sulfate solution. The chromous solution was also analyzed iodimetrically with triiodide solution.

t-**Butyl hydroperoxide** (Lucidol Corp., 90%) was vacuum distilled several times until it assayed[56] to greater than 99% peroxide; b.p. 37–38° (16 mm.), m.p. 3–4°.

(52) (a) F. A. L. Anet and L. Marion, *Can. J. Chem.*, **33**, 849 (1955); (b) F. A. L. Anet and E. Isabelle, *ibid.*, **36**, 589 (1958).

(53) (a) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co. Inc., New York, N. Y., 1962, p. 210; (b) S. Winstein, D. Pressman, and W. G. Young, *J. Am. Chem. Soc.*, **61**, 1645 (1939); (c) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., Amsterdam, 1963, p. 136 ff. (d) J. F. King and R. G. Pews, *Can. J. Chem.*, **42**, 1294 (1964).

(54) (a) C. E. Boord, *J. Am. Chem. Soc.*, **55**, 3293, 4930 (1933), and earlier papers; (b) E. D. Amstutz, *J. Org. Chem.*, **9**, 310 (1942); (c) M. S. Kharasch, L. Biritz, A. Bhattacharya, and N. C. Yang, *ibid.*, **83**, 3229 (1961); M. S. Kharasch, M. Wiener, W. Nudenberg, A. Bhattacharya, T. Wang, and N. C. Yang, *ibid.*, **83**, 3232 (1961); (d) a *cis* elimination is not necessarily implied in any of these reaction sequences; (e) C. H. DePuy, G. N. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964); (f) *cf.* H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 182 (1958); (g) H. M. Walborsky and A. E. Young, *ibid.*, **86**, 3288 (1964); (h) W. C. Kray, Jr., and C. E. Castro, *ibid.*, **86**, 4603 (1964).

(55) H. Lux and G. Illman, *Ber.*, **91**, 2143 (1958).

(56) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

t-Amyl hydroperoxide was prepared from *t*-amyl alcohol and hydrogen peroxide by Milas'[57] procedure.

α,α-Dimethylphenethyl hydroperoxide was prepared[10] from α,α-dimethylphenethyl alcohol (Givaudan Co.) and hydrogen peroxide; m.p. 45–46°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49; hydroperoxide equiv. wt., 166.21. Found: C, 72.5, 72.4; H, 8.5, 8.5; hydroperoxide equiv. wt., 166.3, 167.5.

t-Butyl Hydroperoxide and Chromous Perchlorate.—A stock solution of *t*-butyl hydroperoxide was prepared from 4.5 g. of *t*-butyl hydroperoxide made up in a 100-ml. volumetric flask. Titer was 9.62 ml. of 0.1002 *N* $Na_2S_2O_3$. Chromous perchlorate solution was assayed iodometrically; the titer was 11.1 ml. of 0.1003 *N* $Na_2S_2O_3$. In a 100-ml. round-bottom flask equipped with a dropping funnel, manometer, and vacuum take-off was added a 20-ml. aliquot of *t*-butyl hydroperoxide solution. The flask was evacuated, and a 30-ml. aliquot of chromous perchlorate solution was added dropwise to the rapid magnetically stirred solution placed in a thermostated bath at 20°. The gas evolution was measured, ethane was added as a marker, and a gas sample was analyzed by gas chromatography. An aliquot of reaction mixture was removed with a hypodermic syringe through a rubber septum cap and quenched in a triiodide solution. The difference in the total chromous titer before and after reaction was 193 ml. of 0.1003 *N* $Na_2S_2O_3$. The stoichiometry of the reaction was, therefore, that two chromous ions were oxidized for each hydroperoxide.

The aqueous mother liquor was aerated to bring about the reaction of the chromous ion and was analyzed for total hydroxyl and carbonyl contents. It contained 1.61 mequiv. of alcohol and 8.05 mequiv. of ketone whose sum was equivalent to the *t*-butyl hydroperoxide charged (9.66 mequiv.). The over-all reaction is as follows.

$$10t\text{-}BuO_2H + 20Cr^{+2} \longrightarrow$$
$$8.35t\text{-}BuOH + 1.65CH_3COCH_3 + 1.61CH_4$$
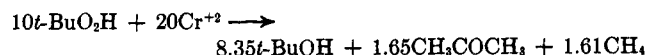
The reaction can also be carried out using a solution of chromic chloride and titanous chloride. A reducing solution was made up of 5.33 ml. of chromic chloride ($CrCl_3 \cdot 6H_2O$) and 4.8 ml. of 2.12 *N* titanous chloride in 20 ml. of water.

t-Butyl Hydroperoxide and Vanadium Salts.—A stock solution of *t*-butyl hydroperoxide (11.4 g.) was made up in a 250-ml. volumetric flask. A 10-ml. aliquot was treated, after degassing, with solutions containing vanadium in various oxidation states.

A solution of vanadic sulfate [$V_2(SO_4)_3$] was prepared by the electrolyte reduction at lead electrodes of vanadyl sulfate solution containing 30 g. of vanadyl sulfate and 15 g. of sulfuric acid in 150 ml. of water. Vanadous sulfate (VSO_4) solution was made by the further reduction of vanadic sulfate and was used immediately after preparation. Vanadyl sulfate solution was made up from 3.7 g. of vanadyl sulfate, in 15 ml. of 2 *N* sulfuric acid. All three vanadium solutions (15 ml.) reacted rapidly with *t*-butyl hydroperoxide.

t-Amyl Hydroperoxide and Ferrous Sulfate.—In a 50-ml. round-bottom flask equipped with a manometer, dropping funnel, and vacuum take-off was added a solution of 1.0 g. of *t*-amyl hydroperoxide in 40 ml. of water. The system was evacuated and a solution of 2.95 g. of ferrous sulfate in 20 ml. of water was added dropwise. Variation in temperature was controlled by immersing the reaction vessel in a water bath maintained at the appropriate temperature. The composition of the gas is given in Table IV (A).
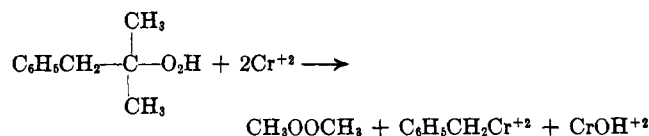
TABLE IV

Gas composn.	%—A—		%—Run—		
	28°	60°	1	2	3[a]
CH_4	0	0.1	1.0	2.0	0.5
C_2H_6	13.2	16.8	73.8	80.8	65.9
C_2H_4	28.6	34.0	8.0	7.0	9.5
$n\text{-}C_4H_{10}$	58.0	49.2	13.8	1.8	17.8

[a] A solution of 0.80 g. of 2-phenyl-2-butyl hydroperoxide in 10 ml. of isopropyl alcohol was added at 59° to a solution of 2.0 g. of ferrous sulfate in 15 ml. of water and 10 ml. of isopropyl alcohol.

The addition of isopropyl alcohol has the effect of increasing the ethane yield as shown below. The reactions were carried out by adding (1) a solution of 3.0 g. of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in 50 ml. of water and 25 ml. of isopropyl alcohol to 1.0 g. of *t*-amyl hydroperoxide in 50 ml. of water at 54°, and (2) a solution of 1.0 g. of *t*-amyl hydroperoxide to a suspension of 3.0 g. of $FeSO_4$ in 5.0 ml. of water and 30 ml. of isopropyl alcohol at 58–64°.

α,α-Dimethylphenethyl Hydroperoxide and Chromous Ion.—Crystalline α,α-dimethylphenethyl hydroperoxide (3.0 g., 18 mequiv.) was dissolved in ether and the ether was vacuum flashed, leaving the hydroperoxide as an oil. Chromous perchlorate solution (1.21 *M*, 24 ml.) was added *via* a hypodermic syringe to the evacuated flask and the reaction mixture was stirred magnetically for 12 hr. at room temperature. A 15-ml. aliquot of ether was added to extract the products which were analyzed by g.l.c. The ethereal solution was found to contain no α,α-dimethylphenethyl alcohol. It contained toluene, bibenzyl, and acetone. The aqueous solution was analyzed for total carbonyl content (acetone) and found to contain 15.2 mequiv. of acetone (total acetone 17.4 mequiv., 96.6%).

The stoichiometry in chromous ion was determined as follows. A solution of *t*-butyl alcohol (50 ml.) containing 1.0 g. of α,α-dimethylphenethyl hydroperoxide and 3.0 ml. of water was chilled to 0°. With rapid stirring and cooling there was added to the evacuated flask (within 2 min.) 20 ml. of a solution of 1.07 *M* $Cr(ClO_4)_2$; the reaction mixture was stirred for 1 hr. at 0°. A 6.0-ml. reaction mixture was extracted with a hypodermic syringe through the rubber septum cap and chromatographed directly through a Dowex (X40) column. The titer of the first 100 ml. was 80.3 ml. of 0.1003 *N* thiosulfate; the second 100 ml. had a titer of 27.0; and the third 300 ml. of eluate had a titer of 41.1 ml. The amount of originally charged chromous ion consumed corresponded to 6.6 mequiv. The stoichiometry of the reaction, therefore, appears to be closely

$$C_6H_5CH_2\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}O_2H + 2Cr^{+2} \longrightarrow$$
$$CH_3OOCH_3 + C_6H_5CH_2Cr^{+2} + CrOH^{+2}$$

The assumption was that $C_6H_5CH_2Cr^{+2}$ reacts with I_2 according to

$$C_6H_5CH_2Cr^{+2} + I_2 \longrightarrow C_6H_5CH_2I + Cr^{+3} + I^-$$
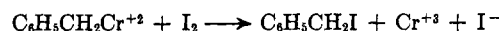
The rapid rate of the reaction was indicated by the fact that the iodine titer was independent of the time (after 5 min.) the components were allowed to stand before the iodine was titrated with thiosulfate.

α,α-Dimethylphenethyl Hydroperoxide and Ferrous Sulfate.—A solution of *t*-butyl alcohol (5.0 ml.), 3.0 ml. of water, and 1.0 g. of α,α-dimethylphenethyl hydroperoxide was chilled to 0°, and the flask was evacuated. A solution of ferrous sulfate (0.82 *M*, 20 ml.) was added *via* a hypodermic syringe to the rapidly stirred solution. After stirring for 1 hr. at 0°, a 20-ml. aliquot of Skelly B was added. The Skelly B solution contained benzyl alcohol (small amount), bibenzyl, acetone, and toluene, but no α,α-dimethylphenethyl alcohol (by g.l.c.).

Diacyl peroxides were prepared by the general method outlined below. In every case, pure peroxide which assayed to greater than 99% was obtained. The infrared spectrum showed a doublet in the region 5.5–5.65 μ and other carbonyl impurities (especially esters) absorbing at 5.8–5.9 μ were absent. The exceptions to these cases were phenylacetyl peroxide[58] and pivaloyl peroxide,[59] which were too unstable to handle neat. After preparation they were dissolved in ethanol at 0° and quickly reduced with chromous solution.

A solution of 158 ml. (2 moles) of pyridine and 50 ml. of ether was cooled to −10° and 62.5 ml. (0.55 mole) of 30% hydrogen peroxide was added portionwise at such a rate that the temperature did not exceed 10°. The mixture was rapidly stirred so that the two-phase system was finely dispersed and 1 mole of acid chloride was added dropwise, keeping the temperature between −5 and −10°. The reaction mixture was stirred for an additional 2 hr. at 0° and carefully neutralized with a chilled dilute sulfuric acid solution. Ether (100 ml.) was added and

(57) N. Milas and D. Surgenor, *J. Am. Chem. Soc.*, **68**, 205 (1946).

(58) P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

(59) H. C. McBay, Thesis, University of Chicago, 1945. This contains no details for the preparation of pivaloyl peroxide; it was only treated in solution.

the peroxide was extracted (throughout this and subsequent operations the solutions were *not allowed to warm to above 0°*). The aqueous solution was extracted further with pentane. The ether and pentane extracts were combined and washed with chilled dilute sulfuric acid, sodium carbonate solution, and water and dried over sodium sulfate. The pentane–ether extract was concentrated on a rotary evaporator first at aspirator pressures and then the final traces of solvent were removed on a vacuum pump. (The flask was kept chilled throughout this operation by rotating it in an ice bath.) The yield of peroxide was 90–95%.

n-Valeryl chloride, Eastman Kodak Co. White Label, was partially converted to the methyl ester. Gas chromatography showed less than 0.3% isomeric (isovaleryl and 2-methylbutyryl) impurities.

Isovaleryl chloride was usually contaminated with 2-methylbutyryl chloride. Eastman Kodak White Label isovaleric acid was converted to the acid chloride with thionyl chloride. Less than 0.4% isomeric impurities were present.

Phenylacetyl chloride, Trubek Laboratories, was redistilled before use.

Pivaloyl Chloride (Enjay Chemical Co.).—Pivalic acid was converted to acid chloride with thionyl chloride (>99.7% isomerically pure).

2-Methylbutyryl chloride, Eastman Kodak Co. White Label, after conversion to the methyl ester showed 1.5% isovaleryl chloride as adulterant. It was corrected for in the final analysis. The peroxide is thermally unstable neat.[47]

t-Butylacetyl chloride was prepared by carbonation of Grignard reagent from neopentyl chloride (Aldrich Chemical Co.), followed by thionyl chloride. Analysis of methyl ester indicated it to be greater than 99.7% pure. The melting point of peroxide[47] was 43.5–44.0°.

Cyclopropanecarbonyl chloride was prepared from cyclopropane carboxylic acid (K and K Laboratories) with thionyl chloride. The melting point of peroxide[60] was 80.0–80.5°.

Cyclopropylacetyl Chloride.—The acid was prepared[61] from ethyl vinylacetate and methylene iodide by the Simmons–Smith procedure, followed by distillation and saponification. The peroxide melted at approximately 5°.[62] It is thermally quite unstable neat.

Cyclobutanecarbonyl chloride (Kaplop Laboratories) was shown by gas chromatography of the methyl ester to be 99.5% pure. The peroxide is described elsewhere.[61]

Allylacetyl chloride was prepared from allylacetic acid (Peninsular Chemical Co.) and thionyl chloride. The peroxide is described elsewhere.[61]

(60) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).
(61) H. Mains, unpublished results.
(62) H. Hart and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

Methylene iodide (National Biochemical Co.), methylene bromide, 1,1-dibromomethane, 1,3-dibromobutane, and 1,3-dibromopropane (Eastman Kodak Co.), and 1,3-diiodopropane (City Chemical Co.) were commercially available samples used as such.

Diacyl peroxides were reduced with chromous sulfate in a 200-ml. round-bottom flask to which was added an aqueous alcohol solution of the peroxide. The free volume to solution ratio was at least 10. It was cooled in ice, and the solution was swept with oxygen-free nitrogen for 15 min. by inserting hypodermic needles through the rubber septum. It was finally evacuated to approximately 10-mm. pressure and the chromous solution was added with a syringe. The flask was put on a mechanical shaker to ensure complete mixing. The reaction was analyzed by adding a known quantity of marker (isobutane for *n*-butane) with a gas-tight syringe, shaking until homogeneous, and sampling the gas mixture for gas chromatographic analysis. Calibration curves (straight lines) were constructed for each gas marker-carbon dioxide combination obtained from a given solvent mixture. Marker gas was chosen so that its solubility characteristics would be as close as possible to the component to be identified (*e.g.*, *n*-butane–isobutane, butene-1–isobutylene, methylcyclopropane–cyclobutane, neopentane–butane, and cyclopropane–*n*-butane). Results obtained in this manner were reproducible and accurate to 3%. Gas chromatography was conducted with both a 50-ft. dimethyl sulfolane on firebrick and a 15-ft. silver nitrate–benzyl cyanide on Chromosorb W column which have sufficiently different characteristics to enable positive identification of the components in the gas mixtures.

After gas analysis, an aliquot was removed with a hypodermic syringe and added to excess ferric chloride solution, which was titrated with standard ceric sulfate. The carboxylatochromium-(III) was analyzed by ion-exchange chromatography on a Dowex-50 sulfonic acid resin (60–100 mesh). Excess chromous ion was destroyed with bromine or oxygen and the carboxylatochromium-(III) was eluted with 1.5 M perchloric acid after first washing with 0.4 M perchloric acid to remove anions and other easily eluted species. The dipositive chromium ions were analyzed by oxidation with alkaline hydrogen peroxide for total chromium. Another aliquot was hydrolyzed, and the liberated acid continuously was extracted with ether and analyzed by gas chromatography (6-ft. Carbowax–didecylphthalate on Chromosorb W treated with hexamethyldisilazane) with a homologous acid as marker.

Iodonium Salts Containing Heterocyclic Iodine[1-3]

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New or improved syntheses are reported for iodonium cations with heterocyclic iodine in five-, six-, and seven-membered rings and for cations with both iodine and oxygen, sulfur, or nitrogen in six-membered rings. Pyrolytic decomposition of the iodonium iodides gave 2,2'-diiododiphenyl compounds in which the rings are attached either directly or by carbon, oxygen, sulfur, or nitrogen.

Prior synthetic methods in the preparation of cyclic iodonium salts have involved replacement of a diazonio group with iodine,[4,5] acid-catalyzed condensation of an

(1) This article is taken from M.S. Theses of G. B. T., 1960, and L. K., 1963.
(2) Diaryliodonium Salts. XXIV. Preceding article: F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, 4442 (1964).
(3) Previously reported ring systems are named according to A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960.
(4) L. Mascarelli and G. Benati, *Gazz. chim. ital.*, **38**, 624 (1908).
(5) N. E. Searle and R. Adams, *J. Am. Chem. Soc.*, **55**, 1649 (1933).

iodoso group with a benzene ring,[6] and the reaction of iodyl sulfate with an appropriate aromatic substrate in strong acid.[7] Only methylene-bridged salts, where *n* = 0, 1, 2, or 3, have been prepared by these methods.

The present work is concerned with an extension of the above methods to produce cyclic iodonium salts with nitrogen, oxygen, and sulfur in six-membered

(6) J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *ibid.*, **78**, 3819 (1956).
(7) W-K. Hwang, *Sci. Sinica* (Peking), **6**, 123 (1957); *Chem. Abstr.*, **51**, 16476 (1957).