[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE CHEMISTRY OF HYDROPEROXIDES. IV. OXIDATION OF TERTIARY AROMATIC ALCOHOLS WITH HYDROGEN PEROXIDE OR HYDROPEROXIDES

M. S. KHARASCH, ANDREW FONO, W. NUDENBERG, AND ALGIRDAS C. POSHKUS

Received December 7, 1949

In a previous paper it was shown that α-cumyl hydroperoxide, when treated in glacial acetic acid with a small amount of perchloric acid, gives phenol and acetone (1).

$$C_6H_5(CH_3)_2C\text{—}OOH \xrightarrow[HClO_4]{HOAc} C_6H_5OH + CH_3COCH_3$$

It is of interest to determine the migration (or elimination) tendencies of various groups in molecules of the type RR′R″C—OOH, where at least two of the groups, R, R′, and R″ are aromatic groups.[1] Because the preparation of such hydroperoxides is rather troublesome, a new approach to the problem was sought.

It was found that when α,α-dimethylbenzyl alcohol, in glacial acetic acid, was treated with *tert*-butyl hydroperoxide or hydrogen peroxide in the presence of a small amount of perchloric acid, considerable heat was evolved, and the alcohol was converted to phenol and acetone. The reaction time was about ten minutes.

$$\begin{array}{ll} & + H_2O_2 \xrightarrow{HOAc\ +\ HClO_4} C_6H_5OH + (CH_3)_2CO + HOH \\ C_6H_5(CH_3)_2COH & \\ & + (CH_3)_3C\text{—}OOH \xrightarrow{HOAc\ +\ HClO_4} C_6H_5OH + (CH_3)_2CO \\ & \qquad + (CH_3)_3COH \end{array}$$

Similar results were obtained (in the absence of perchloric acid) when α-cumyl chloride, the triarylmethyl chlorides, and other substances of the type RR′R″CCl or olefins (RR′C═CH$_2$) and concentrated hydrochloric acid, were treated with hydrogen peroxide in acetic acid (at least one of the radicals R, R′, or R″ must be an aromatic radical).

DISCUSSION

The results summarized in Table I can best be interpreted by assuming that, in the presence of strong acids, tertiary alcohols containing at least one aryl group react with hydrogen peroxide[2, 3] or tertiary alkyl hydroperoxides to give

---

[1] The strictly aliphatic hydroperoxides, when treated with perchloric acid, give mainly the corresponding peroxides. The work leading to this conclusion will be reported in another article of this series.

[2] It has been established that hydrogen peroxide and glacial acetic acid react to give an equilibrium mixture in the presence of a strong acid:

$$CH_3CO_2H + H_2O_2 \rightleftharpoons CH_3CO\text{—}OOH + HOH$$

However, the equilibrium in the absence of a carbinol is attained slowly as compared with the rate of the reactions here studied [D'Ans and Frey, *Ber.*, **45**, 1845 (1912)]; the question therefore arises whether the reactions described are caused by hydrogen peroxide or the

the following intermediate products:[4]

1. $RR'R''COH + H_2O_2 \overset{H^+}{\rightleftharpoons} RR'R''C\text{-}OOH + H_2O$
2. $RR'R''COH + (CH_3)_3C\text{-}OOH \rightarrow RR'R''COOC(CH_3)_3 + H_2O$

In reaction 2, if little of the strong acid is used, the peroxide can be isolated. However, with somewhat larger amounts of the strong acid (perchloric) the products undergo decomposition.

To account for the fact that only small traces of perchloric acid are necessary to produce the rearrangements indicated, the following chain reaction was suggested:

1. $C_6H_5(CH_3)_2C\text{—}OOH \xrightarrow[H^+]{HOAc} H_2O + \underset{(\mathbf{B})}{[C_6H_5(CH_3)_2CO]^+}$
2. $(\mathbf{B}) \rightarrow \underset{(\mathbf{C})}{[C_6H_5O(CH_3)_2C]^+}$
3. $(\mathbf{C}) + C_6H_5(CH_3)_2C\text{-}OOH \rightarrow C_6H_5OH + CH_3COCH_3 + (\mathbf{B})$

Table I discloses that the groups which, according to the latter mechanism, migrate and which, in any case, are eliminated, may be arranged in the same ordered series obtained by the cleavage of unsymmetrical mercurials with hydrochloric acid (2). This series was called "the electronegativity series" of organic radicals.[5]

With two exceptions, this same series of radicals corresponds well with the "migration aptitudes" of radicals in the rearrangements of symmetrical pinacols (3). The discrepancies observed are that, in the rearrangement of symmetrical

---

peracetic acid. It has been established that when α,α'-dimethylbenzyl alcohol, dissolved in acetic acid, is treated with peracetic acid in the presence of a small amount of perchloric acid, only about 50% of phenol was formed; the other oxidation product was probably α-phenyl-α-methylethylene glycol. The addition of small amounts of water to the acetic acid solution caused an increase in reaction time and an increase in the yield of phenol. These results indicate that hydrogen peroxide and not peracetic acid is the active reagent in the oxidation of α,α-dimethylbenzyl alcohol (and other tertiary alcohols) to yield phenol.

[3] Of tremendous importance in all such reactions is the concentration and strength of the acid used, particularly in the case of olefins.

[4] Both the formation of these peroxides (from the hydroperoxides and a tertiary alcohol) and their decomposition in the presence of an acid are readily formulated as follows:

(a) $RR'R''COH + H^+ \rightarrow RR'R''C^+ + H_2O$

(b) $(CH_3)_3C\text{—}OOH + RR'R''C^+ \rightarrow \{[(CH_3)_3C\text{—}OOH]\,[RR'R''C^+]\}$ $(\mathbf{A})$

(c_1) $\mathbf{A} \rightleftharpoons (CH_3)_3COOCRR'R'' + H^+$

(c_2) $\mathbf{A} \overset{RR'R''COH}{\rightleftharpoons} (CH_3)_3COOCRR'R'' + RR'R''C^+ + H_2O$

(c_3) $\mathbf{A} \rightarrow (CH_3)_3COH + [RR'R''CO]^+$

Reactions c_1 and c_2 are reversible; the reverse reaction is favored by increasing the amount of strong acid. The extent to which each one of the reactions occur (c_1, c_2, and c_3) depends further on the strength of the carbon-to-oxygen bond in the peroxide. (The factors governing the decomposition of unsymmetrical peroxides will be discussed in one of the succeeding articles.)

[5] The word "electronegativity" has now many connotations. As originally applied, it indicates the tendency of the organic radical to exist as a negative ion.

pinacols, *o*-tolyl and *o*-anisyl groups migrate less readily than phenyl groups, the reverse of the results obtained by the cleavage of unsymmetrical organomercurials. It is of considerable interest, therefore, that the *o*-tolyl and the *o*-anisyl groups are eliminated preferentially when *o*-tolyldiphenylcarbinol and *o*-anisyl-

TABLE I

REACTIONS OF TERTIARY ALCOHOLS OR OLEFINS WITH HYDROGEN PEROXIDE AND A STRONG ACID[a]

ALCOHOL OR OLEFIN	PRODUCTS[b]		
	PHENOLIC	KETONIC	NON-PHENOLIC, NON-KETONIC
1. α,α-Dimethylbenzyl alcohol	Phenol (95%)	Acetone	None
2. α,α-Diphenylethylene	Phenol (70%)	Acetophenone (68%)	Original olefin (30%)
3. Triphenylcarbinol[c, d]	Phenol	Benzophenone (93%)	Original carbinol (5%)
4. 1-Phenyl-1-*p*-tolylethanol[c]	*p*-Cresol (70%)[e]	Acetophenone	Phenyl-*p*-tolylethylene (20%)
5. α-Phenyl-α-*p*-anisylethylene[c]	*p*-Hydroxyanisole (55%)[e]	Acetophenone	α-Phenyl-α-*p*-anisylethylene (20%)
6. *o*-Anisyldiphenylcarbinol[c]	Guaiacol (60%)	Benzophenone (75%) *o*-Methoxybenzophenone (10%)	Original carbinol (12%)
7. Diphenyl-*o*-tolylcarbinol	*o*-Cresol (80%)[e]	Benzophenone (56%)	Unidentified (30%)
8. Diphenyl-α-naphthylcarbinol[f]	α-Naphthol (70%)[e]	Benzophenone (70%)	Unidentified (30%)
9. 1-Phenyl-1-*o*-tolylethanol	*o*-Cresol (12%)	Acetophenone	α-Phenyl-α-*o*-tolylethylene (80%)
10. 4,4′-Diphenoxytriphenyl[g] carbonium perchlorate		Phenoxybenzophenone	
11. 4-Nitrotriphenyl[g] carbonium perchlorate	Phenol	*p*-Nitrobenzophenone	

[a] The reactions were carried out in glacial acetic acid solution. [b] The quantitative separation of all the reaction products was not always considered essential. In all cases however the presence of each compound listed among the reaction products was demonstrated. [c] *tert*-Butyl hydroperoxide was used in place of hydrogen peroxide (see experimental part). [d] With triphenylcarbinol and hydrogen peroxide some 5–10% of triphenylmethyl peroxide is formed, in addition to the phenol and acetophenone. [e] No phenol could be isolated (see experimental part). [f] Because the phenolic material is easily oxidized, the use of excess hydrogen peroxide is undesirable. [g] These data are taken from the paper by Dilthey, Quint, and Dierichs, *J. prakt. Chem.*, [2], **151**, 25 (1938). No yields are recorded. However, the authors do not mention the formation of products other than those recorded.

diphenylcarbinol are treated with hydrogen peroxide in acetic acid in the presence of small amounts of perchloric acid. Perhaps the discrepancies noted in connection with the *ortho*-substituted pinacols may be due to a steric factor,[6] and not to the weaker "electronegativity" of these radicals.

EXPERIMENTAL

Oxidation of α,α-dimethylbenzyl alcohol. tert-Butyl hydroperoxide (0.05 mole), α,α-dimethylbenzyl alcohol (0.05 mole), and acetic acid (14 cc.) were treated with 0.001 mole of perchloric acid in acetic acid. The temperature of the reaction mixture was maintained below 30°. The peroxide titre reached zero in 10 minutes. The reaction mixture was poured into water, and the resultant mixture was extracted with ether. The ether extract was washed with sodium bicarbonate solution to remove acetic acid, and was then treated with 5% sodium hydroxide solution. No phenol was found. The ether solution was dried, and ether was removed under reduced pressure. The residue was distilled at reduced pressure, and the fraction distilling at 40°/0.2 mm., was collected. This fraction constituted a 95% yield (based on the amount of *tert*-butyl hydroperoxide used) of *tert*-butyl α-cumyl peroxide, n_D^{20} 1.4792.

Anal. Calc'd for $C_{13}H_{20}O_2$: C, 75.10; H, 9.61; mol. wt., 208.

Found: C, 75.10; H, 9.75; mol. wt., 200.

One gram of the unsymmetrical peroxide was reduced by treatment with 0.4 g. of powdered sodium in ether. From the reaction mixture was obtained, after washing with water, 0.6 g. of α,α-dimethylbenzyl alcohol; m.p. 36°, n_D^{20} (supercooled) 1.5219.

When perchloric acid (10 mole-%) is added to the acetic acid solution of the peroxide, the latter is converted to a mixture of phenol, acetone, and α-methylstyrene dimer. Furthermore, when increased amounts of perchloric acid (10 mole-%) are used in the original reaction mixture the same products are formed immediately. Thus *tert*-butyl hydroperoxide (0.05 mole) and α,α-dimethylbenzyl alcohol (0.07 mole) dissolved in 12 cc. of glacial acetic acid, when treated with 0.01 mole of perchloric acid formed phenol (0.025 mole), α-methylstyrene dimer (0.015 mole), and acetone (not isolated).

Oxidation of α,α-diphenylethylene. as-Diphenylethylene (b.p. 162°/16 mm., n_D^{15} 1.6080), 0.016 mole, in 20 cc. of glacial acetic acid was treated with 30% hydrogen peroxide (0.028 mole), and a 70% aqueous solution of perchloric acid (0.01 mole) was added. The reaction mixture was maintained at a temperature below 30°. After 12 hours, the reaction mixture was worked up as usual. There were obtained: phenol (0.011 mole) and acetophenone, identified as the dinitrophenylhydrazone, m.p. 228°.

Oxidation of triphenylcarbinol. Triphenylcarbinol (0.05 mole) suspended in a solution of *tert*-butyl hydroperoxide (0.05 mole) in acetic acid (45 cc.) was treated with 0.0025 mole of perchloric acid. The carbinol dissolved rapidly. After four hours water was added to the reaction mixture. The aqueous suspension was stored at 0° for 12 hours. The solid which separated was collected and dried. It was taken up in boiling 60°-ligroin. Unchanged triphenylcarbinol separated when the ligroin solution was cooled to 4°. The carbinol was collected and the mother liquor was cooled to −80°, whereupon the solid *tert*-butyl triphenylmethyl peroxide separated. Additional amounts of solid were obtained by concentrating the filtrate from the first crop of crystals. The crude peroxide melted at 66°, and was formed to the amount of 85–90%. The recrystallized (ligroin) material melted at 70°.

Anal. Calc'd for $C_{23}H_{24}O_2$: C, 83.1, H, 7.22; mol. wt., 332.

Found: C, 83.23; H, 7.24; mol. wt., 320.

tert-Butyl triphenylmethyl peroxide (5.3 g.) suspended in 24 cc. of glacial acetic acid was treated with 1 cc. of 70% perchloric acid; the temperature was maintained below 30°.

---

[6] Molecular models (Fisher-Hershfelder-Taylor) show that the migration of the phenyl group, in α,β-diphenyl-α,β-di-*o*-tolylethylene glycol, may occur readily, whereas that of an *o*-tolyl group is greatly hindered.

After 45 minutes the reaction mixture was extracted with ether; the ether solution was washed with bicarbonate solution to remove acetic acid. Phenol was extracted from the ether with 5% sodium hydroxide, and, after acidification of the alkaline extract, was identified as its tribromo derivative. The neutral residue from the ether extract was taken up in absolute alcohol. A few drops of water was added to the boiling-alcoholic solution. When the solution cooled, triphenylcarbinol (0.3 g.) crystallized; m.p. 158°; no depression of melting point upon mixture with an authentic sample. Addition of water to the filtrate from the carbinol precipitated 2.7 g. (93%) of crystalline benzophenone; m.p. 46°; no depression upon mixture with authentic sample.

Oxidation of triphenylcarbinol. Triphenylcarbinol (0.01 mole), suspended in a solution of 30% hydrogen peroxide (0.03 mole) and 20 cc. of glacial acetic acid, was treated with perchloric acid (0.01 mole, 30% solution in acetic acid). The triphenylcarbinol dissolved completely in 2–4 hours and then a small amount of solid (5–10%) separated from the solution. This solid, which was insoluble in ether, was recrystallized from benzene; it proved to be triphenylmethyl peroxide, m.p. 175°; the melt is orange-colored. The acetic acid solution of the reaction mixture was worked up in the usual fashion. The oily neutral fraction solidified completely when seeded with a crystal of benzophenone; the crystals melted at 46–47°; yield, 93%. The phenol formed was identified as its tribromo derivative (m.p. 93°).

Oxidation of 1-phenyl-1-p-tolylethanol. 1-Phenyl-1-*p*-tolylethanol (b.p. 120–125°/0.3 mm., n_D^{20} 1.5828) (0.05 mole) and *tert*-butyl hydroperoxide (0.06 mole) were added to 16 cc. of glacial acetic acid. To the resulting solution was added 0.01 mole of perchloric acid in acetic acid (50% solution). Two liquid layers formed when the perchloric acid solution was added. The reaction mixture was maintained at a temperature below 30°, and, after 20 hours, water was added. The resulting mixture was extracted with ether; the ether extract was washed with sodium bicarbonate solution, and then extracted with 5% sodium hydroxide. From the alkaline extract, by acidification, 0.035 mole *p*-cresol was obtained. That phenol was not present, was shown by the following observations: (a) the phenolic fraction gave a negative Liebermann nitroso test; (b) only traces of the fraction were soluble in sodium benzenesulfonate solution (5), and even this material failed to give a Liebermann test; (c) the tribromo derivative melted at 108°.

The neutral ether-soluble fraction was distilled at 0.3 mm. Acetophenone was collected at 42°; n_D^{20} 1.5338 (lit. n_D^{9} 1.5342), dinitrophenylhydrazone, crude, m.p. 228–230° uncorr., agreeing with that of an authentic sample. At 90° and 0.3 mm. α-phenyl-*α-p*-tolylethylene distilled (15–20%, based on the carbinol used); n_D^{20} 1.5862.

Oxidation of α-phenyl-α-anisylethylene. This olefin (6) was prepared by the addition of anisylmagnesium bromide to acetophenone. The Grignard reaction product was decomposed with dilute acetic acid, and was worked up in the usual fashion. The olefin was distilled; b.p. 144–147° at 0.3 mm. The distillate crystallized on cooling; recrystallization from ethanol gave a product melting at 74°. The purified olefin (0.045 mole) and 0.050 mole of *tert*-butyl hydroperoxide in 20 cc. of glacial acetic acid were treated with 0.004 mole of perchloric acid in acetic acid. The temperature was maintained below 30°; after 20 hours, the reaction mixture was worked up as described for the preceding carbinol. The crude phenolic material thus obtained melted at 47–52°; the same materials, after crystallization from 1:1 ligroin-benzene melted at 53°, and did not depress the melting point of hydroquinone monomethyl ether. The *p*-methoxyphenol formed amounted to 0.025 mole. The neutral fraction was treated with ethanol, and from this solution, by cooling to −80°, there was obtained 0.009 mole of unchanged ethylene, m.p. 74°; this material did not depress the melting point of the original ethylene derivative. After distillation of acetophenone from the neutral fraction, there remained some high-boiling tar.

Oxidation of o-anisyldiphenylcarbinol. This carbinol (0.04 mole) and *tert*-butyl hydroperoxide (0.05 mole in 25 cc. of acetic acid) were treated with 0.02 mole of perchloric acid; the temperature was maintained below 30°. After 20 hours, water was added, and the reaction mixture was worked up in the usual way. The alkaline-soluble material (3 g.) was crude guaiacol; the tribromo derivative melted at 117° (recorded, m.p. 116°). The neutral fraction (8.0 g.) was taken up in ethanol, a few drops of water were added, and the unchanged carbinol (0.006 mole) which separated was collected. This recovered carbinol melted at 127°, and did not depress the melting point of an authentic sample. The mixture of ketones which remained in ethanol solution was recovered from the ethanol by addition of water and extraction with ether. After removal of the ether this fraction weighed 6.5 g. The ketone mixture was refluxed with 48% hydrogen bromide in acetic acid (7) in order to hydrolyze any methoxy compound present. The hydrolyzed reaction product was treated with water, extracted with ether, and washed with bicarbonate; then the phenolic ketone was extracted with alkali. By acidification of the alkaline extract, there was obtained 0.004 mole of *o*-hydroxybenzophenone; this material, when recrystallized, melted at 37°. The neutral ketonic material was recrystallized from dilute alcohol; there was thus obtained 0.03 mole of benzophenone, m.p. 47°.

Oxidation of diphenyl-o-tolylcarbinol. The carbinol (4), m.p. 94°, (10.9 g., 0.04 mole) was treated with 30% hydrogen peroxide (5 cc., 0.045 mole) and glacial acetic acid (50 cc.). To the resulting mixture was added 70% perchloric acid (0.01 mole), and the solution was allowed to stand at room temperature for three hours. The reaction mixture was worked up in the usual fashion.

For identification and estimation of the amount of the phenolic materials formed in the reaction the following procedure was used. The phenolic fraction (3.5 g.) was dissolved in 12% sodium hydroxide solution and the resulting solution was treated with 5 g. of chloroacetic acid. This mixture was heated on the steam-bath for 5 hours; during this time an additional 5 g. of chloroacetic acid and sufficient alkali to maintain alkalinity were added. The reaction mixture was cooled, acidified with dilute sulfuric acid, and extracted with ether. The ether solution was extracted with sodium bicarbonate solution; and by acidification of the bicarbonate extract there was obtained 3.6 g. of the *o*-cresoxyacetic acid, m.p. 148–152° (without crystallization). The amount of aryloxyacetic acid formed accounts for 67% of the phenolic fraction. When a model experiment was carried out with pure *o*-cresol the recovery of the aryloxy derivative was 75%. The filtrate from the *o*-cresoxyacetic acid gave less than 0.2 g. of precipitate when treated with bromine water. This result indicates the presence of only insignificant amounts of the more water-soluble phenoxyacetic acid, which readily forms a tribromo derivative insoluble in water. From the neutral fraction (7.0 g.) of the reaction mixture was obtained 4.0 g. of benzophenone, m.p. 47–48°. The residual oil remaining after crystallization of the benzophenone was not further investigated.

Oxidation of α-naphthyldiphenylcarbinol. The carbinol, m.p. 135–136°, (0.04 mole) was treated with 30% hydrogen peroxide (0.045 mole) in glacial acetic acid (75 cc.). To the resulting mixture was added 70% perchloric acid (0.01 mole). The temperature was maintained below 25°. After one hour, the reaction mixture was separated from the small amount of amorphous solid (1.2 g.) which had precipitated. The mixture was then worked up in the usual fashion. The phenolic fraction isolated amounted to 4.0 g. It was identified by conversion to its aryloxyacetic acid derivative as previously described. The naphthoxyacetic acid thus formed melted at 180–184° (crude). No phenol could be detected. From the neutral fraction was obtained, by distillation, 5.0 g. of crystalline benzophenone, m.p. 47–48°, and 3.0 g. of higher-boiling nonketonic oil (b.p. 160–190°/2 mm.). The amorphous solid and the high-boiling oil which amounted to 30% of the starting materials, were not further investigated.

Oxidation of 1-phenyl-1-o-tolylethanol. This carbinol was prepared by addition of *o*-tolylmagnesium bromide to acetophenone; b.p. 137–140° at 0.4 mm., n_D^{20} 1.5862.

Anal. Calc'd for $C_{15}H_{16}O$: C, 84.94; H, 7.55; Mol. wt., 212.

Found: C, 84.77; H, 7.56; Mol. wt., 215.

1-Phenyl-1-*o*-tolylethanol (0.05 mole) and *tert*-butyl hydroperoxide (0.05 mole) were dissolved in 20 cc. of glacial acetic acid. To the solution was added 0.02 mole of perchloric acid. After 2 hours, the reaction mixture was worked up in the usual fashion. The phenolic fraction amounted to 0.006 mole; the properties (color reactions, water-solubility, etc.) of the phenolic fraction were consistent with those of *o*-cresol: The neutral fraction was distilled under reduced pressure. The fraction collected at 40°/0.3 mm. contained the ketones. This fraction was treated with dinitrophenylhydrazine, and the hydrazone was fractionally crystallized. Two fractions were obtained [(a) m.p. 230°; (b) m.p. 233°; (uncorr.)]. These were identical with the derivative obtained from authentic acetophenone. The major portion of the neutral fraction distilled at 108–110° at 0.3 mm., and proved to be α-phenyl-α-*o*-tolylethylene (80 mole-%); n_D^{20} 1.5929; molecular weight (cryoscopic, benzene), 198; calc'd for $C_{15}H_{14}$, 194. Elementary analysis showed the absence of oxygen, and catalytic hydrogenation in ethanol in the presence of Adams' catalyst resulted in the absorbtion of 1 mole of hydrogen; thus, 0.65 g. of material absorbed 77 cc. (corrected) of hydrogen (calc'd for one double bond, 76 cc.).

SUMMARY

1. Tertiary alcohols, containing at least one aromatic group, or the olefins derived therefrom are converted in the presence of non-corresponding hydroperoxides under mildly acidic conditions to unsymmetrical peroxides.

2. Tertiary alcohols, containing at least one aromatic group, or the corresponding olefins can be oxidized under acidic conditions with *tert*-butyl hydroperoxide or hydrogen peroxide to phenolic and ketonic materials. The corresponding hydroperoxides and unsymmetrical peroxides yield the same products and are assumed to be intermediates.

3. With compounds of the type RR'R″COH comparison of the elimination aptitudes of the various groups is possible. The elimination aptitude of groups follows the electronegativity series. The relative aptitudes differ from those derived from the pinacol rearrangement in the case of *ortho*-substituted groups. It is suggested that in the case of the pinacols steric factors also play an important part.

CHICAGO 37, ILLINOIS

REFERENCES

(1) KHARASCH, FONO, AND NUDENBERG, *J. Org. Chem.*, **15**, Paper I of this series.
(2) KHARASCH AND CO-WORKERS, *J. Am. Chem. Soc.*, **48**, 3130 (1926); *J. Org. Chem.*, **3**, 347, 405, 409 (1938).
676—5.5.50 OC 4094 page 11 take 6.1.4C Galley 4X
(3) For leading references see: BACHMAN AND STEINBERGER, *J. Am. Chem. Soc.*, **56**, 170 (1934).
(4) ACREE, *Ber.*, **37**, 993 (1904).
(5) BETTELHEIM, *Svensk. Kem. Tid.*, **54**, 194 (1942) (*Chem. Zentr.*, *1943*,*I*, 984).
(6) HURD AND WEBB, *J. Amer. Chem. Soc.*, **49**, 549 (1927).
(7) STOERMER, *Ber.*, **41**, 322 (1908).