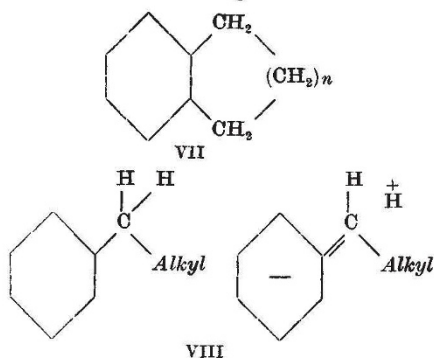Baker–Nathan effect. We deplore the present trend to employ formulæ of the type $H_3 \equiv C—CH = CH_2$ [7] and to neglect the geometrical requirements of hyperconjugation. We conclude by indicating a consequence of this shortcoming.

VII

VIII

Hyperconjugation occurs in the hydrocarbons VIII when the alkyl group (more correctly, the carbon atom which is directly attached to the benzyl group) is in or near the plane of the benzene ring. It is therefore susceptible to steric inhibition by repulsive forces between the alkyl group and the benzene ring, and, decreasing as the bulk of the alkyl group increases, becomes progressively smaller in each successive member of the series VIII (Alkyl = methyl, ethyl, iso-propyl and tert.-butyl). The rates of bromination of these hydrocarbons also decrease in this order, and had Berliner and Berliner fully appreciated the geometrical requirements of hyperconjugation, they would not have invoked a "second order hyperconjugation involving beta hydrogen atoms"[8].

<div align="right">

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[1] Remington, J. Amer. Chem. Soc., **67**, 1838 (1945).
[2] Pauling, "Nature of the Chemical Bond", 139 (Cornell, 2nd edit., 1940).
[3] Ramart-Lucas and Hoch, Bull. Soc. Chim., (5), **2**, 327 (1935). Bicquard, Bull. Soc. Chim., (5), **8**, 55 (1941).
[4] Unpublished observations.
[5] Morton and de Gouveia, J. Chem. Soc., 911, 916 (1934).
[6] Brown, Widiger and Letang, J. Amer. Chem. Soc., **61**, 2597 (1939).
[7] Wheland, "The Theory of Resonance", 235 (1947).
[8] Berliner and Berliner, J. Amer. Chem. Soc., **71**, 1195 (1949).

Autoxidation of Isopropylbenzene

In view of current interest in the autoxidation of hydrocarbons, it seems desirable to record briefly some observations made in these laboratories concerning the autoxidation of isopropylbenzene.

Hock and Lang[1] had previously noted that dry isopropylbenzene was converted to a hydroperoxide (αα-dimethylbenzyl hydroperoxide) on being shaken in an atmosphere of oxygen at 85° C. and irradiated with ultra-violet light :

$$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OOH.$$
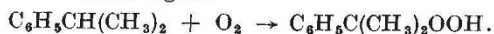
The rate of production of hydroperoxide was slow (about 0·3 mol. per cent per hour) and only limited conversions (about 7 per cent) of hydrocarbon to hydroperoxide were achieved.

During investigations started in 1945, we found that isopropylbenzene could be oxidized comparatively rapidly with oxygen in an alkaline oil-in-water emulsion at 85° C to give the hydroperoxide in good yield. We believe that although the oxidation of organic compounds with air under alkaline conditions has been known for many years, the emulsion oxidation of a hydrocarbon to yield the hydroperoxide as major product is a novel technique. The method has also been applied to other aromatic hydrocarbons[2].

In a representative experiment, a 1 : 2 emulsion of purified isopropylbenzene in an alkaline (initial pH 10·5) aqueous phase containing 0·09 per cent w/v sodium stearate was stirred vigorously at 85° C. and oxygen passed through the mixture. After an induction period of 1·5 hr. absorption of oxygen commenced, the rate increasing with increasing hydroperoxide concentration up to a figure of 6·3 mol. oxygen per hour per 100 mol. isopropylbenzene after a total time of 14·5 hr. The concentration of peroxide (determined iodometrically in acetic acid under carbon dioxide) was 30 per cent molar, the efficiency of conversion of oxygen to hydroperoxide being 85 per cent. The product was then saturated with carbon dioxide and the hydrocarbon phase separated.

Isolation of the hydroperoxide from the oxidation products could be achieved by fractional distillation of the hydrocarbon phase under reduced pressure, preferably in the presence of a little solid sodium carbonate as stabilizer. In some cases the method of Hock and Lang (loc. cit.) was used, namely, the precipitation of the sodium salt with 25 per cent aqueous sodium hydroxide, and regeneration of the free hydroperoxide from its salt by treatment with acid. Quantitative recovery of the hydroperoxide was approached, however, only after several treatments of the hydrocarbon phase with alkali, since the free hydroperoxide is a very weak acid. Confirmation of the structure of the hydroperoxide was obtained by repeating the degradations described by Hock and Lang (loc. cit.), namely, by reduction with sodium sulphite or bisulphite to phenyl dimethyl carbinol, and by decomposition with 10 per cent sulphuric acid to phenol and acetone. Minor quantities of acetophenone, phenyl dimethyl carbinol and α-methylstyrene were identified during the working-up of our oxidation products.

This oxidation reaction is analogous to other radical chain autoxidations[3]. The induction period is eliminated by the addition of the hydroperoxide itself, or of other organic peroxides with a suitable decomposition-rate under the conditions of the autoxidation (for example, lauryl, benzoyl). Phenol inhibits the oxidation, and the reaction is sensitive to certain metals (lead and copper) which increase the rate of hydroperoxide decomposition. Beyond about 35 per cent conversion the oxidation-rate reaches a maximum, and thereafter declines. There is also a limit to the hydroperoxide concentration which can be achieved, this being of the order of 50 per cent molar.

More detailed investigations of the reaction have been made, including the effect of variations in the emulsifier, phase ratio, temperature and pH of the aqueous phase, and these will be published elsewhere.

We are indebted to the directors of the Distillers Company, Ltd., for permission to publish this letter.

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        Epsom, Surrey.   June 15.

[1] Hock and Lang, Ber., **77**, 257 (1944).
[2] The Distillers Co., Ltd., Hall and Quin, Brit. Pat. 610,293 (Oct. 1 1948) and other applications pending.
[3] See, for example, Waters, Ann. Reps. Chem. Soc., **42**, 136 (1945)