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THE REACTION OF METHYL AND t-BUTOXY RADICALS WITH BENZENE

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Abstract—Mass spectroscopic analysis shows that diphenyl and C_{13} and C_{14} hydrocarbons are produced when di-t-butyl peroxide decomposes in a very dilute benzene solution. In contrast, when acetyl peroxide decomposes in benzene, only C_{14} hydrocarbons are produced. Thus it appears that methyl radicals react with benzene through an addition mechanism, but t-butoxy radicals abstract hydrogen from benzene with the production of phenyl radicals. The higher molecular weight products from the decomposition of di-t-butyl peroxide in benzene can be explained as products of the combination reactions of phenyl and methylcyclohexadienyl radicals.

INTRODUCTION

In an earlier paper, Brook and Glazebrook[1] reported that the decomposition of di-t-butyl peroxide in toluene-α-d_3 gave a more complex mixture of products than resulted from decomposition in toluene. Deuteration of the methyl group makes it less sensitive to attack by hydrogen-abstracting agents and, as a result, the free radicals liberated from the peroxide attacked the benzene ring. When the product of the reaction was analysed by mass spectroscopy, it was found to contain dibenzyl-d_4 and a range of other hydrocarbons derived from the coupling of benzyl-α-d_2, methylphenyl-α-d_3 and methylmethyl-d_3-cyclohexadienyl radicals. The formation of a cyclohexadienyl-type radical by the addition of a methyl radical to toluene-α-d_3 is readily explained by current theories of homolytic aromatic substitution,[2–4] but the formation of methylphenyl-α-d_3 radicals by the abstraction of hydrogen from the benzene ring is unexpected.

It therefore seemed desirable to check these observations by decomposing di-t-butyl peroxide in benzene. If phenyl radicals are formed, they should dimerize or attack the benzene forming C_{12} hydrocarbons; if methyl- or t-butoxycyclohexadienyl radicals are formed they should cause the formation of higher molecular weight compounds containing thirteen or more carbon atoms. Since these compounds can be readily distinguished from C_{12} hydrocarbons by mass spectrometry, it should be easy to decide whether phenyl or substituted cyclohexadienyl radicals have taken part in the reaction.

The decomposition of di-t-butyl peroxide, however, produces two reagent radicals, t-butoxy and methyl radicals, and there may therefore be some doubt which of these radicals was responsible for a particular hydrogen abstraction reaction. Fortunately, it is possible to resolve these questions by generating methyl radicals in benzene from acetyl peroxide, and by analysing the higher molecular weight reaction products from this reaction in the same way.

[1] J. H. T. Brook and R. W. Glazebrook, *Trans. Faraday Soc.* **56**, 1014 (1960).
[2] D. R. Augood and G. H. Williams, *Chem. Rev.* **57**, 77 (1957).
[3] C. Walling, *Free Radicals in Solution* p. 482. Wiley, New York (1957).
[4] G. H. Williams, *Homolytic Aromatic Substitution*. Pergamon, London (1960).

EXPERIMENTAL

Reagents. "AnalaR" benzene was shown by gas-liquid chromatography (GLC) to contain saturated hydrocarbons and toluene in small amounts. It was satisfactorily purified by recrystallization at 0°. After 4 recrystallizations, the benzene contained less than 20 ppm of toluene and was free from other impurities.

Di-t-butyl peroxide (DTBP) (from L. Light and Co. Ltd.) had less than 1% of impurity.

Acetyl peroxide was prepared by the method of Price and Morita.[5] The peroxide was not isolated, but was prepared as a solution in benzene.

Analysis

(i) *Determination of acetone, t-butanol and toluene.* After the decomposition of about 0·2 g DTBP in 10 g benzene, sealed *in vacuo* in a glass tube, 0·5 ml samples of the resulting solution were developed on a wide-bore GLC column (50 cm × 1·5 cm) of dinonyl phthalate on Celite 545. The emergent fractions of acetone, t-butanol and toluene were trapped in U-tubes cooled in liquid air. The concentrated samples were then vaporized into a Griffin and George GLC apparatus, with a polyethylene glycol/Celite 545 packing, for analysis. This procedure avoided swamping the analytical GLC apparatus with benzene.

(ii) *Determination of methane.* Methane was determined after decomposing about 0·2 g DTBP in 10 g benzene in a glass tube equipped with a break-seal. The tube was attached to a gas burette and cooled in a slurry of solid carbon dioxide. The seal was broken, and the tube warmed to room temp and then cooled to −78°. Gas evolution was measured on the burette. The gas was shown by mass spectrometric analysis to be essentially methane, with no ethane.

(iii) *Examination of "dimer" products.* (a) 0·2 g of DTBP, or the equivalent amount of acetyl peroxide, in 300 ml benzene (0·004 molar), was either sealed *in vacuo* in glass ampoules or sealed in a steel bomb under N_2 ("white-spot" grade), after thorough removal of oxygen by repeated freezing and melting. The samples were heated in oil baths for four half-lives[6,7] of the peroxide and then transferred to a distillation flask, where the bulk of the excess benzene was removed (atm. press. under a current of N_2). The residues were placed in a small distillation apparatus and the remainder of the benzene was evaporated under N_2.

The volatile portion of the residues was then distilled into a sample tube at a pressure of 0·1 mm Hg, with a pot temp not exceeding 130°. The sample tube was then sealed to await further processing. The sealed sample was subsequently analysed by mass spectrometry, either as such or after dehydrogenation or hydrogenation.

(b) Dehydrogenation was accomplished by adding the sample, and 1 ml of undecane, to 1 g of 5% Pt on SiO_2 catalyst, and refluxing under a slow stream of N_2 for 3 hr. At the temp used, 195°, cracking and isomerization of the hydrocarbons was unlikely to occur. The dehydrogenated products were then recovered by chromatography on Davidson 923 silica gel. After development with light petroleum spirit, the aromatics were desorbed with ether and, after evaporation of the ether, examined mass spectrometrically.

(c) Hydrogenation was carried out in a small shaking apparatus at atm. temp and press., with cyclohexane as solvent and Adams PtO_2. The products were examined mass spectrometrically. As the spectrum was more complicated than that of the dehydrogenated products, the hydrogenation procedure was used on two samples only.

The mass spectrometer analyses were performed on an Associated Electrical Industries Ltd. model MS 2(H) mass spectrometer. Instrument conditions were as follows: ionizing current—30 μÅ; ionizing voltage (uncorrected)—10 volts; ion accelerating voltage—2000 volts; source temp—230° C. Magnet scanning was used throughout. Samples were admitted via an all-glass heated inlet of the gallium covered sinter type[8] at a temp of 150°C. This temp was considered adequate to vaporize the whole of the distillates (b.p. up to 130°C at 0·1 mm) without fractionation of the species present.

The ionizing voltage used in the present study was selected by observing the spectra of pure biphenyl at progressively decreasing ionizing voltage. The maximum voltage (10 volts) for which

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[5] C. C. Price and H. Morita, *J. Amer. Chem. Soc.* **75**, 3686 (1953).

[6] J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Amer. Chem. Soc.* **70**, 1336 (1948).

[7] J. A. Offenbach and A. V. Tobolsky, *J. Amer. Chem. Soc.* **79**, 278 (1957).

[8] J. H. Beynon, *Mass Spectrometry* p. 162. Elsevier, Amsterdam (1960).

only the parent molecule ions were produced was used for all subsequent quantitative observations. Under these conditions, homologues of biphenyl or higher polyphenyls would not be expected to produce intense fragment ions.[9]

For identification purposes, spectra of all samples were also obtained at 70 volts. Under these conditions, the presence of biphenyl and methyl biphenyl in the dehydrogenated samples was confirmed by comparison with reference spectra.[10] No reference spectra of the partially aromatic species are available hence their identity is somewhat less certain.

RESULTS

1. *Determination of acetone, t-butanol and toluene in the products*

Table 1 records the yields of acetone, t-butanol and toluene in experiments in which the temp and the initial concentration of DTBP were varied. Small corrections have been made to allow for the incomplete decomposition of peroxide in the experiments.

TABLE 1. VOLATILE PRODUCTS FROM THE DECOMPOSITION OF DTBP IN BENZENE

Temperature, °C	Initial peroxide concentration, mole/kg	Acetone	t-Butanol	Toluene	Recovery, %
		mole/mole peroxide decomposed			
110	0·196	1·32	0·50	—	91
130	0·119	1·40	0·42	0·45	91
135	0·309	1·40	0·38	0·40	90
135	0·175	1·40	0·32	0·40	86
135	0·111	1·41	0·30	0·44	85

85–91% of DTBP was accounted for as acetone and t-butanol. This recovery is a little low by comparison with the 95–96% recoveries which may be observed in tests with hydrocarbons having more reactive hydrogen atoms than those of benzene, and indicates that some 5–10% of the butoxy radicals have been incorporated in reaction products which have not been identified.

The yield of butanol at 135° is not independent of the initial peroxide concentration. The rather greater yield at the highest peroxide concentration suggests that the butoxy radical abstracts some hydrogen from the reaction products. The butanol yield diminishes with rising temp because of the greater tendency of butoxy radicals to decompose to acetone and methyl radicals.

2. *Determination of methane*

The apparatus used was too crude to make generally reliable analyses for methane. In two experiments 1·35 mmoles methane were produced from the decomposition of 2·57 mmoles DTBP, and 1·01 mmole methane from 1·79 mmoles DTBP, both in 10 g benzene, at 135°. These yields correspond to 0·51 and 0·56 mole per mole DTBP respectively. The gas was shown by mass spectrometric analysis to contain no ethane.

3. *Analysis of "dimer" reaction products*

In order to preserve as far as possible the initial reaction products from further attack by t-butoxy and methyl radicals, experiments were conducted with very dilute solutions of DTBP (or acetyl peroxide) in benzene, and care was taken to avoid oxidation of the dimeric products when the benzene and lighter reaction products were distilled off.

Mass spectrometric analysis of the distilled dimer fraction with an inlet system temp of 150° and at low ionizing voltages showed strong peaks at mass numbers 78, 92 and 106 corresponding to benzene, toluene and xylene (Fig. 1). These compounds are unlikely to be present, and the peaks were probably due to fragmentation products of substituted cyclohexadienes. Their presence complicates the analyses. It was therefore desirable to stabilize the cyclohexadienes before analysis, and this was accomplished by hydrogenation or dehydrogenation procedures. The dehydrogenated

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[9] H. E. Lumpkin, *Analyt. Chem.* **30**, 321 (1958).

[10] American Petroleum Institute, Research Project 44, Catalogue of Mass Spectral Data.

TABLE 2. MASS-SPECTROMETRIC ANALYSIS OF DEHYDROGENATED DIMER FRACTION FROM THE DECOMPOSITION OF DTBP AND ACETYL PEROXIDE IN BENZENE

Peroxide concentration: 5×10^{-3} mole/litre

Peroxide	Reaction temperature, °C	Normalized peak heights for species*						
		Diphenyl	Methyl-diphenyl	Dimethyl-diphenyl	Trimethyl-diphenyl	Terphenyl	Methyl-terphenyl	Dimethyl-terphenyl
DTBP	115	42	33	21	2	0·5	1·5	—
DTBP	135	21	38	30	—	3	8	—
DTBP	135	33	29	31	2	1	2	0·5
DTBP	135	32	33	24	—	3	5	0·8
DTBP	150	14	41	38	3·5	1	2	0·5
Ac_2O_2	80	0	14	80	2	—	1·0	0·4
Ac_2O_2	100	0	0	97	2	←	1·0	→
Ac_2O_2	100	0	0	97	2	←	1·0	→

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* Substitution isomers not distinguished mass-spectrometrically.

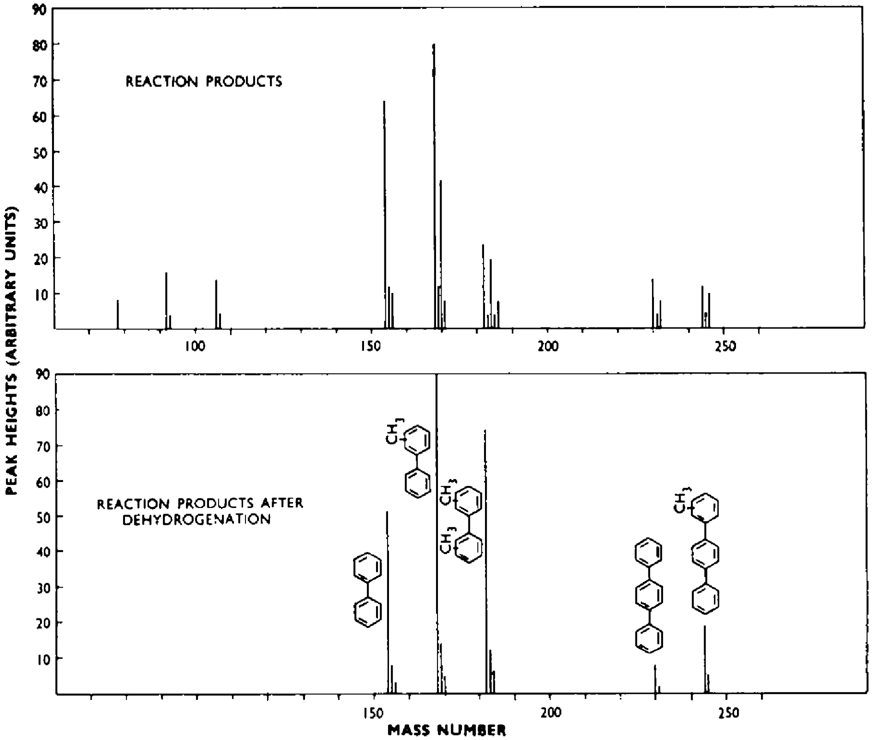


FIG. 1

samples gave very simple mass spectra (Fig. 1), completely free from fragment ions, and it was found convenient to apply this procedure before analysis of the dimer fraction was attempted.

Mass spectrometric analyses of the dehydrogenated fractions are shown in Table 2 in which the relative peak heights are taken to represent the relative abundance of the various components. The three experiments with DTBP at 135° do not show good repeatability. The distillation stage in the work-up procedure is probably responsible for this, as spectra on residual products have been more closely reproducible. However, for semi-quantitative purposes, the results serve to show what products are present, and which predominate.

A full analysis of the hydrogenated products is shown in Table 3. The distribution of isomers shown is speculative: the presence of components of different molecular weight is shown by the spectrum. The assumption that peak heights represent abundances of the various species is perhaps less tenable than for the related, fully aromatic species.

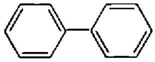
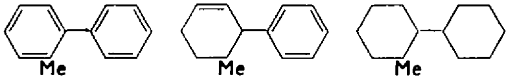
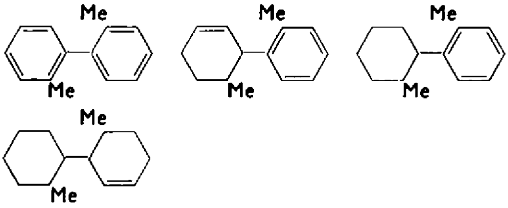
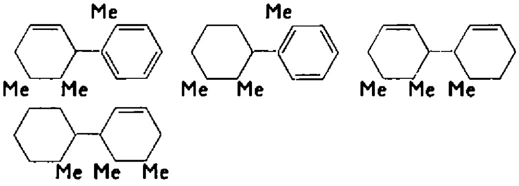
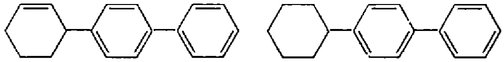
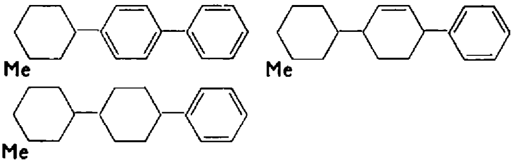
Product balances for the reactions are presented in Table 4. For brevity, a composite table is shown. The yields of t-butanol, acetone, methane and toluene are derived from experiments at a peroxide concentration of 0·175 mole/kg, and the yields of dimer products, based upon an average composition of the dehydrogenated dimer, were derived from experiments at peroxide concentrations of 5×10^{-3} mole/litre.

DISCUSSION

The decomposition of di-t-butyl peroxide in benzene solution yields t-butoxy radicals as the primary product. Most of these radicals decompose in their turn to yield acetone and methyl radicals but of those that do not, about half appear as t-butanol, having abstracted hydrogen from some species in solution, and half are not accounted for. The methyl radicals formed by the decomposition of the t-butoxy radicals are the predominant reagent radicals in the system, and their fate is accounted for in the product balance: very roughly one third appears in the final products as

TABLE 3. MASS-SPECTROMETRIC ANALYSIS OF HYDROGENATED DIMER FRACTION FROM DECOMPOSITION OF DTBP IN BENZENE AT 135°

Peroxide concentration: 5×10^{-8} mole/litre

Number of carbon atoms	%*	Compounds present† (roughly equal amounts in each group)
12	39	
13	40	
14	15	
15	2	
18	1	
19	2·5	

* Assuming equal sensitivities.

† Isomer distribution unknown.

methane, one third appears as toluene, and one third is incorporated in hydrocarbon products in the C_{12}–C_{20} molecular weight range.

The formation of methane and toluene has been studied before[11,12] and, accordingly, we have concentrated on the examination of the hydrocarbons of higher molecular weight which are formed in quite large amounts. Our earlier work[1] suggests that they should be formed by the coupling of free radicals derived from benzene, and that their identification should reveal what radicals have been present in the system.

However, caution should be exercised before drawing conclusions from the mass spectrum of unknown compounds, since they may rearrange or break up under electron bombardment, and in particular, a misleading impression may be given of the relative amounts of the species present if the parent peak (at the mass number corresponding to the molecular weight) is small. The most satisfactory way of treating

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[11] M Levy and M. Szwarc, *J. Amer. Chem. Soc.*, 77, 1949 (1955).

[12] M. Szwarc, *J. Phys. Chem.*, 61, 40 (1957).

TABLE 4. PRODUCT BALANCE FOR REACTION OF 50 MMOLES DTBP WITH BENZENE AT 135°

Product	Weight, g	mmoles	Hydrogen gain or loss (mg atoms)
t-Butanol	—	16	+16
Acetone	—	70	—
Methyl radicals[a]	—	70	—
Methane	—	28	+28
Toluene	—	20	−20
C_{12}–C_{16} hydrocarbons[b]	2·70	18·7	−19
C_{18}–C_{20} hydrocarbons[c]	0·42	1·7	—
Undistilled polymer	0·85	—	—
Loss of t-BuO· (to polymer?)[a]		14	
Loss of CH_3·		1	
Gain of hydrogen (from polymer?)		—	5

[a] t-Buo· = t-BuOH + acetone + loss; CH_3· = acetone.

[b] On average, one mole of dimer contains 1 mole methyl radicals.

[c] One mole of C_{18}–C_{20} hydrocarbons attributed 1 mole methyl radicals; hydrogen deficit not estimated.

The loss of t-butoxy radicals observed in these experiments, averaging 14%, is probably to be accounted for in the appreciable undistilled polymer fraction. The formation of this polymer is more pronounced in the experiments with DTBP than in the corresponding acetyl peroxide decompositions.

the products from the decomposition of di-t-butyl peroxide in benzene is to dehydrogenate them under mild conditions, so as to convert cyclohexadienes to the fully aromatic species which are known to give only parent peaks in the mass spectrometer. It is then possible to identify the aromatic hydrocarbons with certainty.

The value of doing this is well illustrated by the results in Fig. 1. The mass spectrum of the untreated reaction products shows fragmentation peaks at relatively low mass which are missing from the spectrum of the dehydrogenated reaction products. The peaks due to C_{13} and C_{14} hydrocarbons are larger, with respect to the C_{12} peak, in the spectrum of the dehydrogenated products, and it is evident that the original C_{13} and C_{14} hydrocarbons have decomposed quite extensively in the mass spectrometer.

The peaks at mass numbers 154, 168 and 182 in the mass spectrum of the dehydrogenated products correspond to diphenyl, methyldiphenyl and dimethyldiphenyl. The presence of diphenyl shows that phenyl radicals have been formed in the reaction between di-t-butyl peroxide and benzene. In contrast, the decomposition of acetyl peroxide in benzene (Table 2) yields no diphenyl and it follows that phenyl radicals are produced by the reaction of t-butoxy radicals, rather than methyl radicals, with benzene. The diphenyl may have been formed either by the reaction of phenyl radicals with benzene to give diphenyl and phenylcyclohexadiene,[13] or by the combination of two phenyl radicals. The formation of the C_{14} hydrocarbon is obviously due to the coupling of two C_7 radicals and may be attributed to the combination of two methylcyclohexadienyl radicals; and, judging from the products formed in the acetyl peroxide experiments in which phenyl radicals are not generated, the C_{13} hydrocarbon is produced by the combination of phenyl and methylcyclohexadienyl radicals, rather

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[13] D. F. de Tar and R. A. J. Long, *J. Amer. Chem. Soc.* **80**, 4742 (1958).

than by the attack of methylcyclohexadienyl radicals upon benzene. In none of the experiments did the relative proportions of C_{12}, C_{13} and C_{14} hydrocarbons approach a binomial distribution, as would have been expected if they had been formed exclusively by the combination and cross-combination of phenyl and methylcyclohexadienyl radicals. It is therefore likely that the C_{12}, C_{13} and C_{14} products are formed by two types of reaction, the combination and cross-combination of the radicals and the reaction of phenyl radicals with benzene, and it is difficult to estimate the relative amounts of phenyl and methylcyclohexadienyl radicals produced in the reaction.

The examination of the reaction products after dehydrogenation has proved quite satisfactory insofar as the mass spectrum obtained is simple and easily interpreted, but the disadvantage of this approach is that it does not discriminate between cyclohexadienes and aromatic species originally present. This could be overcome by hydrogenating the reaction products before they are submitted to mass spectrometric analysis, so as to convert cyclohexadienes to the easily recognised cyclohexanes.

The results of hydrogenation experiments proved to be more complex. The C_{12} hydrocarbon found was diphenyl. The mixture of C_{13} hydrocarbons produced contained methyldiphenyl, methylphenylcyclohexene (derived from the hydrogenation of methylphenylcyclohexadiene) and methylcyclohexylcyclohexane. The C_{14} hydrocarbons comprised dimethyldiphenyl and three hydrocarbons containing hydrogenated rings, namely, dimethylphenylcyclohexene and the corresponding cyclohexane and dimethylcyclohexenylcyclohexane. It therefore appears that the hydrogenation of cyclohexadienes to cyclohexanes did not proceed to completion, and that some of the cyclohexadienes dehydrogenated on the catalyst, or during the isolation procedure.[14] Qualitatively, however, the hydrogenation experiments showed that the C_{13} and C_{14} hydrocarbons hydrogenated extensively and therefore were probably cyclohexadienes. The experiments failed to confirm the presence of phenylcyclohexadiene in the original reaction products although this must have been formed from the reaction of phenyl radicals with benzene.[13]

From these experiments we conclude that t-butoxy radicals abstract hydrogen atoms from benzene to produce phenyl radicals, but methyl radicals add to benzene, in accordance with predictions based on kinetic studies.[12] It seems certain that methyl radicals under our conditions are quite unable to abstract hydrogen from benzene, but we have not been able to show with a similar degree of certainty that methylcyclohexadienyl radicals are produced. The results are however quite consistent with the formation of these radicals.

At present, it is not possible to advance reasons why the reactions of t-butoxy and methyl radicals towards benzene should be so dissimilar. There is not enough known about the possible transition states nor, of course, whether other alkoxy radicals behave in the same way as t-butoxy. The bond-dissociation energies of C–O bonds in ethers[15] are typically 6–9 kcal lower than those of the C—C bonds in similar hydrocarbons.[16] The t-butoxy radical may, therefore, bond more readily to hydrogen than to carbon, but other factors which are not yet well understood may in fact determine the course of the reaction.

[14] M. Eberhardt and E. L. Eliel, *J. Org. Chem.* **27**, 2289 (1962).

[15] P. Gray and A. Williams, *Chem. Rev.* **59**, 239 (1959).

[16] T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworth (1954).