

Thermolysis of Bis(diarylmethylenecarbamoyl) Peroxides

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Diacyl peroxides of structure $(XC_6H_4)_2C=N-C(=O)OOC(=O)-R$ ($R=(XC_6H_4)_2C=N$, $X=H$ (**1**), $X=2-CH_3$ (**3**), $X=4-CH_3$; $R=4-ClC_6H_4$, $X=H$ (**2**)) have been prepared by the reaction between the corresponding carbamoyl chloride and hydrogen peroxide-urea complex in the presence of pyridine or between the carbamoyl chloride and 4-chloroperbenzoate in anhydrous ether at low temperature. Thermolysis of **1**—**3** follows first order kinetics. The large rates of thermolysis of **1** and **3** relative to those of bis(diphenylmethylenecarbonyl) peroxide have been ascribed to steric compressions of **1** and **3** in the ground state and to the concerted cleavage of three bonds. Stable diphenylmethylenecarbonyl radicals do not substitute in toluene by themselves but they do with the aid of aryloxy radicals. The iminyl radicals abstract hydrogen from the methyl group of toluene, and the rate constant has been estimated to be 5×10^2 — 2×10^3 $M^{-1}s^{-1}$ at 50 °C.

The rates of the addition reactions of acyloxy radicals to benzene relative to those of their decomposition reactions to give carbon dioxide and aryl or alkyl radicals have been studied.¹⁾ During the course of the studies it has been found that some of the ortho substituents in aryloxy radicals such as methoxyl and bromo groups exhibited an increase in the activation energies for the decomposition of aryloxy radicals.²⁾ The activation energy of the decomposition of cinnamoyloxy radicals was also higher than that of benzoyloxy radicals.²⁾ Studies on these phenomena could disclose the exact manner of the carbon dioxide cleavage of acyloxy radicals. Investigation of methylenecarbamoyloxy radicals would enable clarification of the nature of the $=N-CO_2$ bond in comparison with the $=CH-CO_2$ bond. Since the bond dissociation energies of $C-N$ are 2—9 kcal/mol smaller than those of $C-C$ bonds,³⁾ some amount of concerted multibond fission in the thermolysis of the peroxides having a $=N-CO_2$ structure is expected. This work also aimed to confirm the reactivity of N-centered radicals, of which increasing interest has been recently shown in reviews on aminyl radicals,⁴⁾ hydrazynyl radicals,⁵⁾ and aminium radicals.⁶⁾

Results and Discussion

Preparation of Bis(diarylmethylenecarbamoyl) Peroxides. The preparations of bis(diarylmethylenecarbamoyl) peroxides were difficult due to the hydrolysis of carbamoyl chloride. Carbamoyl chlorides, when treated with a hydrogen peroxide-urea complex⁷⁾ and pyridine in anhydrous ether under cooling at -20 °C were however successful in the preparation of the peroxides.

Bis(di-2-methylphenylmethylenecarbamoyl) peroxide (**3**) is very labile and on standing at room temperatures turns yellow in a few minutes. The CH-analysis of the peroxide agrees fairly well with the calculated values, but the active oxygen determinations gave values below 100%: the di-2-methylphenyl compound **3** gave 67%, the di-4-methylphenyl peroxide **5** 85%, and the diphenyl peroxide **1** 86%, in comparison with bis(diphenylmethylenecarbonyl) peroxide (**4**) 97%. The low values of active oxygen suggest a fast breakdown of the $=N-CO_2$ bond, yielding iminyl radicals, which are reduced slowly.

Product Studies. Products formed in the thermo-

lysis of **1** and **2** in toluene at 50 and 100 °C, respectively, are given in Table 1.

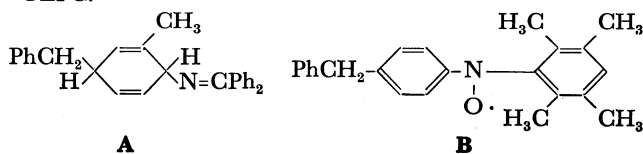
During the thermolysis of **2** the absorption bands at 1740, 1700, and 1280 cm^{-1} , presumably the 4-chlorobenzoate of benzophenone oxime and 4-chlorobenzoic acid appear, and increase in intensities. The same appearance of absorption bands, however, was not found in the case of **1**.

Diphenylmethylenecarbonyl radicals abstract hydrogen from the methyl group of toluene. Diphenylmethylenecarbamoyloxy radicals, if formed, lose carbon dioxide very rapidly, so that the carbamoyloxy radicals hardly add to the solvent toluene. The fast cleavage of carbon dioxide from diphenylmethylenecarbamoyloxy radicals was partly suggested by the iodometric determination of active oxygen, giving 67—86% of the theoretical value, and partly by the experiments, attempting to prepare methyltetraphenylmethanes by the reaction between **1** and triphenylmethyl radicals in toluene. This reaction is applicable to benzoyl peroxide,^{1a)} but it was not successful in the case of **1**.

TABLE 1. PRODUCTS FORMED IN THE THERMOLYSIS OF BIS(DIPHENYLMETHYLENECARBAMOYL) PEROXIDE AND OF 4-CHLOROBENZOYL DIPHENYLMETHYLENECARBAMOYL PEROXIDE IN TOLUENE^{a)}

Product	Peroxide	
	$(Ph_2C=NCOO)_2$ at 50 °C	$ClC_6H_4COOOCN=$ CPh_2 at 100 °C
$Ph_2C=NH$	71.5	26.3
$Ph_2C=N-CH_2Ph$	14.7	0.8
$(Ph_2C=N-)_2$	35.2	3.2
$PhCH_2C_6H_4CH_3$ -(3)	1.2	—
$PhCH_2CH_2Ph$	0	5.0
$Ph_2C=N-C_6H_4CH_3$ -(2)	0	1.8
-(3)	0	2.5
-(4)	0	1.4

a) Yield in mol % per mole peroxide, determined by GLPC.



Although benzoyloxy radicals add to the solvent toluene under these reaction conditions, they do not appreciably abstract hydrogen from toluene. In the thermolysis of **1** therefore it is expected that the hydrogen abstraction by diphenylmethylenecarbamoyloxy radicals does not occur and diphenylmethylenamine would be formed solely by the reaction of the iminyl radicals.

Hydrogen sources responsible for the high yield of diphenylmethylenamine from **1** and **2** have not been explained well: some of the diphenylmethylenamine could be formed in secondary reactions. In the thermolysis of **1** a small amount of *m*-tolylphenylmethane was found (1.2%). Its precursor would be an adduct of the benzyl radical to toluene trapped by the diphenylmethylenamine radicals, **A**, which on heating will give diphenylmethylenamine and *m*-tolylphenylmethane. A similar addition of benzyl radicals to benzene has been observed in spin trapping experiments of the thermolysis of azobisphenylmethane in benzene in the presence of 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene), yielding nitroxide **B**.⁹⁾

Bis(diphenylmethylen)hydrazine has been reported to give diphenylmethylenamine and other compounds on heating at 375–500 °C.⁹⁾ During the GLPC determination of bis(diphenylmethylen)hydrazine at 220 °C, however, no formation of the imine was observed. In the thermolysis of **2** the presence of the ester of benzophenone oxime was suggested by IR spectra, and the suggestion was that the ester might give diphenylmethylenamine in the GLPC determination.

In the thermolysis of **1**, 3,3'-dimethylbiphenyl was not detected. If the iminyl radicals can add to toluene to give (diphenylmethylenamino)methylcyclohexadienyl radicals, the cyclohexadienyl radicals could subsequently dimerize and decompose yielding dimethylbiphenyl and diphenylmethylenamine. The formation of biphenyl and ammonia by the reaction mechanism between amino radicals and benzene has been suggested.¹⁰⁾

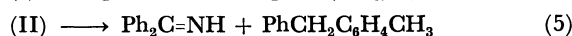
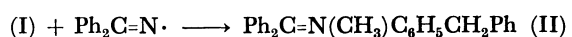
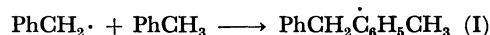
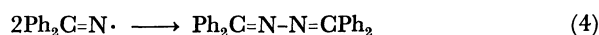
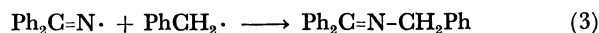
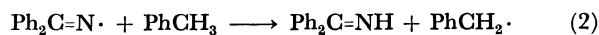
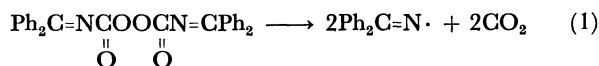
Further marked differences between the products from **1** and **2** are that no bibenzyl and no (diphenylmethylenamino)toluenes were formed from **1**, but were produced from **2**. The (diphenylmethylenamino)toluenes from **2** were composed of more meta isomer than ortho and para derivatives. The substitution at the meta position of toluene by diphenylmethylenamino radicals agrees with the findings of Ishikawa *et al.*¹¹⁾ in the photolysis of the benzoate and the 4-chlorobenzoate of benzophenone oxime in toluene. The substitution of diphenylmethylenamino radicals proceeds probably *via* the intermediate aroyloxy-cyclohexadienyl radicals as in the case of the homolytic triphenylmethylation of toluene in the reaction between triphenylmethyl radicals and benzoyl peroxide in toluene.^{1a)} Diphenylmethylenamino radicals do not substitute in toluene by themselves but they do with the aid of aroyloxy radicals.

During the thermolysis of **2** the concentration ratio (PhCH₂·)/(Ph₂C=N·) will be larger than that in the case of **1**, since the half moiety of the peroxide mole-

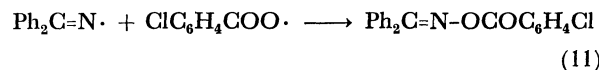
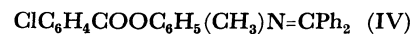
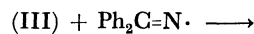
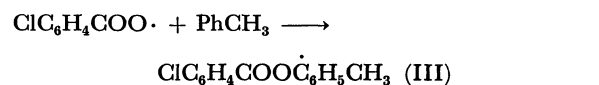
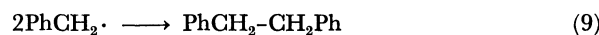
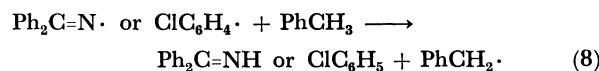
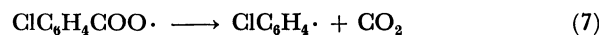
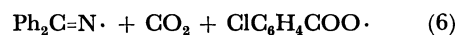
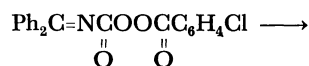
cule **2** is chlorobenzoyloxy and 4-chlorophenyl radicals derived from the aroyloxy radicals are effective in abstracting hydrogen. Two benzyl radicals more frequently combine together in the thermolysis of **2** than in the case of **1**.

For the thermolysis of **1** and **2** the following scheme can be formulated.

For **1**



For **2**



Reactions (3) and (4).

Kinetic Studies. Peroxides **1**–**4** were decomposed in benzene and in toluene under nitrogen. The rate of decomposition was followed by observing the decrease in absorption bands $\nu_{\text{C}=\text{O}}$ (1775 cm⁻¹), $\nu_{\text{O}=\text{O}}$ (1095 cm⁻¹ for **1** and **3**, 1065 cm⁻¹ for **4**), and $\nu_{\text{C}-\text{O}}$ (1195 and 1120 cm⁻¹ for **2**). The change of toluene for benzene caused no effect in the rates. The decompositions followed first order kinetics and the activation parameters are given in Table 2. The extent of the free radical decomposition of **1** was 99% (DPPH) and 90% (Galvinoxyl) at 50 °C. The value for **2** was 81% (DPPH). These results indicate homolytic reactions for **1** and **2**, accompanied by a small degree of cage reaction for **2** (about 20%). Reaction 11 in the Scheme is a cage reaction.

The very fast and nearly complete homolyses of **1** and **2** are characterized by small activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$. *t*-Butyl peroxy-carbamate were reported to decompose *via* a homolytic pathway to the extent of 73–95%,¹²⁾ although the ESR studies on the

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THERMOLYSIS OF **1**, **2**, **3**, AND **4** TOGETHER WITH THOSE OF BENZOYL PEROXIDE AND *t*-BUTYL DIPHENYLMETHYLENEPEROXYCARBAMATE

Peroxide	k^a min ⁻¹	Temp °C	ΔH^* ^{b)} kcal/mol	ΔS^* ^{c)} cal/mol, deg
1	$1.06 \cdot 10^{-2}$	40	24.2	+ 1
2	$1.91 \cdot 10^{-3}$	50	27.7	+ 6
3	$3.87 \cdot 10^{-2}$	40	21.9	+ 5
4	$2.24 \cdot 10^{-2}$	50	25.4	+ 12
(C ₆ H ₅ COO) ₂	$1.16 \cdot 10^{-4}$	60	32.7	+ 13.3 ^{d)}
	$7.02 \cdot 10^{-4}$	78 ^{e)}		
Ph ₂ C=NCOOBu ^t O	$1.09 \cdot 10^{-5}$ ^{f)}	50	29.8	+ 7

a) Error $\pm 3\%$ for **1**–**4**. b) Error ± 0.8 kcal/mol. c) Error ± 2 eu. d) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958). e) G. B. Gill and G. H. Williams, *J. Chem. Soc.*, **1965**, 995. f) Calculated using the rate constant $22.1 \times 10^{-4} \text{ s}^{-1}$ at 130 °C and the ΔH^* . (cf. Rüchardt and R. Pantke, *Ann.*, **762**, 88 (1971)).

photochemical decomposition of *t*-butyl *N*-alkylperoxy-carbamates showed the presence of the alkylbutyloxyamino radicals instead of the alkylamino radicals.¹³⁾ Examination of the decomposition of **1** in toluene at 50 °C by the ESR technique showed formation of diphenylmethylenamino radicals in about 10^{-5} M from the peroxide in 3×10^{-2} molar concentration. The spectrum of the iminyl radical (triplet of septets, a_N 10.20 G and a_H 0.34 G) agrees exactly with those reported by Hudson *et al.*,¹⁴⁾ in the study of thiocarbamate of benzophenone oxime.

The activation enthalpies and entropies of **1** and **3** are smaller than those of benzoyl peroxide, and the situation is the same for **2** but to a smaller extent. These results suggest a concerted cleavage of three bonds in a manner similar to those of peresters investigated by Bartlett and Hiatt.¹⁵⁾ The activation enthalpy for peroxide **4** is about 5 kcal/mol smaller than that of benzoyl peroxide, contrary to almost the same value of activation entropy for both peroxides. This indicates an appreciable assistance in thermolysis caused by the phenyl groups, resulting in an elevation of the energy of the ground state due to steric compression. Steric compression by phenyl groups is also expected in the peroxides **1**–**3**. In **1**–**3** some reorganization of bonds is operating in the transition state, leading to a decrease in the activation entropy: partial formation of stable free radicals Ph₂C=N· and carbon dioxide will be the cause of the reorganization of the bonds.

The methyl substituents in the peroxide **3** make the steric compression more serious and the conformations of tolyl groups in the ground state resembles those of ditolylmethylenamino radicals as suggested by Symons.¹⁶⁾ A much smaller ΔH^* and a moderate decrease in ΔS^* arises from these situations.

The smaller rate constant for **2** than that for **1** implies a marked contribution of the diphenylmethylenamino group to the thermolysis rate. In general the rates of decomposition of asymmetric diacyl peroxides are larger than the symmetric ones, owing to the polar effect of asymmetric structure in the transition state. Walling *et al.*¹⁷⁾ and Leffler and More¹⁸⁾ have discussed the effect of the polar nature in the transition state.

The effect of the asymmetric structure of **2** on the rate of decomposition is probably a minor one in the presence of the diphenylmethylenamino group.

Promotion of the decomposition by non-bonding electrons on nitrogen atoms through donation to the O–O bond will be of minor importance because the conformation **C** is more hindered than that of **D** owing to the bulkiness of the diphenylmethylenamino groups. In the conformation **C** the phenyl groups P₁, P₂, P₁', and P₂' come near to each other more seriously than the phenyl groups P₂ and P₁' do in the conformation **D**. Consequently the former conformation will be destabilized more than the latter. The participation of the non-bonding electrons on nitrogen in electron donation to the O–O bond would be facilitated if the σ^* orbital of the O–O bond overlaps strongly with the non-bonding orbital of nitrogen. The favorite conditions for overlapping can be expected more in conformation **C** than in **D**. (Fig. 1).

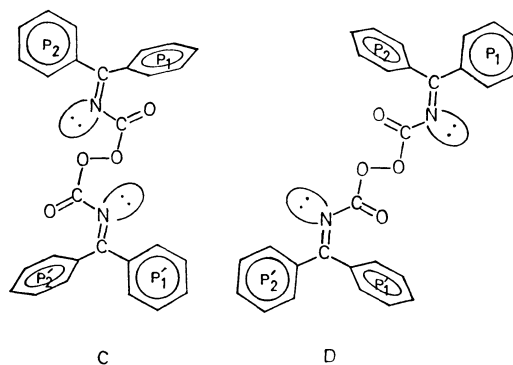


Fig. 1.

Estimation of Rate Constant of Hydrogen Abstraction Reaction of Diphenylmethylenamino Radical from Methyl Group of Toluene.

The main products of the thermolysis of **1** in toluene at 50 °C were diphenylmethylenamine, 71.5%, *N*-(diphenylmethylenamino)benzylamine, 14.7%, and bis(diphenylmethylenamino)hydrazine, 35.2%. Although the yield of diphenylmethylenamine was as high as 71.5%, the formation of the methylenamine was not solely confined to Reaction 2. If all diphenylmethylenamine were produced by the process, Reaction

2, then the termination reaction products of benzyl radicals, which were formed in the Reaction 2, should be detected in an equal amount as diphenylmethylenamine. *N*-(Diphenylmethylene)benzylamine and *m*-tolylphenylmethane have been determined together in 15.9% and a large amount of benzyl radicals (about 55%) could not be explained. For simplification it has been assumed that diphenylmethylenamine radicals abstract hydrogen from toluene to an extent to yield benzyl radicals in *ca.* 15% per mole peroxide and that diphenylmethylenamine was also produced *via* an unknown parallel process, 55%. Based on these assumptions the rate constant k_2 of the reaction sequences of Eqs. 2—4 can be estimated assuming a steady state in benzyl radicals, if k_4 and the stationary concentration of the diphenylmethylenamine radicals (N) were known. Thus the Relation 12 is obtained:

$$\frac{d(\text{ketazine})/dt}{d(\text{diphenylmethylenbenzylamine})/dt} = \frac{k_4(\text{N})^2}{k_3(\text{N})(\text{benzyl radical})} = \frac{k_4(\text{N})^2}{k_2(\text{N})(\text{toluene})} \quad (12)$$

The value of k_4 was reported to be $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at -35°C .¹⁹ At 50°C k_4 will be $10^9 \text{ M}^{-1} \text{ s}^{-1}$. The stationary concentration of the iminyl radicals was assumed by ESR technique to be 10^{-5} M at 50°C in toluene when a solution of **1** in $3 \times 10^{-2} \text{ M}$ was used. Setting (toluene) = 10 M, gives

$$k_2 = 5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}.$$

This is the lower limiting value of k_2 . Another estimation will give maximum of k_2 , if we assume that Reaction 2 is the sole process for the formation of diphenylmethylenamine and that benzyl radicals in 55% per mole are ignored in the determination. From Relation 13,

$$\frac{d(\text{ketazine})/dt}{d(\text{diphenylmethylenamine})/dt} = \frac{k_4(\text{N})^2}{k_2(\text{N})(\text{toluene})}, \quad (13)$$

$$k_2 = 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}.$$

The rate constant $5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ of diphenylmethylenamine radicals for the hydrogen abstraction reaction from toluene at 50°C is larger than the value $23 \text{ M}^{-1} \text{ s}^{-1}$ of trichloromethyl radicals from cyclohexane at 40°C ,²⁰ and $2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ of *t*-butylperoxy radicals from toluene at 30°C .²¹ These can be explained in terms of heats of reaction using bond dissociation energies,²² N-H , $\text{PhCH}_2\text{-H}$, $\text{Cl}_3\text{C-H}$, $\text{C}_6\text{H}_{11}\text{-H}$, and *t*-BuOO-H of ≥ 95 , 85, 96, 94, and 90 kcal/mol, respectively.

Experimental

Peroxides. Diarylmethylenecarbamoyl chlorides were prepared by the reaction between diarylmethylenamine and phosgen or oxalyl chloride by the method of Samaraj and others.²³ To a mixture of diarylmethylenecarbamoyl chloride and a 20% excess of hydrogen peroxide-urea complex⁷ in dry ether was added at -20°C a 20% excess of pyridine in ether under stirring. Stirring was continued for 5 h and the mixture treated to the usual work up. Recrystallization of peroxide was effected from dichloromethane-methanol.

$(\text{Ph}_2\text{C}=\text{NCOO})_2$ (**1**). Yield 18%. Mp $108\text{--}108.5^\circ \text{C}$,

dec. Active oxygen determined by iodometry was 86% of the theoretical value. Found: C, 74.71; H, 4.52; N, 6.21%. Calcd for $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_4$: C, 74.99; H, 4.50; N, 6.25%.

$4\text{-ClC}_6\text{H}_4\text{COOCON}=\text{CPh}_2$ (**2**). Sodium 4-chloroperbenzoate, prepared from peracid and sodium hydride, was set in dry ether at -15°C and to this was added diphenylmethylenecarbamoyl chloride. Yield 66%. Mp $98.5\text{--}99^\circ \text{C}$, dec. Found: C, 66.34; H, 3.54; N, 3.70%. Calcd for $\text{C}_{21}\text{H}_{14}\text{NO}_4\text{Cl}$: C, 66.41; H, 3.72; N, 3.68%.

$((2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{C}=\text{NCOO})_2$ (**3**). Yield 16%. Mp $78\text{--}80^\circ \text{C}$, dec. Active oxygen by iodometry 67%. Found: C, 75.77; H, 5.50; N, 5.40%. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_4$: C, 76.18; H, 5.59; N, 5.55%.

$(\text{Ph}_2\text{C}=\text{CHCOO})_2$ (**4**). Diphenylmethylenecacetyl chloride, prepared from 1,1-diphenylethylene and oxalyl chloride,²⁴ was transformed to peroxide. Mp $98\text{--}99^\circ \text{C}$, dec. Yield 23%. Active oxygen 97.1%. Found: C, 80.60; H, 4.85%. Calcd for $\text{C}_{30}\text{H}_{22}\text{O}_4$: C, 80.70; H, 4.97%.

$((4\text{-CH}_3\text{C}_6\text{H}_4)_2\text{C}=\text{NCOO})_2$ (**5**). Yield 3%. Mp $103\text{--}105^\circ \text{C}$, dec. Active oxygen 85%. Found: C, 75.75; H, 5.90; N, 5.42%. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_4$: C, 76.18; H, 5.59; N, 5.55%.

Authentic Compounds for GLPC. *Diphenylmethylenamine*: Prepared from diphenylmethylenamine hydrochloride and sodium methylate. Bp $121\text{--}122^\circ \text{C}/0.5 \text{ Torr}$. Mp $59\text{--}63^\circ \text{C}$.²⁵

Diphenylmethylenbenzylamine: Obtained from benzophenone and benzylamine, Mp $60\text{--}61^\circ \text{C}$.²⁶

Bis(diphenylmethylenene)hydrazine: Prepared from benzophenone and hydrazine. Mp $164\text{--}165^\circ \text{C}$.²⁷

N-(*o*-, *m*-, and *p*-Diphenylmethylenamine)toluenes: Toluidine and benzophenone were heated in the presence of fused zinc chloride for 2 h at 150°C . Mp $48.5\text{--}50^\circ \text{C}$ (*o*-),²⁸ $77\text{--}78^\circ \text{C}$ (*m*-),²⁸ and $45\text{--}46^\circ \text{C}$ (*p*-).²⁸

m-Tolylphenylmethane: Obtained by the method of Lamneck, Jr., and Wise.²⁹ Bp $86\text{--}86.5^\circ \text{C}/0.5 \text{ Torr}$.

GLPC Measurements. The products of thermolysis of peroxides were determined by GLPC using a JGC-1100 (JEOL) type apparatus, 3-m column of Apiezon L (5% on Chromosorb W(AW)) at 220°C , and 3-m column of Apiezon L (1.5% on Chromosorb W(AW)) at 154°C . Helium as carrier gas.

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