

**Table II.** Dependence of Observed Second-Order Rate Constant in the Presence of Pyrophosphate Buffer on Sodium Ion Concentration. Rate of Oxidation of Tetramethylene Sulfide<sup>a</sup>

Na <sup>+</sup> , <i>M</i>	pH	<i>k</i> <sub>obsd</sub> , <i>M</i> <sup>-1</sup> sec <sup>-1</sup>
0.04	8.64	255
0.06	8.56	210
0.08	8.49	185
0.10	8.40	160
0.12	8.34	135

<sup>a</sup> Initial total tetramethylene sulfide =  $5 \times 10^{-4}$  *M*; initial total  $I_2 = 2.5 \times 10^{-6}$  *M*; total pyrophosphate buffer = 0.005 *M*; ionic strength maintained at 0.145 with tetramethylammonium chloride; *k*<sub>obsd</sub> measured spectrophotometrically; temp, 25.0°.

ally with increasing basicity of the nucleophiles; however, in the case of arsenate this relationship does not hold. The species  $HAAsO_4^{2-}$  is a weaker base than  $HPO_4^{2-}$  but shows a slightly higher catalytic activity than the phosphate species.

The triply charged species  $HP_2O_7^{3-}$  appeared to be much less catalytically active than the anions  $HPO_7^{2-}$  and  $P_2O_7^{4-}$ . This observation may be rationalized at least in part on the basis of observed hydrogen bond<sup>9</sup> formation between the phosphate groups in the  $HP_2O_7^{3-}$  species.

Since the species  $P_2O_7^{4-}$  has been shown to form complexes<sup>10</sup> with Na<sup>+</sup> and K<sup>+</sup>, its catalytic activity may be

(9) J. A. Wolhoff and J. T. G. Overbeek, *Rec. Trav. Chim.*, **78**, 759 (1959).

(10) G. Schwarzenbach and J. Zurc, *Monatsh.*, **81**, 202 (1950).

expected to be strongly influenced by the presence of these ions. Experimental support of such an effect can be seen in Table II which shows some observed second-order rate constants in the presence of constant pyrophosphate buffer but at several sodium chloride concentrations.

The ionic strength was maintained constant with tetramethylammonium chloride. The rate decreases considerably with an increase of the sodium concentration; the exact catalytic activity, however, was not determined because of the complexity of the system resulting from the change in pH with changing sodium concentration.

### Experimental Section

**Reagents.** Tetramethylene sulfide (impurities 0.05 ± 0.05 mole %) were obtained as a specially purified sample from the U. S. Bureau of Mines, Laramie, Wyo.<sup>11</sup> Commercial tetramethylene sulfide purified by passage over neutral aluminum oxide (activity I, Woelm) followed by fractionation in a spinning-band column yielded essentially the same rate constant. All other chemicals were reagent grade. Water was purified by redistilling tap-distilled water from potassium permanganate solution acidified with sulfuric acid.

**Rate Studies.** In general usual spectrophotometric procedures commonly employed for rate measurements were followed. For slower runs reactants were mixed separately and then poured into the spectrophotometric cell. For faster reactions the solutions were mixed directly by injection in the cell.

All pH measurements were made to 0.01 unit. For pH-Stat rate determinations special precautions were taken to exclude atmospheric carbon dioxide and were carried out under nitrogen.

(11) The authors wish to thank the U. S. Department of Interior, Bureau of Mines, for generously providing these samples.

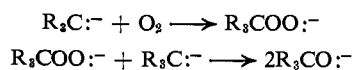
## The Oxidation of Carbanions. I. Oxidation of Triaryl Carbanions and Other Tertiary Carbanions<sup>1</sup>

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**Abstract:** The rate of oxidation of triphenylmethane in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) solution is shown to be equal to the rate of ionization of the hydrocarbon to the carbanion. The oxidation reaction is rate controlled by the ionization process. Some evidence is presented to indicate that the rapid process by which the carbanion is consumed is of a free radical or electron-transfer nature. The ionization of triphenylmethane in the solvent employed is first order in hydrocarbon and in potassium *t*-butoxide. The base appears to be completely dissociated in this solvent system. The deuterium isotope effect in the ionization is 9.5 at 25°. The effects of structure and solvents on the products and rates of oxygenation of some other tertiary carbanions are considered.

The reaction of molecular oxygen with tertiary benzylic anions has not been extensively studied. It is potentially a very simple reaction of some synthetic utility because the only expected oxidation products are the hydroperoxide or the carbinol.



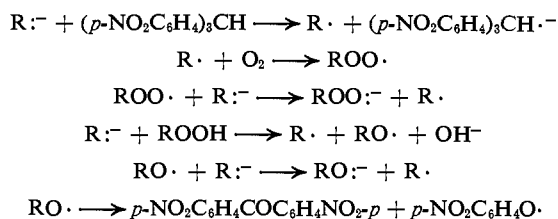
(1) Reactions of Resonance Stabilized Anions. XXIV. Work supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

Thus, it was found possible to convert *p*-nitrocumene in dimethyl sulfoxide (DMSO) solutions containing potassium *t*-butoxide to the carbinol by reaction with oxygen at room temperature.<sup>3</sup> Tris(*p*-nitrophenyl)methane has been converted to a mixture of the hydroperoxide, alcohol, and *p*-nitrophenol by reaction with oxygen in ethanolic potassium hydroxide solution,<sup>4</sup> by a process that shows many characteristics of a

(2) National Science Foundation Predoctoral Fellow, 1963–1966.

(3) G. A. Russell, A. J. Moye, E. G. Janzen, S. Mak, and E. R. Talaty, *J. Org. Chem.*, in press.

branched chain reaction,<sup>3,4</sup> initiated by electron transfer.<sup>5,6</sup>



Sprinzak has oxidized 9-phenyl-, 9-methyl-, 9-ethyl-, and 9-benzylfluorene in pyridine solutions containing Triton B and noted the absorption of 1 mole of oxygen per mole of carbanion at 0° with the formation of the hydroperoxide.<sup>7</sup> At 40° the reaction yielded mainly alcohol and only slightly more than 0.5 equiv of oxygen was required. Triphenylmethylsodium has been reported to react with oxygen in ether to form triphenylcarbinol and trityl peroxide in varying yields,<sup>8</sup> while tritylmagnesium bromide is reported to be converted to the peroxide by oxygen.<sup>9</sup>

1,1-Diphenylethylpotassium reacts with oxygen to form 1,1-diphenylethanol and a small amount of the 2,2,3,3-tetraphenylbutane.<sup>10</sup> The dilithium adduct of tetraphenylethylene is converted to the unsaturated compound by oxygen in ether<sup>11</sup> while the dilithio adduct of 9,10-dimethylantracene reacts with oxygen in 1,2-dimethoxyethane to yield 9,10-dimethylantracene and some of the 9-hydroperoxy-9,10-dimethylantracene.<sup>11b</sup>

We have previously reported that a variety of aralkyl hydrocarbons that are unreactive toward oxygen in the presence of alkoxide ion in alcohol solution can be readily oxidized in DMSO solution.<sup>12</sup> In the present paper we consider this reaction in greater detail in regard to the scope of the reaction and the nature of the rate-determining and product-controlling steps.

## Results

### Products and Rates of Oxidation of Triphenylmethane.

Table I summarizes the products and initial rates of oxidation of triphenylmethane in basic solutions containing initially 100% excess of potassium *t*-butoxide.

Table I points out the greater ionizing power of HMPA and DMSO. Pure DMSO could not be employed as a solvent because it reacts readily with oxygen in the presence of potassium *t*-butoxide, presumably due to the presence of the methylsulfinylcarbanion (CH<sub>3</sub>-SOCH<sub>2</sub><sup>-</sup>).<sup>12</sup>

Surprisingly, although the reaction in DMSO (80 vol. %)-*t*-BuOH (20 vol. %) showed the same stoichiometry

(4) M. F. Hawthorne and G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

(5) G. A. Russell and E. G. Janzen, *ibid.*, in press.

(6) G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Selective Oxidation Processes," *Advances in Chemistry Series*, No. 51, American Chemical Society, Washington, D. C., 1965, p 112.

(7) Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958).

(8) G. A. Russell and E. Marcus, *Ber.*, **47**, 1664 (1914); C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.*, **47**, 2739 (1925); W. E. Bachman and F. Y. Wiselogle, *ibid.*, **58**, 1943 (1936).

(9) J. Schmidlin, *Ber.*, **39**, 628 (1906).

(10) K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924).

(11) (a) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914); (b) H. Hock and F. Ernst, *ibid.*, **92**, 2732 (1959).

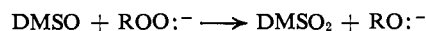
(12) (a) G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smenzowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962); (b) G. A. Russell and A. G. Bemis, *Chem. Ind.* (London), 1262 (1965).

Table I. Oxidation of Triphenylmethane at 25 ± 1 °a

Solvent (%) <sup>b</sup>	Initial rate <sup>c</sup>	Stoichiometry <sup>d</sup>	Product (%) <sup>e</sup>
<i>t</i> -BuOH	<0.01	...	...
Pyridine	0.16 <sup>f</sup>	1.0	Hydroperoxide (80), peroxide (10)
Pyridine (80)- <i>t</i> -BuOH (20)	0.02	...	...
DMF (80)- <i>t</i> -BuOH (20)	0.39	1.0	Hydroperoxide (87) <sup>g</sup>
DMSO (80)- <i>t</i> -BuOH (20)	1.10	1.0	Alcohol (95)
HMPA (80)- <i>t</i> -BuOH (20)	1.28	1.0	Hydroperoxide (58)
HMPA	2.3 <sup>h</sup>	1.0	Hydroperoxide (77)

<sup>a</sup> 0.1 M [triphenylmethane]<sub>0</sub>, 0.2 M potassium *t*-butoxide, in the presence of oxygen at 749 mm. <sup>b</sup> DMF = dimethylformamide, *t*-BuOH = *t*-butyl alcohol, DMSO = dimethyl sulfoxide, HMPA = hexamethylphosphoramide. <sup>c</sup> Moles of oxygen/mole of triphenylmethane/min. <sup>d</sup> Moles of oxygen/mole of [triphenylmethane]<sub>0</sub>. <sup>e</sup> Yield of recrystallized product. <sup>f</sup> Heterogeneous. <sup>g</sup> The initially isolated product was a 1:2 complex of DMF and triphenylmethyl hydroperoxide in 91% yield. <sup>h</sup> Minimum rate.

as in the other solvents, the product was triphenylcarbinol in the DMSO-containing solvent but the hydroperoxide in the other solvents. This suggested that dimethyl sulfoxide was reducing the hydroperoxide to the alcohol.



Triphenylmethyl hydroperoxide can be recovered in quantitative yield from DMSO in the absence of base. In the presence of base and DMSO, it is converted to the alcohol in 94% yield without the evolution of oxygen. Dimethyl sulfone is difficult to recover from DMSO solution but in the experiment a 30% yield of the sulfone was obtained.

This result suggests a unique role for DMSO as a solvent for carbanion oxidations. It can reduce the first-formed hydroperoxide to the alcohol before decomposition reactions occur.

The effect of the nature of the base employed in DMSO solution is summarized in Table II.

Table II. Initial Rate of Oxidation of Triphenylmethane as a Function of the Structure of the Base in DMSO (80 vol. %)-*t*-BuOH (20 vol. %) Solution at 25 ± 1 °a

Base	Concn, M	Initial rate <sup>b</sup>
KOH	Saturated soln	0.06
LiOC(CH <sub>3</sub> ) <sub>3</sub>	0.10	0.15
NaOC(CH <sub>3</sub> ) <sub>3</sub>	0.10	0.32
KOC(CH <sub>3</sub> ) <sub>3</sub>	0.10	0.82
(CH <sub>3</sub> ) <sub>4</sub> NOC(CH <sub>3</sub> ) <sub>3</sub>	0.20	1.10
KOC(CH <sub>3</sub> ) <sub>3</sub>	0.20	1.10
NaOCH <sub>3</sub>	0.20	0.18

<sup>a</sup> 0.1 M [triphenylmethane]<sub>0</sub> in the presence of oxygen at 749 mm. <sup>b</sup> Moles of oxygen/mole of triphenylmethane/min.

Table III summarizes product, stoichiometry, and initial rate data for the oxidations of several other aralkyl hydrocarbons containing *tertiary* hydrogen atoms.

**Table III.** Oxidation of Aralkyl Hydrocarbons at  $25 \pm 1^\circ$  in the Presence of Potassium *t*-Butoxide<sup>a</sup>

Hydrocarbon	Solvent (%)	Initial rate <sup>b</sup>	Stoichiometry <sup>c</sup>	Product (%) <sup>d</sup>
Diphenyl- $\alpha$ -naphthylmethane	DMSO (80)- <i>t</i> -BuOH (20)	1.64	1.0	Alcohol (95)
9-Phenylfluorene	DMSO (80)- <i>t</i> -BuOH (20)	3.2 <sup>e</sup>	1.0	Alcohol (73)
9-Phenylfluorene	<i>t</i> -BuOH	0.44	0.72	<i>f</i>
9-Phenylfluorene	HMPA	3.26 <sup>e</sup>		...
9-Methylfluorene	DMSO (80)- <i>t</i> -BuOH (20)	3.9 <sup>e</sup>	1.0	Alcohol (79)
9-Methylfluorene	<i>t</i> -BuOH	0.36	0.95	Hydroperoxide (70)
9-Methylfluorene	HMPA	3.5 <sup>e</sup>	0.87	...
1,1-Diphenylethane	DMSO (80)- <i>t</i> -BuOH (20)	0.02	0.57	...
1,1-Diphenylethane	HMPA	0.61	0.84	Alcohol
1,1-Diphenylethane	<i>t</i> -BuOH	<0.01		
Diphenylacetic acid	DMSO (80)- <i>t</i> -BuOH (20)	0.86	1.0	Benzilic acid (74)
Methyl diphenylacetate	DMSO (80)- <i>t</i> -BuOH (20)	3.1 <sup>e,g</sup>	1.0	Benzilic acid (83)
1,1-Diphenylacetone	DMSO (80)- <i>t</i> -BuOH (20)	1.87	1.27	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(OH)-CH <sub>2</sub> SOCH <sub>3</sub> (40)
<i>sym</i> -Tetraphenylethane	DMSO (80)- <i>t</i> -BuOH (20)	0.025 <sup>g</sup>	1.4	Tetraphenylethylene (96), KO <sub>2</sub> , K <sub>2</sub> O <sub>2</sub>

<sup>a</sup> 0.1 *M* hydrocarbon, 0.2 *M* potassium *t*-butoxide, in oxygen at 749 mm. <sup>b</sup> Moles of oxygen/mole of hydrocarbon/min. <sup>c</sup> Moles of oxygen absorbed/mole of hydrocarbon. <sup>d</sup> Yield of recrystallized product based on hydrocarbon. <sup>e</sup> Extremely rapid rate, may be minimum rate. <sup>f</sup> See ref 7. <sup>g</sup> 0.05 *M* of substrate.

**Table IV.** Oxidation of Triphenylmethane<sup>a</sup>

Temp, °C	Solvent (%)	[R <sub>3</sub> CH] <sub>0</sub> , <i>M</i>	[(CH <sub>3</sub> ) <sub>3</sub> CO <sup>-</sup> ], <i>M</i>	<i>k</i> <sub>1</sub> , sec <sup>-1</sup>	$\frac{k_t = k_1}{[(CH_3)_3CO^-]},$ l./mole sec
24.5	DMSO (80)- <i>t</i> -BuOH (20)	0.10	0.20	0.0268	0.134 ± 0.003 <sup>b</sup>
24.5	DMSO (70)- <i>t</i> -BuOH (30)	0.10	0.20	0.0078	0.04
24.5	DMSO (60)- <i>t</i> -BuOH (40)	0.10	0.20	0.00254	0.013
27 ± 1	DMSO (52)- <i>t</i> -BuOH (48)	0.10	0.20	0.00084	0.0042
24.5	DMSO (25)- <i>t</i> -BuOH (75)	0.10	0.20	0.000044	0.0002
29.5	DMSO (80)- <i>t</i> -BuOH (20)	0.0492	0.197	0.0361	0.179
29.5	DMSO (80)- <i>t</i> -BuOH (20)	0.0492	0.234	0.0378	0.170
34.5	DMSO (80)- <i>t</i> -BuOH (20)	0.0492	0.0936	0.0219	0.234
24.5	DMSO (80)- <i>t</i> -BuOH (20)	0.0242 <sup>c</sup>	0.197	0.0341	0.173
24.5	DMSO (80)- <i>t</i> -BuOH (20)	0.10 <sup>d</sup>	0.20	0.00286 <sup>e</sup>	0.0143

<sup>a</sup> 25 ml of solution in the presence of oxygen at 749 mm. <sup>b</sup> Average of several experiments. <sup>c</sup> Diphenyl- $\alpha$ -naphthylmethane. <sup>d</sup>  $\alpha$ -Deuteriotriphenylmethane, 93.3%  $\alpha$ -*d* by mass spectrometry. <sup>e</sup> Slope of log plot during latter stages of reaction. The plot shows an initial steeper slope due to 6.7% of triphenylmethane. This kinetic method of analysis of two competing pseudo-unimolecular reactions was first applied by H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, 73, 1318 (1951).

#### Kinetics of the Oxidation of Triphenylmethane.

The oxidation of triarylmethanes in basic solution is an excellent reaction to treat in a kinetic manner because of the clean stoichiometry. Due to the absorption of 1 mole of oxygen per mole of triphenylmethane (R<sub>3</sub>CH), the instantaneous [R<sub>3</sub>CH]<sub>*t*</sub> = [R<sub>3</sub>CH]<sub>0</sub> - [O<sub>2</sub>]<sub>absd</sub>. Indeed, a plot of log [R<sub>3</sub>CH]<sub>*t*</sub> vs. time gives a straight line for a reaction thermostated at 24.5° (see Figure 1 of ref 12b) and containing a 10-fold excess of base to [R<sub>3</sub>CH]<sub>0</sub>. Values measured in this way for a pseudo-unimolecular rate constant (*k*<sub>1</sub>) together with a value of *k*<sub>*t*</sub> calculated by dividing *k*<sub>1</sub> by [(CH<sub>3</sub>)<sub>3</sub>CO<sup>-</sup>] are given in Table IV.

It was found that the slopes of the tangents drawn at the beginning of the smoothed oxygen absorption curves (initial rates) provided as accurate kinetic data as the actually measured rate constants. Moreover, the initial rate data is free from effects of a change in the concentration of base. A series of experiments performed at  $25 \pm 1^\circ$  are summarized in Table V and demonstrate that the reaction is independent of oxygen concentration above a saturation pressure of 402 mm, independent of the presence of nitrobenzene, and is first order in both triphenylmethane and potassium *t*-butoxide. Similar data were obtained when di-

phenyl- $\alpha$ -naphthylmethane was employed in place of triphenylmethane.

The data of Tables IV and V indicate a simple kinetic picture for the oxidation of triphenylmethane. The rate expression is

$$\frac{-d[R_3CH]}{dt} = \frac{-d[O_2]}{dt} = k_t[R_3CH][KOC(CH_3)_3]$$

There is a decided isotope effect,  $k_t((C_6H_5)_3CH)/k_t \times ((C_6H_5)_3CD) \cong 9.5$ , and the activation parameters for triphenylmethane are  $\Delta H^* = 9.8 \pm 0.5$  kcal/mole and  $\Delta S^* = 29.4$  eu. The isotope and activation parameters<sup>13</sup> are consistent with the ionization of triphenylmethane being the rate-controlling step of the reaction. Another series of experiments are in accord with this interpretation. The oxidation of fluorene in basic solution is strongly catalyzed by nitroaromatics<sup>6,12</sup> and in the absence of oxygen electron transfer between the fluorene anion and nitroaromatics can be observed by electron spin resonance.<sup>14</sup> Elec-

(13) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, 1, 16 (1963).

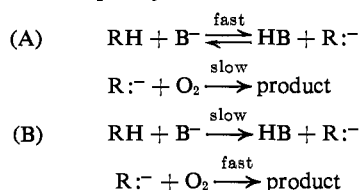
(14) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, 86, 1807 (1964).

Table V. Oxidation of Triphenylmethane in Dimethyl Sulfoxide (80)-*t*-Butyl Alcohol (20) at 25 ± 1°

[Triphenylmethane] <sub>0</sub> , moles/l.	Potassium <i>t</i> -butoxide, moles/l.	O <sub>2</sub> pressure, mm	Initial rate <sup>a</sup> × 10 <sup>4</sup>	<i>k</i> <sub>1</sub> , <sup>b</sup> sec <sup>-1</sup>	<i>k</i> <sub>1</sub> = <i>k</i> <sub>1</sub> /[(CH <sub>3</sub> ) <sub>3</sub> (COK)], l./mole sec	Initial rate/[R <sub>3</sub> CH] <sub>0</sub> × [KOC(CH <sub>3</sub> ) <sub>3</sub> ], l./mole sec
0.025	0.05	749	1.27	0.007	0.14	0.102
0.025	0.05	609	1.31	0.0073	0.15	0.105
0.025	0.05	402	1.81	0.0082	0.16	0.145
0.025	0.05	749	1.33 <sup>c</sup>	0.0075	0.15	0.106
0.025	0.10	749	2.02	0.0103	0.10	0.081
0.025	0.20	749	6.42	0.034	0.17	0.128
0.05	0.20	749	11.6	0.0296	0.15	0.116
0.10	0.20	749	22.5	0.0341	0.17	0.113
0.049	0.045	749	2.65	0.0578	0.13	0.120
0.049	0.09	749	5.2	0.0116	0.13	0.118
0.049	0.135	749	7.85	0.0213	0.15	0.129

<sup>a</sup> Moles of oxygen absorbed/l. sec. <sup>b</sup> From plots of log ([R<sub>3</sub>CH]<sub>0</sub> - [O<sub>2</sub>]<sub>absd</sub>) vs. time. <sup>c</sup> In the presence of 0.098 *M* nitrobenzene.

tron transfer can be detected from the triphenylmethide anion and nitrobenzene,<sup>14</sup> but no catalysis of the rate of oxidation of triphenylmethane is observed when nitrobenzene is added (Table V). Thus, the rate of oxidation of fluorene can be considered to follow Scheme A and triphenylmethane Scheme B.



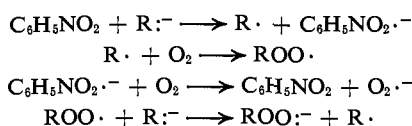
Some pertinent results on oxidations performed in the presence of nitrobenzene are summarized in Table VI.

Table VI. Oxidations in Basic Solution in the Presence of Nitrobenzene at 25 ± 2°

Hydrocarbon ( <i>M</i> )	Solvent (%)	KOC-(CH <sub>3</sub> ) <sub>3</sub> , <i>M</i>	C <sub>6</sub> H <sub>5</sub> -NO <sub>2</sub> , mM	Ratio of initial rates in presence and absence of nitrobenzene
Fluorene (0.1)	<i>t</i> -BuOH	0.20	4.8	2.1
Fluorene (0.12)	<i>t</i> -BuOH	0.24	9.8	4.5
Triphenylmethane (0.025)	DMSO (80)- <i>t</i> -BuOH (20)	0.05	98	1.0 ± 0.05 <sup>a</sup>
<i>α</i> - <i>d</i> -Triphenylmethane (0.025)	DMSO (80)- <i>t</i> -BuOH (20)	0.20	98	0.93
9-Methylfluorene (0.10)	<i>t</i> -BuOH	0.20	195	6.3 <sup>b</sup>
1,1-Diphenylethane (0.10)	DMSO (80)- <i>t</i> -BuOH (20)	0.20	195	1.3

<sup>a</sup> Average of several experiments. <sup>b</sup> Catalyzed rate very rapid, may be a minimum value.

The catalysis by nitrobenzene in Scheme A is obvious for a free radical chain oxidation.



Evidence for the regeneration of nitroaromatics by reaction with oxygen has been given.<sup>15</sup>

The absence of catalysis by nitroaromatics in the oxidation of triphenylmethane could mean that a free radical chain is not involved, or that whenever a triphenylmethane molecule is ionized it reacts immediately with oxygen by a free radical mechanism or otherwise, with the rate of oxidation controlled solely by the rate of ionization. If so, oxidation in basic solution represents a novel approach to the determination of ionization rate constants. That indeed the rate of oxidation is limited by the rate of ionization of triphenylmethane was proven by a comparison of the rates of oxidation and deuterium exchange for *α*-*d*-triphenylmethane. *α*-*d*-Triphenylmethane was prepared and found to contain 6.7% *α*-hydrogen by mass spectrometry. At 27 ± 0.2°, a solution 0.049 *M* in this *α*-*d*-triphenylmethane and 0.256 *M* in potassium *t*-butoxide was allowed to react for 165 sec in DMSO (80%)–*t*-BuOH (20%) solution. The solution was quenched with water and the *α*-*d*-triphenylmethane analyzed by mass spectrometry to contain 39.1% *α*-deuterium. Of the original deuterium, 58% had exchanged with an average rate of 1.60 × 10<sup>-4</sup> mole/l. sec which would correspond to a second-order rate constant (*k*<sub>1</sub>) equal to 0.0205 l./mole sec. This can be compared with the value of 0.0143 found at 24.5° in oxidation (Table IV).

Under exactly the same conditions employed for the exchange studies, 0.635 mmole of oxygen was absorbed by 25 ml of solution in 165 sec at an average rate of 1.54 × 10<sup>-4</sup> mole/l. sec and a consumption of 53% of the initial triphenylmethane and *α*-deuteriotriphenylmethane present. Even if all of the triphenylmethane present was consumed in 165 sec (using a value of *k*<sub>1</sub> (Table IV) of 0.15 predicts that 99.5% of the triphenylmethane would have been consumed) 0.565 mmole of *α*-*d*-triphenylmethane (51.4% of the initial quantity) must have been consumed. We believe these experiments agree within experimental uncertainty and prove that the rate of ionization of *α*-*d*-triphenylmethane is equal to its rate of oxidation in basic solution. Undoubtedly the same is true for triphenylmethane itself.

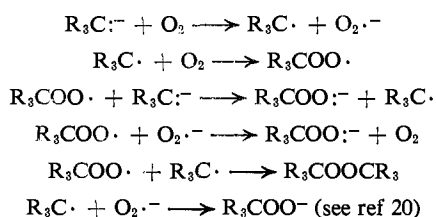
## Discussion

The oxidation of triphenylmethane in solutions of potassium *t*-butoxide in DMSO–*t*-butyl alcohol must

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involve a carbanion intermediate. The rates are very rapid whereas the free radical chain oxidation of triphenylmethane is extremely sluggish even at elevated temperatures<sup>16</sup> due to the reversibility<sup>17</sup> of the reaction of oxygen with the triphenylmethyl radical.<sup>16</sup> Long kinetic chains involving the tritylperoxy radical are impossible in the oxidation of triphenylmethane in the presence or absence of base. That oxidation in basic solution does not involve any attack of peroxy radical on un-ionized triphenylmethane is indicated by the equality of ionization and oxidation rates and by the fact that competitive oxidations of triphenylmethane and cumene in basic DMSO-*t*-butyl alcohol solutions do not consume any of the cumene (unfortunately the relative reactivities of cumene and triphenylmethane toward a peroxy radical are unknown); toward the bromine atom or trichloromethyl radical triphenylmethane is actually slightly less reactive than cumene.<sup>18</sup>

Because the slow step is the rate of ionization of the hydrocarbon, our results on the oxidation of triphenylmethane have no mechanistic bearing on the question of whether the triphenylmethide is consumed by a radical mechanism or by a one-step process involving a change of multiplicity and a violation of multiplicity rules. Because of our results with more acidic hydrocarbons,<sup>6,19</sup> where a free radical chain mechanism can be demonstrated, we feel that the oxidation of triphenylmethane in basic solution involves short chains involving such steps as



The more acidic 9-methyl- and 9-phenylfluorenes which show nitrobenzene catalysts must certainly involve such a process. However, we cannot exclude a cage-type reaction such as,<sup>21</sup>  $R_3C\cdot + O_2 \uparrow \rightarrow [R_3C\cdot \uparrow + O_2\cdot^- \uparrow \rightarrow R_3C\cdot \downarrow O_2\cdot^- \uparrow] \rightarrow R_3COO\cdot$ , particularly in view of the most recent results on the rapidity of spin relaxation in caged processes.<sup>22</sup> However, it is not clear why in the case of fluorene we would have a radical chain reaction whereas for triphenylmethane, which should give a more stable radical, the radical cannot escape from the cage. Moreover, the reaction of molecular oxygen with the phenalene anion<sup>23</sup> or 2-phenylbis(biphenylene)allyl anion<sup>24</sup> does lead to production of the radicals.

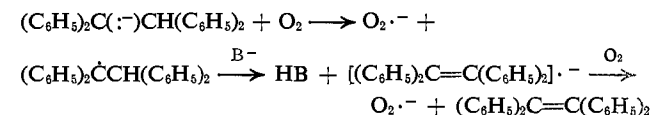
In pyridine solution, we do find products indicative of termination steps  $((C_6H_5)_3COOC(C_6H_5)_3)$  for a

radical process. Probably this is connected with the fact that pyridine forms a complex with superoxide ion<sup>25</sup> and could prevent or greatly diminish the rate of reaction of a peroxy radical with the superoxide ion. Alternately, the complexing effect of pyridine could be considered to destroy the original triphenylmethyl radical-superoxide ion cage.

The dehydrogenation of *sym*-tetraphenylethane to produce  $K_2O_2$  and  $KO_2$  is also not consistent with a cage process which should produce a hydroperoxide or the olefin plus peroxide dianion.



The formation of superoxide ion is quite consistent with a radical process.



The stoichiometry is consistent with a reaction proceeding in about equal parts by aralkyl hydroperoxide (giving  $K_2O_2$ ) and radical anion (giving  $KO_2$ ).

It is believed that the initial rates of oxidation summarized in Table III reflect the rates of ionization except for the nine-substituted fluorenes. The rate of oxidation of diphenylacetic acid certainly implies unusual stability for the anion, presumably because of carbonate-like symmetry as suggested by Cram.<sup>26</sup> In DMSO (80%) or pure HMPA containing excess potassium *t*-butoxide, 3,3-diphenylpropionic acid failed to ionize. The series of acidities (tertiary hydrogen atoms only) is apparently:  $(C_6H_5)_2CHCH_2CO_2^- < (C_6H_5)_2CHCH_3, (C_6H_5)_2CHCH(C_6H_5)_2 < (C_6H_5)_3CH, (C_6H_5)_2CH-\alpha-C_{10}H_8, (C_6H_5)_2CHCO_2^- < 9\text{-phenylfluorene}, (C_6H_5)_2CHCOCH_3, (C_6H_5)_2CHCO_2Et$ .

The kinetics of ionization and isotope effect in the ionization of  $\alpha$ -*d*-triphenylmethane are surprisingly simple in DMSO (80%)-*t*-butyl alcohol (20%). In 100% DMSO the reaction of strong bases with weak carbon acids is quite different as evidenced from the lack of an isotope effect for hydrogen-deuterium exchange in 2-methyl-3-phenylpropionitrile<sup>27</sup> and hydrogen-tritium exchange in toluene.<sup>28</sup> Our isotope effect of  $\sim 9.5$  for ionization of  $\alpha$ -*d*-triphenylmethane compares favorably with the isotope effect of 10–12 for  $k_H/k_D$  calculated by Streitwieser and Van Sickle for exchange of toluene with lithium cyclohexylamide in cyclohexylamine.<sup>29</sup>

Effects of the nature of the cation associated with the *t*-butoxide ion and the effect of solvent on the rate of proton transfer (Tables I, II, and IV) appear fairly standard. Dimethyl sulfoxide and hexamethylphosphoramide are obviously superior solvents for promoting the basicity of the *t*-butoxide ion. Since potassium and tetramethylammonium *t*-butoxide gave the same rate of ionization, we believe that potassium *t*-butoxide is appreciably dissociated in DMSO (80%)-*t*-butyl alcohol (20%) in agreement with the kinetic

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dependence on potassium *t*-butoxide to the first power. The lithium and sodium salts are apparently appreciably associated in this solvent (Table II). A plot of the log of the rate of ionization of triphenylmethane *vs.* the composition of solvent in terms of per cent DMSO gives a straight line as was found in the racemization of 2-methyl-3-phenylpropionitrile over the same solvent range.<sup>30a</sup>

The rate constant for protonation of triphenylmethide ion by *t*-butyl alcohol in DMSO solution has been estimated as  $\sim 10^6$  l./mole sec by Ritchie and Uschold.<sup>30b</sup> Since oxygen ( $\sim 0.01$  M) competes overwhelmingly with *t*-butyl alcohol ( $\sim 2$  M), it follows that the attack of oxygen on the triphenylmethide ion occurs with a rate constant greater than  $10^9$  l./mole sec, perhaps at a diffusion-controlled rate. *The triphenylmethide ion reacts with oxygen more readily than the triphenylmethyl radical!*<sup>16</sup>

## Experimental Section

Melting points are uncorrected and were taken on a Fisher-Jones hot stage. All mass spectra were recorded on an Atlas MAT CH-4 instrument, at low ionizing voltages.

The rates of oxidation were measured by observing the volume of oxygen absorbed per unit of time. The volumes were corrected to standard temperature and pressure and converted to moles.

**Oxidation Procedure.** The oxidations were performed at 749 mm except where otherwise noted and at ambient temperatures (unless thermostated) in a 125-ml creased flask, equipped with an addition flask and a degassing apparatus (see Figure 23 of ref 6). The oxidation flask was vigorously shaken on a wrist action shaker (see Figure 22 of ref 6). The shaking motion in a creased flask on this shaker causes the solution to become frothy and provides much better contact between oxygen and the liquid phase than with paddle or bar stirrers. The flasks were connected by Tygon tubing to a manifold containing an oxygen inlet valve, a gas buret equipped with a mercury leveling bulb, a closed-end mercury manometer, and a vacuum connection. Solutions of base were placed in the creased flask, and oxygen was introduced through the center tube which extended below the surface of the solution. Prior to the start of a reaction, oxygen was allowed to bubble through the basic solution and then escape *via* a three-way stopcock. In some cases the whole flask was immersed in a thermostated oil bath for 20 min prior to the start of an oxidation. The flask was then removed from the bath and placed on the shaker just before starting the oxidation. In this manner more exact temperature control was achieved. The substrate was placed in the 10-ml retort-shaped addition flask and was added to the creased flask by rotating the addition flask just prior to starting the shaker. Oxygen absorption was recorded as a function of reaction time. When oxygen absorption had ceased, the contents of the flask were poured into water, the flask rinsed with water, and the solutions combined. In some cases dilute hydrochloric acid was added until the solution achieved pH 5. Water-insoluble products were filtered from the aqueous solution and soluble products separated by extraction.

**Reagents.** Sodium was dissolved in *t*-butyl alcohol obtained commercially, and oxygen was bubbled through the resulting solution for 24–48 hr. The *t*-butyl alcohol was then distilled from the basic solution. This process was repeated once with sodium and again with potassium. The oxygenated solution from the first treatment (before distillation) was black and contained floating dark solids. After the third treatment the solution was only faintly yellow. The purified *t*-butyl alcohol was stored over calcium hydride. A solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared by dissolving a weighed amount of freshly cleaned potassium in a known volume of the purified *t*-butyl alcohol. An aliquot of the resulting solution was titrated with standardized hydrochloric acid. Solutions of base prepared in this manner contained less hydroxide ion than those made by dissolving commercial potassium *t*-butoxide in *t*-butyl alcohol as shown by much

slower rates of hydrolysis of methyl *p*-toluate in the former solution. Potassium *t*-butoxide from Mine Safety Appliance Corp. was used as base in solvents containing no alcohol. Tetramethylammonium *t*-butoxide was prepared by the treatment of 0.02 mole of tetramethylammonium bromide in 56 ml of DMSO with 20 ml of a 1.0 N solution of potassium *t*-butoxide in *t*-butyl alcohol. Potassium bromide (2.59 g, 0.0219 mole) was removed by filtration. Dimethyl sulfoxide obtained from Crown Zellerbach Corp. was distilled under vacuum at 60–70° from calcium hydride and stored over calcium hydride. Dimethylformamide was dried over calcium hydride. Hexamethylphosphoramide obtained from Tennessee Eastman Corp. was distilled and stored over calcium hydride. Pyridine was of analytical reagent grade and was stored over potassium hydroxide pellets. Sodium and lithium *t*-butoxides were prepared by dissolving the corresponding alkali metal in purified *t*-butyl alcohol. Sodium methoxide was used as obtained from Matheson Coleman and Bell. Potassium hydroxide, 85% from Mallinckrodt, was ground to a powder before use.

Purified solvents stored over calcium hydride gave identical oxidation rates as those freshly distilled.

Triphenylmethane was obtained from Matheson Coleman and Bell and was recrystallized twice from 95% ethanol, mp 93°. Diphenyl-1-naphthylmethane was prepared by addition of 1-naphthylmagnesium bromide to benzophenone, followed by HI reduction of the crude alcohol, mp (after recrystallization from aqueous ethanol) 139–141°, lit.<sup>31</sup> 139–140°. 9-Methylfluorene was prepared by the alkylation of 9-sodiofluorene with methyl iodide.<sup>32</sup> The product was recrystallized three times from Skelly B, mp 46–47°, lit.<sup>32</sup> 45–47°. 9-Sodiofluorene was made by the addition of sodium to fluorene in ether, and was filtered and washed several times with ether.<sup>32</sup> 9-Phenylfluorene was prepared from fluorenone,<sup>33</sup> and recrystallized from alcohol, mp 148°. *sym*-Tetraphenylethane was prepared by treating benzhydryl bromide with zinc in ethyl acetate.<sup>34</sup> Recrystallization from benzene gave the product, mp 210–211°, lit.<sup>34</sup> 211°. Methyl diphenylacetate was prepared by acid-catalyzed esterification of diphenylacetic acid with methanol. The ester, after recrystallization from 95% ethanol, had mp 60–61°, lit.<sup>35</sup> 60°. 1,1-Diphenylethane was prepared by addition of methylmagnesium bromide to benzophenone, which on acid work-up gave the olefin. Catalytic hydrogenation gave 1,1-diphenylethane,  $\geq 98\%$  pure by glpc after distillation. 1,1-Diphenylacetone was used as obtained from Aldrich Chemical Co., and diphenylacetic acid from Eastman.

**Isolation of Oxidation Products.** After oxygen absorption had ceased, the oxidates were poured into water. In many cases a precipitate formed which could be filtered from the aqueous solution. In this manner, triphenylcarbinol, mp 165–165.5°, was isolated from the oxidation of triphenylmethane in DMSO (80%)–*t*-butyl alcohol (20%); (80:20 DMSO); diphenyl-1-naphthylcarbinol, mp 134–135° from diphenyl-1-naphthylmethane; and tetraphenylethylene, mp 213–214° (after recrystallization from benzene) from tetraphenylethane. Acidification with dilute hydrochloric acid of the hydrolyzed oxidates made filtration easier, but did not effect the nature of products from oxidations in 80:20 DMSO. Benzoic acid, mp 149–151° (after recrystallization from benzene), was isolated by ether extraction of the acidified hydrolysates from the oxidations of diphenylacetic acid and methyl diphenylacetate in 80:20 DMSO. 1,1-Diphenyl-2-methylsulfinylethanol (the dimethyl sulfoxide–benzophenone adduct), mp 147–148° (recrystallization from a mixture of chloroform and cyclohexane), lit.<sup>36</sup> 147–148°, was isolated by chloroform extraction from the oxidation of 1,1-diphenylacetone in 80:20 DMSO. The above products had superimposable infrared spectra and undepressed mixture melting points with authentic samples of these materials.

**Oxidation of Triphenylmethane.** Addition of the oxidates of triphenylmethane in hexamethylphosphoramide (HMPA) or HMPA (80%)–*t*-butyl alcohol (20%) to water resulted in the precipitation of triphenylmethyl hydroperoxide, mp 84.5–85.5° (after recrystallization from Skelly B). These products had identical infrared spectra and undepressed mixture melting points with an authentic sample of triphenylmethyl hydroperoxide, prepared by the action

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of 90% hydrogen peroxide on triphenylmethyl chloride, which had mp 84.5–85.5° (after recrystallization from Skelly B), lit.<sup>37</sup> 81–83°. The addition of the oxidate of triphenylmethane in dimethylformamide (80%)–*t*-butyl alcohol (20%) to water gave a precipitate which, after recrystallization from Skelly B, had mp 60–61°. *Anal.* Found: C, 78.83; H, 6.31; N, 1.82.

The infrared spectrum (chloroform) was an exact superposition of the spectra of triphenylmethyl hydroperoxide and dimethylformamide. The oxidation product had identical infrared spectrum, melting point and undepressed mixture melting point with a material prepared by dissolving authentic triphenylmethyl hydroperoxide in DMF, precipitation with water, and recrystallization from Skelly B. When this material (formed in either manner) was dissolved in Skelly B, washed with water, and the Skelly B layer dried and concentrated, triphenylmethyl hydroperoxide was obtained. This material must thus be a complex, and for a 2:1 triphenylmethyl hydroperoxide:DMF complex the theoretical analysis is (for C<sub>41</sub>H<sub>39</sub>NO<sub>5</sub>): C, 78.72; H, 6.24; N, 2.24.

If the oxidates from oxidation of triphenylmethane in 80:20 DMSO, HMPA, 80:20 HMPA, or 80:20 DMF are acidified after addition to water, only triphenylcarbinol (identical in all respects with an authentic sample) is isolated. The oxidate from the oxidation of triphenylmethane in pyridine was added to water and filtered, and the filtrate extracted with benzene. The residue had an infrared spectrum (potassium bromide) superimposable with an authentic sample of trityl peroxide prepared by the method of Gomberg,<sup>38</sup> mp 185–186°, lit.<sup>38</sup> 185–185°, mmp 185–186°. From the benzene extract, triphenylmethyl hydroperoxide (identical melting point, superimposable infrared spectrum, and undepressed mixture melting point with an authentic sample) was isolated. When the aqueous oxidate of the oxidation of triphenylmethane in pyridine was acidified, the same yield of trityl peroxide was obtained, but triphenylcarbinol was the product from the benzene extract.

**Oxidation of 9-Methylfluorene.** The oxidate from the oxidation of 9-methylfluorene in 80:20 DMSO was added to water and filtered, mp 160–167°. After recrystallization from Skelly B, the product had mp 174–175°, and had a superimposable infrared spectrum and undepressed mixture melting point with authentic 9-methyl-9-fluorene, lit.<sup>39</sup> mp 174°. The addition of the oxidate from the oxidation of 9-methylfluorene in *t*-butyl alcohol to water precipitated a material, which after recrystallization from Skelly B melted at 152–154°. The infrared spectrum (chloroform) was similar but not identical with that of 9-methyl-9-fluorene and showed hydroxyl bands at 2.89 (sharp) and 3.05  $\mu$  (broad) in contrast to hydroxyl bands at 2.78 (sharp) and 2.94  $\mu$  (broad) for 9-methyl-9-fluorene. Other bands for the oxidation product of 9-methylfluorene in *t*-butyl alcohol were in general identical with those observed for 9-methyl-9-fluorene. The shift in hydroxyl bands to higher wavelength is similar to that observed between triphenylcarbinol (2.75  $\mu$ , sharp) and triphenylmethyl hydroperoxide (2.88  $\mu$ , sharp), and leads to the assignment that this product is 9-hydroperoxy-9-methylfluorene, lit.<sup>40</sup> mp 150°, possibly containing a small amount of 9-methyl-9-fluorene. The oxidation product from 9-methylfluorene in HMPA was a mixture of the alcohol and hydroperoxide from the infrared spectrum.

**Oxidation of 9-Phenylfluorene.** After the oxidation of 9-phenylfluorene in 80:20 DMSO was complete, the reaction mixture was poured into water, and the resulting precipitate filtered, mp 84–85° (after recrystallization from Skelly B and benzene). The product was 9-phenyl-9-fluorene since it had an identical melting point, an

undepressed mixture melting point, and a superimposable infrared spectrum with an authentic sample of this alcohol. The infrared spectrum showed hydroxyl absorptions at 2.78 (sharp) and 2.98  $\mu$  (broad). The hydrolyzed oxidate from 9-phenylfluorene in *t*-butyl alcohol was extracted with ether and the ether layer separated and dried. The ether was removed, leaving a sticky gum which defied attempts at crystallization from Skelly B and benzene. An infrared spectrum of this material showed a hydroxyl absorption at 2.86  $\mu$  (sharp). Since treatment with sodium sulfite converted this material into 9-phenyl-9-fluorene, it is believed to be 9-hydroperoxy-9-phenylfluorene or a mixture of the hydroperoxide and alcohol. The infrared shift of the hydroxyl band to higher wavelength is also in accord with this assignment.

**Oxidation of 1,1-Diphenylethane.** After oxygen absorption ceased, the reaction mixture from the oxidation of 1,1-diphenylethane in HMPA was added to water. This aqueous mixture was extracted with ether, the ether layer dried, and the ether removed under vacuum. The residue was recrystallized several times from Skelly B, mp 80–82°. The infrared showed hydroxyl absorption at 2.77  $\mu$  (sharp), and was superimposable with the infrared of a sample of 1,1-diphenylethanol. The possibility that the corresponding hydroperoxide was also present before recrystallization was not investigated.

**Deuterium-Hydrogen Exchange of Triphenylmethane- $\alpha$ -d.** Triphenylmethane- $\alpha$ -d was prepared by the addition of 3.6 ml of deuterium oxide (99.6%) to triphenylmethylsodium prepared by the reaction of 30 g of trityl chloride (recrystallized from a mixture of 8 parts of heptane, 1 part of acetyl chloride) in 150 ml of ethyl ether (sodium dried) with sodium-mercury alloy prepared from 6 g of sodium and 54 g of mercury. The trityl chloride was allowed to react with the amalgam for 140 min and then quenched with the deuterium oxide. After 17-hr contact with the deuterium oxide (red coloration discharged within 5 min) an excess of water was added and triphenylmethane- $\alpha$ -d, mp 90–91°, was recovered by evaporation of the ether solution. Recrystallization from 95% ethanol gave mp 91–92°, lit.<sup>41</sup> (for triphenylmethane) 93°. An infrared spectrum of this deuterated compound showed no  $\alpha$ -hydrogen atom. Analysis by mass spectroscopy gave the following data: (*m/e*, relative intensity) 244, 4.4; 245, 59.7; 246, 13.7. After correction for C<sup>13</sup> contribution, the triphenylmethane was calculated to be 93.3%  $\alpha$ -d.

The triphenylmethane- $\alpha$ -d was exchanged in the apparatus used for oxidation and under prepurified nitrogen. In the sidearm, 0.30 g of triphenylmethane (93.3%  $\alpha$ -d) in 10 ml of dimethyl sulfide was placed, and the sidearm fitted to the oxidation flask containing a 0.246 *N* solution of potassium *t*-butoxide in 10 ml of DMSO and 5 ml of *t*-butyl alcohol. The oxidation apparatus was purged with prepurified nitrogen and at time zero the sidearm flask tipped to admit the triphenylmethane and the shaker started. After 2.50 min the shaker was stopped and enough water added to precipitate the triphenylmethane (about 100 ml). The precipitated triphenylmethane was filtered, dried, and recrystallized from 95% ethanol, mp 91–92°. Analysis by mass spectroscopy gave the following data: (*m/e*, relative intensity) 244, 15.4; 245, 13.2; 246, 2.4. After correction for C<sup>13</sup> contribution, the triphenylmethane was calculated to be 39.1  $\alpha$ -d.

**Acknowledgments.** Initial oxidations of triphenylmethane in DMSO were performed by Dr. E. G. Janzen. The rates of oxidation of triphenylmethane in 80:20 DMSO with lithium *t*-butoxide and sodium *t*-butoxide are results of Dr. R. Konaka. 1,1-Diphenylethane was prepared by Dr. J. Hunt.

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