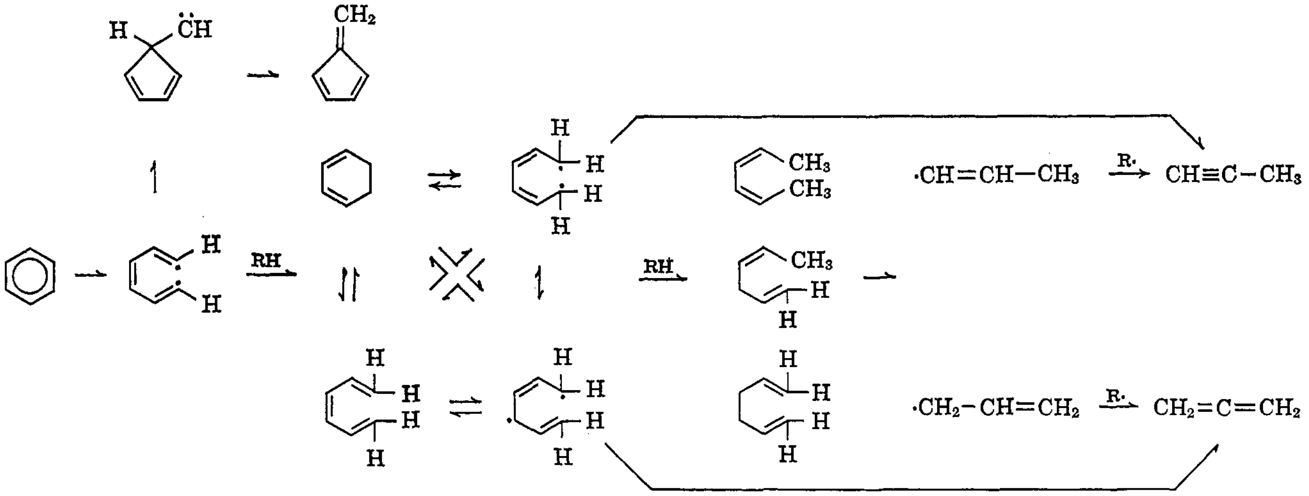
SCHEME II



Acknowledgment.—We wish to acknowledge the financial support of this work by the Dunlop Research Centre, Toronto, Canada. We thank Dr. John Doyle and Mr. Fred Swift, Jr., for their invaluable help. We also thank Dr. Edward Buchanan for running the emission spectra and Dr. T. H. Kinstle of the University of Illinois for the mass spectrographic analysis.

Physical and Chemical Properties of the α-Methoxydiphenylmethyl Radical

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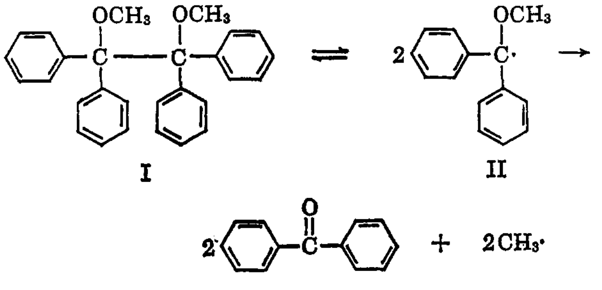
Received April 26, 1965

The α-methoxydiphenylmethyl radical, resulting from homolytic dissociation of 1,2-dimethoxy-1,1,2,2-tetraphenylethane, has been found to possess sufficient stability as to enable examination of its electron spin resonance spectrum and to permit trapping by reaction with carbon tetrachloride and with oxygen. The reaction with carbon tetrachloride leads to formation of benzophenone, presumably through an α-chloro ether intermediate. Reaction with oxygen results in formation of both benzophenone and methyl benzoate.

The α-methoxydiphenylmethyl radical (II) has been presumed to be the intermediate in the thermal decomposition of 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) to benzophenone and methyl radicals.[1] Evidence has now been obtained for the existence of the α-methoxydiphenylmethyl radical (II) by both spectroscopic and chemical methods.



(1)

The α-methoxydiphenylmethyl radical (II) possesses sufficient stability as to permit examination by electron spin resonance spectroscopy. A steady-state concentration of this radical of approximately 2×10^{-4} M was obtained by heating 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) in hexachlorobutadiene at 139° (Figure 1). Hyperfine splittings (a_H) are shown in Table I, along with spin density values (ρ_i) calculated from $\rho_i = a_{H_i}/Q$, with $Q = 23.8$.[2] Considering the six *ortho* and *para* (H_A), the four *meta* (H_B), and the three methyl group hydrogen atoms to form three sets of equivalent hydrogen atoms and using the observed hyperfine splittings, a spectrum essentially identical with that observed can be calculated. The H_A and H_B splittings are in good agreement with the modified molecular orbital treatment of Lefebvre.[3] Using the relationship, $\rho_A = (1 - \rho_B)C_{OA}^2 + \rho_B$, where C_{OA} is the HMO-LCAO coefficient at H_A and ρ_B is the experimental negative spin density at H_B, a value of 0.146 can be calculated for the positive spin density at H_A. This is in good agreement with the experimental value of 0.141.

TABLE I

ELECTRON SPIN RESONANCE DATA

	Splitting, gauss	Spin density
H_A	3.37	0.141
H_B	1.23	−0.052
$-CH_3$	0.33	0.014

Hyperfine splitting arising from the methyl group hydrogen atoms can be accounted for by assigning a

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[1] G. E. Hartzell and E. S. Huyser, *J. Org. Chem.*, **29**, 3341 (1964).

[2] H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

[3] R. Lefebvre, H. H. Dearman, and H. M. McConnell, *ibid.*, **32**, 176 (1960).

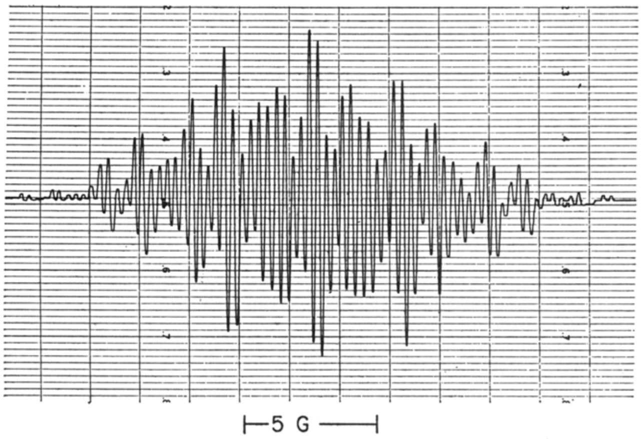
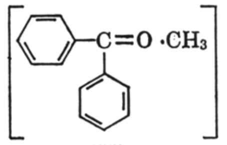


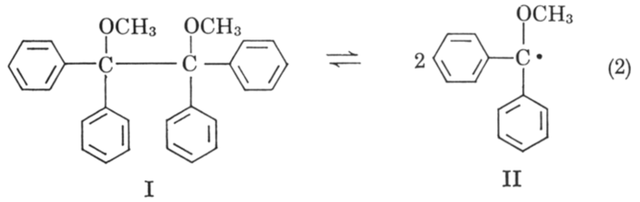
Figure 1.—Electron spin resonance spectrum of the α-methoxydiphenylmethyl radical.

spin density to the oxygen atom using the α–β model.[4] According to this model, an unpaired electron in a p-orbital on an α-carbon atom effects splitting from hydrogen atoms attached to a β-carbon atom by the relationship, $a_{\mathrm{H}} = \rho_\alpha B \cos^2 \theta$. In this case, ρ_α is the spin density on the α-atom, θ is the angle of the carbon–hydrogen bond projected on the p-orbital containing the unpaired electron, and B is a constant ranging from 40 to 62 gauss.[4,5] These values were developed for a carbon–carbon bond system and their applicability to an oxygen–carbon system may be questionable. However, using B = 47 gauss, a value of 0.014 can be calculated for the spin density on the oxygen atom.

The small hyperfine splitting of the methyl group hydrogen atoms may also be interpreted as arising from a small contribution of the valence-bond structure III, in which the carbon–oxygen bond has partial double bond character and the methyl group possesses partial free-radical character.



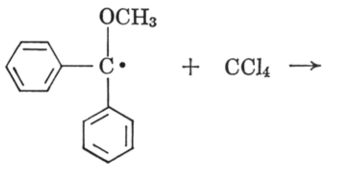
III



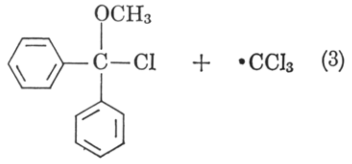
I

II

(2)

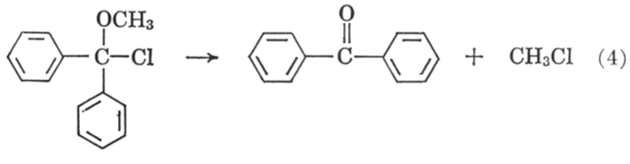


II



IV

(3)



IV

(4)

The α-methoxydiphenylmethyl radical (II) has been trapped in the reaction of 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) with carbon tetrachloride at 79°.[6] The ultimate products of the reaction are benzophenone and methyl chloride. Although these same products could ultimately result from reaction 1 in carbon tetrachloride, the rate of the reaction is approximately 10^3 times faster than would be expected from the radical-elimination process.[1] The reaction with carbon tetrachloride is thought to proceed by the sequence of reactions 2–4. The α-methoxydiphenylmethyl radical (II), formed in a rapid equilibrium step (2), undergoes a relatively slow displacement reaction (3) on carbon tetrachloride to produce α-chlorodiphenylmethyl methyl ether (IV). The latter is known to decompose upon heating to benzophenone and methyl chloride.[7] The presence of an intermediate in this reaction was observed by the growth of a singlet peak in the n.m.r. spectrum of the reaction mixture as the 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) disappeared, which subsequently diminished as benzophenone was formed. Figure 2 shows the concentrations of 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I), the intermediate IV, and benzophenone as a function of time. Interruption of the reaction at the point of maximum concentration of the intermediate by quenching with water resulted in rapid hydrolysis of IV to additional benzophenone and complete disappearance of the singlet peak for the intermediate in the n.m.r. spectrum. The aqueous phase gave a positive silver nitrate test for halide ion.

No reaction occurs upon heating 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) either in benzene or in chloroform at 80° for 24 hr., except for the equilibrium step (1). The nonreactivity of the α-methoxydiphenylmethyl radical (II) in these solvents is not surprising, in view of their small chain-transfer constants as compared with that of carbon tetrachloride.[8]

The α-methoxydiphenylmethyl radical (II) was also trapped by reaction with oxygen in benzene solution at 80°. The initial product is presumably a peroxide (V) which decomposes ultimately to form both methyl benzoate and benzophenone by different routes. A possible sequence of reactions is shown (5–7). The α-methoxydiphenylmethoxy radical (VI) may form methyl benzoate by elimination of a phenyl radical. Benzophenone may arise from decomposition of a

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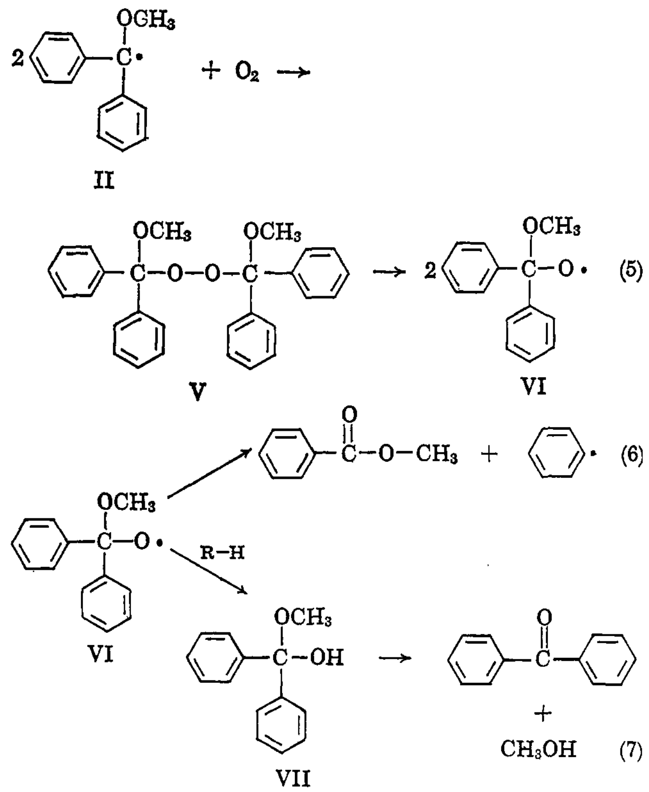
[4] C. Heller and H. M. McConnell, *J. Chem Phys.*, **32**, 1535 (1960).

[5] H. Fischer, *Z. Naturforsch.*, **19**, 866 (1964).

[6] It was observed that exposure of solutions of 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) in carbon tetrachloride to light at 25° resulted in slow formation of benzopinacolone. Independent experiments showed that HCl was capable of effecting the rearrangement, analogous to the normal acid-catalyzed rearrangement of benzopinacol. It is assumed that the rearrangement in carbon tetrachloride is caused by liberation of HCl under ultraviolet radiation, since the presence of 2,6-lutidine prevented the rearrangement.

[7] F. Straus and H. Heinze, *Ann.*, **493**, 191 (1932); F. Straus and H. J. Weber, *ibid.*, **498**, 101 (1932).

[8] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 153.



hemiketal formed from hydrogen abstraction by radical VI. No reaction was observed in benzene in the absence of oxygen.

The relative stability of the α-methoxydiphenylmethyl radical as well as the apparently rapid equilibration of this radical with its dimer suggest that the rate-determining step in the thermal decomposition of I may be the elimination of the methyl radical and not the homolytic dissociation as was previously suggested.[1]

Experimental

1,2-Dimethoxy-1,1,2,2-tetraphenylethane (I).—1,2-Dimethoxy-1,1,2,2-tetraphenylethane was prepared by reaction of diphenylmethyl methyl ether with di-*t*-butyl peroxide.[1]

Electron Spin Resonance Spectra.—Spectra were obtained using conventional e.s.r. equipment on solutions of 1,2-dimethoxy-1,1,2,2-tetraphenylethane in hexachlorobutadiene at 139°. Approximately 2×10^{-4} *M* concentrations of the radical II were observed. The value of *g* for the radical was 2.0030.

Reaction of 1,2-Dimethoxy-1,1,2,2-tetraphenylethane with CCl_4.—A 0.121 *M* solution of 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) was prepared by weighing out 2.395 g. (6.06 mmoles) of I and diluting to a total volume of 50 ml. with CCl_4. The infrared spectrum of this solution showed the absence of any carbonyl compounds. The only aliphatic protons in the n.m.r. spectrum were those of the methoxy groups at −2.99 p.p.m. (TMS as internal reference). The reaction mixture was heated under nitrogen at 79°. Samples were withdrawn periodically over a period of 6 hr. and analyzed for benzophenone by infrared spectra (C=O at 1660 cm.$^{-1}$) and for α-chlorodiphenylmethyl methyl ether (IV) (–OCH_3, δ = −3.38 p.p.m.) and 1,2-dimethoxy-1,1,2,2-tetraphenylethane (–OCH_3, δ = −2.99 p.p.m.) by n.m.r. Data obtained are presented in Figure 2. Final analysis of the reaction mixture after 6 hr. showed at least an 85% yield of benzophenone.

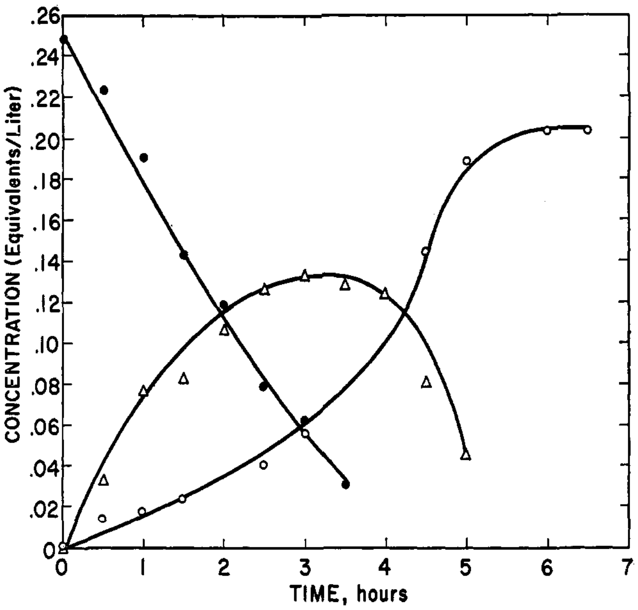


Figure 2.—Reaction of 1,2-dimethoxy-1,1,2,2-tetraphenylethane with CCl_4 at 79°: ●, 1,2-dimethoxy-1,1,2,2-tetraphenylethane; △, α-chlorodiphenylmethyl methyl ether; ○, benzophenone.

In a separate experiment, the mixture was rapidly cooled after 3-hr. reaction time. Infrared analysis showed the solution to be 0.08 *M* in benzophenone. The singlet peak corresponding to the α-chloro ether intermediate (IV) at −3.38 p.p.m. was present in the n.m.r. spectrum. This reaction mixture was then shaken with 100 ml. of water for 10 min. The water wash gave a positive test for halide ion with silver nitrate reagent. The CCl_4 layer was now found to be 0.12 *M* in benzophenone, and the n.m.r. peak at −3.38 p.p.m., corresponding to the α-chloro ether, had disappeared.

Benzophenone, produced in these reactions, was isolated as its 2,4-dinitrophenylhydrazone and found to be identical with an authentic sample.

Reaction of 1,2-Dimethoxy-1,1,2,2-tetraphenylethane with Oxygen.—A solution of 0.1 g. (0.25 mmole) of 1,2-dimethoxy-1,1,2,2-tetraphenylethane (I) in 2.0 ml. of benzene was heated at 80° for 4.5 hr. while sparging a gentle stream of oxygen into the solution. The benzene was allowed to evaporate and a residue was obtained, the n.m.r. spectrum of which showed essentially all of I to have reacted. The residue was separated by vapor phase chromatography into three major components, two of which possessed infrared spectra identical with those of authentic samples of methyl benzoate and benzophenone. Yields of methyl benzoate and benzophenone were approximately 28 and 38%, respectively, as indicated by vapor phase chromatography and n.m.r. analyses.