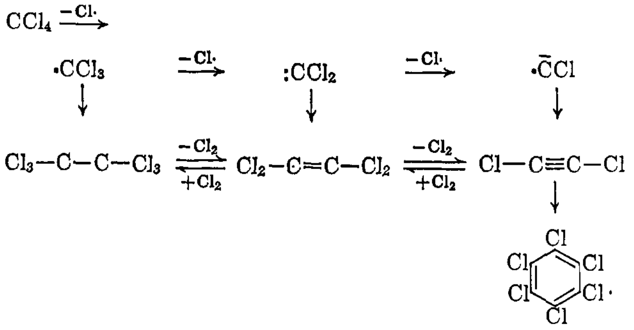
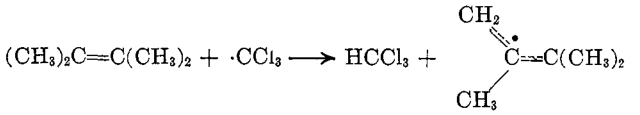
by the formation of hexachlorobenzene. By contrast, at 800° dichloroacetylene is observed but no tetrachloroethylene.[12] These products may be formed according to the following reaction scheme.



Any one of the three reactive species, the trichloromethyl radical, dichlorocarbene, or chloromethyne, could be the primary species responsible for the products. Coupling of the trichloromethyl radical would give hexachloroethane. It has been shown that thermal dechlorination of hexachloroethane to tetrachloroethylene takes place readily,[18] so that this path for the radiofrequency decomposition is not unreasonable. Dichlorocarbene, shown to be present in carbon tetrachloride pyrolysis by mass spectral analysis,[14] must be considered as another possible highly reactive intermediate.

An increase of the ratio of radiofrequency power per gaseous particle in the discharge zone produced a higher yield of tetrachloroethylene at the expense of hexachloroethane. This may be interpreted as either that the trichloromethyl radical was better able to eject another chlorine atom or that hexachloroethane was better able to lose chlorine.

It has been observed, however, that the generation of dichlorocarbene in the gas phase produces, among other products, some hexachlorocyclopropane.[19] We were not able to detect any hexachlorocyclopropane in our products. When tetramethylethylene was present in the gas phase immediately downstream from the discharge zone during the reaction, or when the products from the reaction were allowed to impinge on a liquid nitrogen cold finger immediately past the discharge zone and coated with tetramethylethylene, no dichlorotetramethylcyclopropane was obtained. Instead, chloroform was observed among the products. These



$$(CH_3)_2C{=}C(CH_3)_2 + \cdot CCl_3 \longrightarrow HCCl_3 + \overset{\dot{C}H_2}{\underset{CH_3}{C}}{\cdots}C(CH_3)_2$$

results can only be interpreted to mean that the trichloromethyl radical is the primary reactive species responsible for the formation of the observed products and that if dichlorocarbene is produced, it is undetectable by these experiments.

Acknowledgment.—This research was supported in part by the Dunlop Research Centre, Toronto, Canada, whose generosity is gratefully acknowledged.

[18] F. S. Dainton and J. K. Ivin, *Trans. Faraday Soc.*, **46**, 295 (1950).

[19] W. I. Beran, J. M. Birchall, G. N. Gilmore, and R. N. Hazeldine, Abstracts of Papers, International Symposium on Reaction Mechanisms, Cork, Ireland, July 20–25, 1964, p. 35.

The Reaction of Benzene in a Radiofrequency Glow Discharge[1]

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The action of a glow discharge produced by radiofrequency energy on benzene in the gas phase at room temperature produces a complex mixture of products, the most prevalent of which are poly(*p*-phenylenes), biphenyl, fulvene, acetylene, allene, and methylacetylene. By employing deuterium as a trapping agent for the phenyl radical, deuterated benzene was formed in high yield. The emission spectrum of the phenyl radical was observed.

Extensive studies on the decomposition of inorganic and organic compounds in an electric discharge have been carried out.[2,3] There has been little or no work, however, on the decomposition of complex organic compounds in a microwave of radiofrequency glow discharge.[4]

The reaction of benzene under electron impact in an electrode discharge tube gives a variety of products, most of which are of higher molecular weight than benzene.[5] The reaction of benzene in an electrodeless system, a microwave discharge, has also been shown to afford higher molecular weight products as well as appreciable fragmentation products.[6] In this paper, we report some observations on the reaction of benzene in a glow discharge produced by a radiofrequency field.

Experimental

Apparatus.—The apparatus was made up of Pyrex glass, and its manipulation was effected as previously described.[7] The radiofrequency generator, which operates at 14 Mc. with an output up to 600 w. provided the energy for the discharge. The reaction tube was connected to a series of traps which were set at −20, −70, −80, and −196°.

Radiofrequency Decomposition Reaction of Benzene.—A sample tube containing 30 g. of thiophene-free benzene was frozen at −30°. In 7.5 hr., 19.63 g. of benzene was passed through the radiofrequency field. The approximate residence

[1] Presented at the International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964; Abstracts of Papers, p. 53.

[2] G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

[3] C. L. Thomas, G. Egloff, and J. C. Morrell, *Chem. Rev.*, **28**, 1 (1941).

[4] A. M. Bass and H. P. Broida, Ed., "Formation and Trapping of Free Radicals," Academic Press Inc., New York, N. Y., 1960.

[5] H. Schüler, K. Prchal, and E. Kloppenburg, *Z. Naturforsch.*, **15a**, 308 (1960).

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[6] A. Streitwieser, Jr., and H. R. Ward, *J. Am. Chem. Soc.*, **84**, 1065 (1962); **85**, 539 (1963).

[7] For a more detailed description of the apparatus, see F. Swift, Jr., R. L. Sung, J. Doyle, and J. K. Stille, *J. Org. Chem.*, **30**, 3114 (1965).

TABLE I

PROPERTIES OF POLYMER PRODUCT

	Found, %					
	Carbon	Hydrogen	Mol. wt.	Softening point, °C.	Infrared, cm.$^{-1}$	λ_{max}, mμ
Polymer 1 (extracted with benzene)	79.19	7.40	2180	200	796, 756, 700	282
Polymer 2 (extracted with toluene)	86.47	6.93	4760	200	862, 800, 756, 700	286

time of each molecule in the discharge zone was 0.025 sec.; the average rate of benzene passing through the field was 1×10^{-5} mole/sec. The pressure in the tube was 0.2 mm.

Biphenyl.—The compound collected in the −20° trap, which was recrystallized from methanol–water, melted at 69–70°. The melting point of a mixture of this material with an authentic sample of biphenyl was not depressed. The infrared spectra of the compound from the −20° trap and the authentic sample were identical.

Fulvene.—The products from the −70 and −80° traps were combined and subjected to fractional distillation under nitrogen. The fraction boiling at 79–80° was collected. The visible and ultraviolet spectra of the yellow distillate were taken; the ultraviolet spectrum of the yellow compound in benzene solution was observed differentially against pure benzene. The spectra showed maxima at 247 and 360 mμ, lit.[8,9] λ_{max} 242 and 362 mμ.

A mixture of 87 ml. of the yellow distillate obtained from several runs, 19 mg. (0.202 mmole) of maleic anhydride, and 1 mg. of hydroquinone was heated to the reflux temperature until the solution was faintly colored. The benzene was then removed under reduced pressure. To the residue was added 5 ml. of 5% sodium hydroxide solution and the resulting solution was extracted three times with chloroform. The basic solution was acidified with dilute hydrochloric acid, and the acidified solution was extracted with ether. The ether extract was dried and the ether was then removed under reduced pressure. The residue was recrystallized from a mixture of chloroform and petroleum ether (b.p. 38–60°). A yield of 12.7 mg. (35.2%) of the adduct, 7-methylene-5-norbornene-2,3-dicarboxylic acid, which melted at 149–150°, was obtained. The diacid was hydroscopic.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.86; H, 5.15. Found: C, 61.05; H, 5.20.

The infrared spectrum of the adduct showed maxima at 1555, 874, and 712 cm.$^{-1}$. The n.m.r. spectrum in hexadeuteriodimethyl sulfoxide (Varian Model A-60) showed peaks at τ 3.64 (=CH—), 5.64 (=CH_2), 6.62 (CH α to CO_2H), and 6.72 (CH bridgehead), relative to TMS, in the ratio of 2:2:2:2. The peaks were assigned by comparing the n.m.r. spectrum of the Diels–Alder adduct of the yellow compound with that of norbornene-2,3-dicarboxylic acid.[10]

An authentic sample of the fulvene–maleic anhydride adduct could not be prepared according to the method of Bryce-Smith.[9,11] An authentic sample of the adduct was prepared from fulvene obtained by the sodium methoxide catalyzed condensation of cyclopentadiene and formaldehyde.[12] The reaction was carried out as described except that one-fourth the amounts were employed. After the steam distillation of the reaction mixture, the cold distillate was extracted with 500 ml. of Freon 113 (b.p. 47.6°) and dried. To the Freon solution was added 1.0 g. of maleic anhydride and a few crystals of hydroquinone. The solution was heated to the reflux temperature until the solution became colorless (1.5 hr.). The solvent was removed and the fulvene–maleic anhydride adduct was isolated and purified as described for that product obtained from the radiofrequency reaction. The authentic product, m.p. 147–149°, exhibited properties identical with those of the adduct obtained from fulvene generated in the radiofrequency reaction.

Acetylene, Allene, and Methylacetylene.—The compounds from the −196° trap were separated into the lower boiling and higher boiling gases. The lower boiling gases were analyzed by a gas chromatograph. With a tetraisobutylene column, a column temperature of 25°, and a gas flow rate of helium at 30 cc./min., three components were found. By comparing the retention times with those of authentic samples, the three components were identified as acetylene, allene, and methylacetylene. The infrared spectra (Perkin-Elmer Model 421) of all three components were taken. The infrared spectrum of the first component (acetylene) showed characteristic acetylenic carbon–hydrogen stretchings at 3270 and 3310 cm.$^{-1}$ and was identical with the spectrum of an authentic sample of acetylene. The infrared spectrum of the second component showed the characteristic allenic carbon–carbon double bond stretchings at 1940 and 1960 cm.$^{-1}$. The infrared spectrum of an authentic sample of allene was identical with that of the second component. The spectrum of the third component, present in a very small quantity, showed the acetylenic carbon–hydrogen stretchings at 3270 and 3310 cm.$^{-1}$ plus the regular carbon–hydrogen stretching near 3000 cm.$^{-1}$.

Over 95% of the high-boiling gas was found to be benzene and the remaining small amount was a complex mixture of products.

Polymers.—The solid material in the reaction tube contained a benzene-soluble polymer and a toluene-soluble polymer, both of which showed no carbon–carbon double bond stretching in the infrared. Some of the physical properties of the polymers are tabulated in Table I.

This decomposition produced a 10% conversion to products: polymers, 5%; biphenyl, 2%; fulvene, 1%; acetylene, 1%; allene, 1%; and methylacetylene, trace.

The emission spectrum of the glow discharge of benzene during the radiofrequency decomposition reaction was taken with the Cary Model 14 spectrophotometer by using the discharge in place of the source light (Figure 1).

Deuteration of Benzene.—Three experiments were carried out. In expt. 1, dry deuterium (prepared by the electrolysis of deuterium oxide) was passed into the reaction tube 0.6 cm. above the radiofrequency field during the radiofrequency decomposition reaction of benzene. In expt. 2, deuterium was passed into the reaction tube immediately above the radiofrequency field during the radiofrequency decomposition reaction. In the third experiment, deuterium was passed into the reaction tube below the radiofrequency field and mixed with benzene prior to entering the discharge zone. In all three experiments, the usual procedure was applied as in the radiofrequency decomposition of benzene, and, as nearly as possible, deuterium was added in an equal molar amount. The products obtained were analyzed by a mass spectrometer. The results are tabulated in Table II.

TABLE II

MASS SPECTROSCOPIC ANALYSIS

No. of deuterium atoms/benzene	Product composition, %		
	Expt. 1	Expt. 2	Expt. 3
0	16.7	14.1	14.5
1	83.2	85.7	85.4
2	0.07	0.16	0.13

Discussion

Benzene reacts to the extent of 10% in a glow discharge produced by a radiofrequency field to give polymer (5%), biphenyl (2%), fulvene (1%), allene (1%), methylacetylene (trace), and acetylene (1%). Minor amounts of other products are present in the reaction mixture. Of particular interest is the observation that this reaction differs from that produced by a microwave generator.[6] The latter technique affords a lower conversion (5%) to products, half of which are low molecular weight materials the remainder of which are the higher molecular weight products: toluene, ethylbenzene, and phenylacetylene. One major difference in the two techniques is that a helium carrier gas was employed in the microwave decomposition, while no

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[8] J. M. Blair and D. Bryce-Smith, *Proc. Chem. Soc.*, 287 (1957).

[9] H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

[10] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[11] H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 1409 (1960).

[12] D. Meuche, M. Neuenschwander, H. Schaltegger, and H. U. Schlunegger, *Helv. Chim. Acta*, **47**, 1211 (1964).

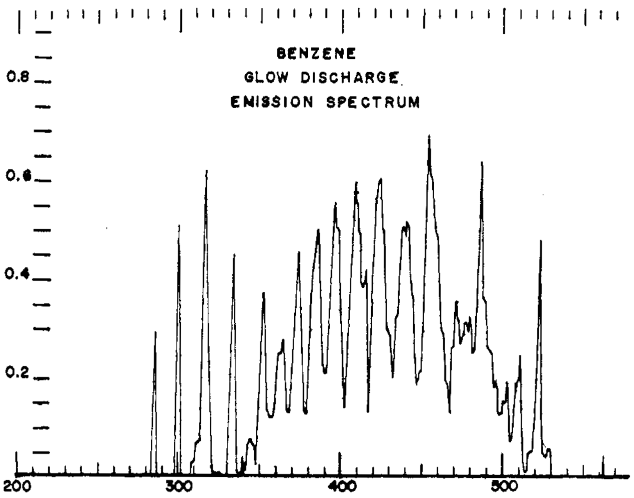


Figure 1.

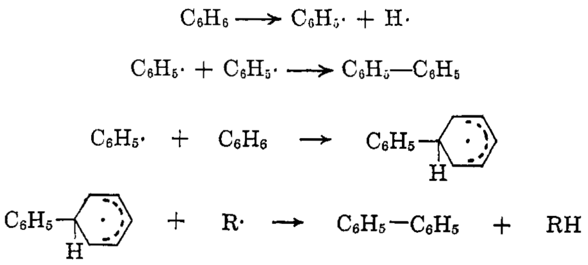
carrier gas was employed in the radiofrequency discharge.

The fulvene obtained from this reaction exhibited an ultraviolet spectrum in benzene and certain chemical characteristics identical with those reported for fulvene obtained from the photolysis of benzene.[8,9] Our adduct of fulvene and maleic anhydride (after hydrolysis to the acid) exhibited a different melting point (149–150°) from that obtained by Bryce-Smith (105–110°).[9] We were unable to prepare an authentic sample of the adduct by following the reported procedure[9,11] but obtained an authentic sample of the adduct by generating fulvene from cyclopentadiene and formaldehyde with a sodium ethoxide catalyst.[12] The 7-methylene-5-norbornene-2,3-dicarboxylic acid thus obtained was identical with the adduct resulting from fulvene generated by the radiofrequency discharge. The n.m.r. spectrum of the adduct verifies its structure. The melting range (105–110°) reported by Bryce-Smith was attributed to a mixture of *exo* and *endo* isomers[9]; we apparently obtained a single isomer.

The infrared spectra of the polymers showed no carbon–carbon double bond stretching, but instead showed characteristic aromatic maxima. The ultraviolet maxima for *p*-terphenyl and *p*-quaterphenyl are 280 and 300 mμ, respectively.[13] The maxima for the benzene-soluble polymer was 282 mμ and that for the toluene-soluble polymer was 286 mμ. The infrared spectra of the polymers showed a band at 860–800 cm.$^{-1}$ which corresponds to two adjacent hydrogens.[14] This band has been shown to shift toward lower wave length with increasing number of consecutive *para* linkages present. Both the benzene-soluble and toluene-soluble polymers showed maxima near 800 cm.$^{-1}$. These results indicate that the polymers are predominately poly(*p*-phenylenes) of different average molecular weight. Their high apparent thermal stability has made them difficult to analyze.

The products formed in this reaction may arise from two different initial bond-breaking reactions. The poly(*p*-phenylenes) and biphenyl are evidently formed as a result of an initial carbon–hydrogen bond-breaking reaction (Scheme I).

SCHEME I



The smaller fragments and fulvene may be formed through the carbon–carbon bond-breaking reactions shown in Scheme II.

The formation of 1,3,5-hexatriene as an intermediate in the reaction series originating from an initial carbon–carbon bond breaking (Scheme II) is reasonable, since 1,3,5-hexatriene has been reported to be formed from the photochemical decomposition of benzene in a rigid matrix at liquid nitrogen temperatures.[15,16] There is some question, however, as to whether the triene product was, in fact, fulvene.[9] Both fulvene and 1,3,5-hexatriene may be formed from the common diradical.

The emission spectrum of the phenyl radical generated by various techniques and from a variety of aromatic nuclei has been reported.[17,18] Unfortunately, the spectra obtained from the various aromatic nuclei are all very similar, so that it is not possible to draw any conclusions as to the authenticity of our spectrum by comparison with those spectra reported.[17] However, the chemical evidence supports the presence of a phenyl radical as a reactive species arising from the decomposition.

The high recovery of benzene from the glow discharge could be the result of several factors. An efficient recombination of phenyl and hydrogen radicals or the intramolecular coupling of the hexatrienyl diradical, once formed, with energy transfer to a third body or by light emission, would produce no over-all change. The failure of carbon–hydrogen or carbon–carbon bond rupture to take place at all or at least to a small extent (10%) would also account for the apparently unaltered benzene.

When deuterium was introduced just downstream from the discharge zone, an efficient incorporation (85%) of deuterium into benzene was accomplished. This suggests that an effective production of phenyl radicals was being carried out in the discharge zone, but that recombination with a hydrogen atom was taking place much more efficiently than, for example, phenyl radical coupling to give biphenyl. Dilution with deuterium allowed the abstraction of a deuterium atom from D_2 to form deuteriobenzene. The fact that a greater incorporation of deuterium was not obtained when deuterium was passed through the zone with benzene is not surprising. Deuterium would not be expected to absorb energy nearly as well as benzene[6] and could be expected to pass through the zone unaffected by the electromagnetic field.

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[13] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1964.

[14] R. R. Doss and P. W. Solomon, *J. Org. Chem.*, **29**, 1569 (1964).

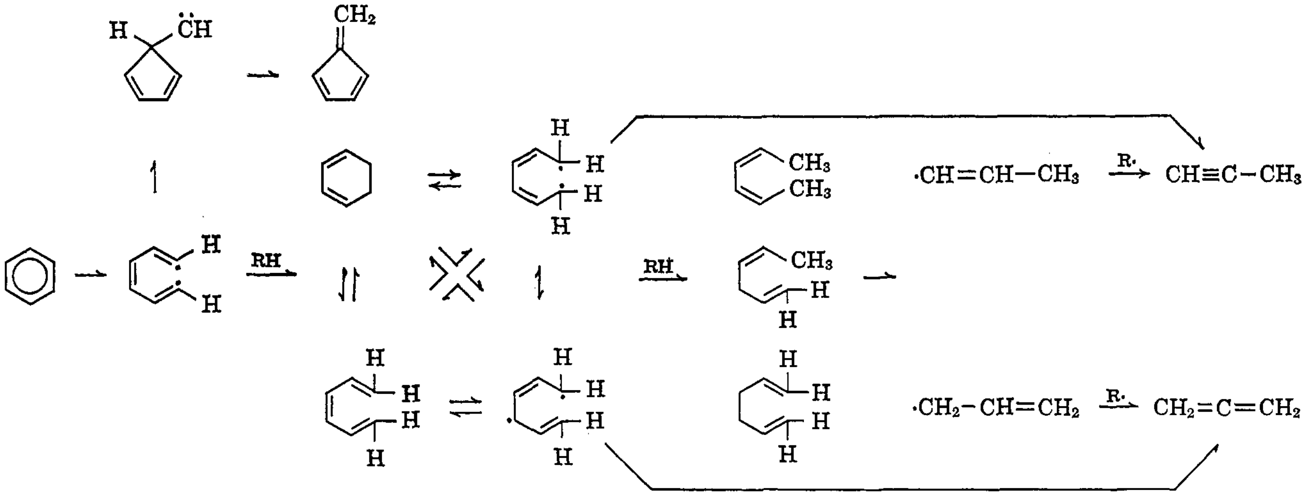
[15] G. E. Gibson, N. Blake, and M. Kalm, *J. Chem. Phys.*, **21**, 1000 (1953).

[16] I. Norman and G. Porter, *Proc. Roy. Soc.* (London), **A230**, 399 (1955).

[17] H. Schüler and L. Reinbeck, *Z. Naturforsch.*, **4a**, 577 (1949).

[18] S. H. Bauer and C. F. Aten, *J. Chem. Phys.*, **39**, 1253 (1963).

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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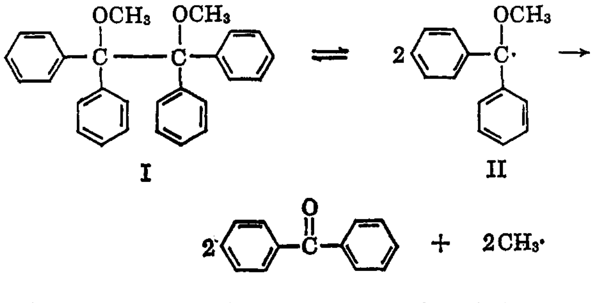
The α-methoxydiphenylmethyl radical, resulting from homolytic dissociation of 1,2-dimethoxy-1,1,2,2-tetraphenylethane, has been found to possess sufficient stability as to enable examination of its electron spin resonance spectrum and to permit trapping by reaction with carbon tetrachloride and with 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).