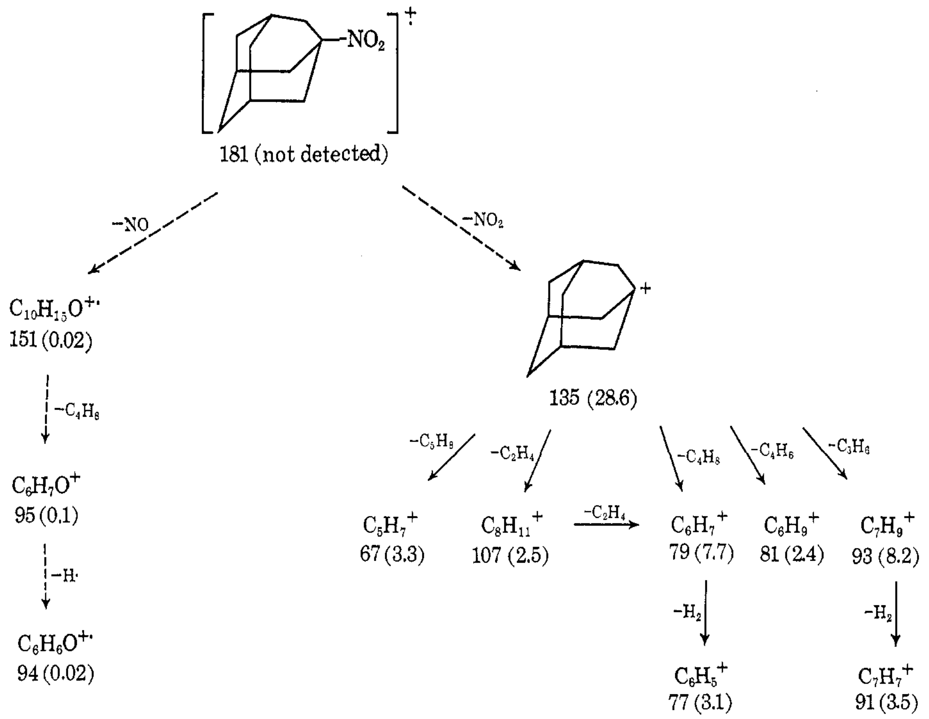
Scheme II



produced. The postulate that phenol is formed by the decomposition of the adamantyloxy radical finds a parallel in the mass spectrum of 1-adamantanol, in which the most abundant ion is $C_6H_7O^+$ (mass 95) formed by loss of $C_4H_9\cdot$ from the molecular ion.[2]

The product distribution from the pyrolysis of 1-nitroadamantane differs from that of adamantane[1] in that the latter produced substantial amounts of naphthalene and alkylnaphthalenes. These products presumably stem from initial carbon–carbon bond cleavages leading to reaction intermediates other than those derived from the adamantyl radical. The gaseous products also differ in that no methane was observed from the pyrolysis of adamantane,[1] whereas methane was one of the major gaseous products from the thermal decomposition of 1-nitroadamantane. This absence of methane is surprising since methylnaphthalenes were reported as products.

We are presently studying the reactions of adamantyl radicals formed *via* hydrogen abstraction by alkyl and aryl radicals derived from nitro derivatives at elevated temperatures.

Experimental Section

1-Nitroadamantane.—To a stirred solution of 123 ml of 40% peracetic acid and 450 ml of benzene was added over a 60-min period 30 g (0.2 mol) of 1-aminoadamantane in 300 ml of benzene. The solution was then heated under reflux for 3 hr and poured into 500 ml of water. The organic layer was separated, washed twice with 200 ml of 10% aqueous sodium hydroxide and 200 ml of 10% hydrochloric acid, and then washed with 100 ml of water. The benzene solution was dried over sodium sulfate. Evaporation of the benzene gave 28 g of crude product which was recrystallized from methanol to give 24 g (67% yield) of 1-nitroadamantane, mp 157–158° (lit.[4] mp 158.5–159°).

The pyrolysis reactions were run in a Vycor tube filled with Vycor chips in an electric furnace under pure dry nitrogen with contact times of 7–13 sec. The vapors were condensed in a flask at 0° and samples of the uncondensed effluent gases were collected for mass spectral analysis. The reaction tube was washed with chloroform, which was later removed by distillation. The condensates and the residues from the chloroform washes were analyzed by gas chromatography and directly coupled gas chromatography–mass spectrometry.[5]

In a typical experiment, 1-nitroadamantane (5.45 g, 0.030 mol) was passed through a Vycor tube at 600° under a nitrogen flow of 20 cc/min with a contact time of 11.1 sec. The 1-nitroadamantane was introduced into the reaction tube by boiling it in a bulb connected to the tube and having the nitrogen sweep the vapors into the reaction zone. The vapors were condensed in a flask at 0° (2.17 g). A sample of the uncondensed effluent gases was collected for mass spectral analysis halfway through the reaction. The reaction tube was washed with chloroform which was removed by distillation to give 0.60 g of residue. The condensate and the residue were then analyzed by gas chromatography and directly coupled gas chromatography–mass spectrometry. The column used in the gas chromatography work consisted of 10% OV 17 on Chromosorb W.

Mass Spectrometry.—The mass spectrum of 1-nitroadamantane was measured with 70-V electrons on a Consolidated Model 21-103 instrument, with the source at 250° and the inlet system at 150°. At inlet temperatures above 200°, thermal degradation of the sample occurred.

Registry No.—1-Nitroadamantane, 7575-82-8.

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[4] G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961).

[5] E. K. Fields and S. Meyerson, *ibid.*, **33**, 4487 (1968).

Electronic Effects of a Phosphorane Substituent[1]

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Taft and his coworkers have shown that the ^{19}F chemical shifts of *m*- and *p*-fluoro-substituted aromatics

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can be related to the substituents interaction with the π system by induction and resonance.[3] Recently this technique has been applied to various phosphorus-containing substituents.[4,5] These studies have included tri- and tetrasubstituted phosphorus compounds. Two pentasubstituted compounds, *m*- and *p*-fluorophenyltetrafluorophosphoranes, were also investigated.

The reaction of trisubstituted phosphorus compounds with diethyl peroxide provides a general route to phosphoranes.[6] This method has now been used to prepare tris-*p*-fluorophenyldiethoxyphosphorane (**1**) and tris-*m*-fluorophenyldiethoxyphosphorane (**2**). The quantities

$$\int_{\mathrm{H}}^{m\text{-X}}, \int_{\mathrm{H}}^{p\text{-X}}, \text{ and } \int_{m\text{-X}}^{p\text{-X}}$$

have been determined by recording the ^{19}F nmr spectra of **1** and **2** with fluorobenzene as an external standard. Using these data, σ_I, the inductive parameter, and σ_R, the resonance parameter, have been calculated. The values are +0.147 and +0.059, respectively. Positive values indicate that the substituent, $P(OC_2H_5)_2(C_6H_4F)_2$, is electron withdrawing both by induction and resonance. The magnitude of the parameters is so small that it is clear that the substituent has little effect on the π system. By comparison the substituent, $P(C_6H_4F)_2$ has σ_I +0.26 and σ_R −0.01 and $P(O)(C_6H_4F)_2$ has σ_I +0.45 and σ_R +0.12.[5] These values indicate that both substituents withdraw electrons by induction and the latter has some resonance interaction, although it is not strong. The σ_I value found for PF_4 (0.45) indicates that it is an inductive electron-withdrawing group and is of similar strength to PF_2 (0.39) and PCl_2 (0.44). Interestingly, the σ_R (0.35) for PF_4 was the largest observed in an extensive study of phosphorus-containing substituents. The difference between the pπ–dπ interactions in the two pentasubstituted phosphorus compounds is certainly remarkable and other systems should be studied.

Experimental Section

Preparation of 1 and 2.—The phosphines were prepared from the appropriate Grignard reagent and phosphorus trichloride. Their properties agreed well with those reported in the literature.[5] Tris-*p*-fluorophenylphosphine, 0.195 g (0.000616 mol), in 0.2 ml of methylene chloride in a cooled nmr tube was treated with 0.07 ml of diethyl peroxide. The course of the reaction was followed by ^{31}P and ^{1}H nmr spectroscopy.[7] The +9.2 absorption of the phosphine diminished and new absorptions appeared at +55 (**1**) and −26 (corresponding to oxide); the ratio was 6:1. Crystallization of **1** occurred and solvent was added to give a homogeneous solution. The ^{1}H nmr spectrum showed a characteristic apparent quintet for the methylene hydrogens of the ethoxy group at 2.58 ($J_{PH} = J_{HH} = 7$ Hz). The methyl protons were found at 0.77 ($J_{HH} = 7$ Hz). The ^{19}F nmr spectrum (94.1 MHz) showed an absorption at −2.18 ppm relative to fluorobenzene as external standard.

Tris-*m*-fluorophenylphosphine, 0.181 g (0.000572 mol), in 0.3 ml of methylene chloride was allowed to react with 0.07 ml of diethyl peroxide. Once again the phosphine absorption, +5, disappeared and that of **2**, +55, and its corresponding oxide, +25, formed in a ratio of 5:1. The ^{1}H nmr spectrum had an apparent quintet at 2.63 ($J_{PH} = J_{HH} = 7$ Hz) and a triplet at 0.80 ($J_{HH} = 7$ Hz). The ^{19}F absorption was found at −0.44 ppm relative to external fluorobenzene.

Comparative Nmr Measurements.—In this study fluorobenzene was used as an external standard rather than as an internal standard. The change in means of measuring the chemical shifts does not have an appreciable effect on σ_I and σ_R. It was found, for example, that σ_I for *m*-fluorotriphenylphosphine, *ca.* 1.06 *M* in methylene chloride with fluorobenzene as external standard, was +0.27 (lit.[5] +0.26) and σ_R −0.01 (lit.[5] −0.01).

Registry No.—**1**, 27531-53-9; **2**, 27570-95-2.

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[3] (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963); (b) R. W. Taft, E. Price, J. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

[4] J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968).

[5] A. W. Johnson and H. L. Jones, *ibid.*, **90**, 5232 (1968).

[6] (a) D. B. Denney and D. H. Jones, *ibid.*, **91**, 5821 (1969); (b) D. B. Denney, D. Z. Denney, B. C. Chang, and K. L. Marsi, *ibid.*, **91**, 5243 (1969).

[7] All ^{31}P spectra are reported in parts per million relative to 85% phosphoric acid.

Long-Range Effects in the Proton Nuclear Magnetic Resonance Spectra of Allenes

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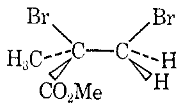
It is well known that the pmr spectrum of an acyclic compound containing both a methylene group and a neighboring asymmetrically (or pseudoasymmetrically) substituted atom can be considerably more complex than would be expected on the basis of simple spin–spin coupling rules. Thus the methylene protons in methyl 2,3-dibromo-2-methylpropionate (**1**) give rise to an AB pattern, rather than a singlet, because the time-averaged magnetic environments of the two protons differ, and no rotational processes can occur to bring about exchange between these two environments.[2] In this case the methylene protons are said to be diastereotopically related, and as such are, in theory, distinguishable by nmr.



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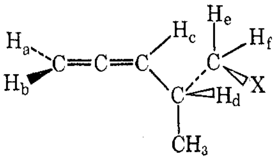
In connection with our study of homoallenic participation,[3] we had occasion to synthesize 2-methyl-3,4-pentadien-1-ol (**2a**), the derived acetate **2b**, and tosylate **2c**. The pmr spectra of these compounds[4] are



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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.

[2] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966. It is important to realize that this effect can be observed whether or not the compound has been optically resolved.

[3] (a) T. L. Jacobs and R. Macomber, *J. Amer. Chem. Soc.*, **91**, 4824 (1969). (b) The solvolytic properties of **2c** have been investigated and are reported separetely, along with synthetic details: R. S. Macomber, *ibid.*, **92**, 7101 (1970).

[4] Spectra were recorded using a Varian A-60 instrument, with samples 15% in carbon tetrachloride containing 1% TMS.