polar structure.[7] The 18 H^1 of the six methyl groups attached to nitrogen gave a doublet, J_{HP} = 9.7 c.p.s., at τ 7.17, when the H^1 n.m.r. spectrum was examined in $CDCl_3$.

The DEOM–TA 1:1 adduct, IV, reacted further with a second molecule of the keto ester II. Consequently, when the aminophosphine was added slowly to the ester, even in a 1:1 mole ratio, little 1:1 adduct IV resulted, in particular in THF[2] solution at 20°. The details of this reaction[3] will be given in the final paper of this series.

The orange triketone–TA adduct[5] V, m.p. 119–120°, was insoluble in hexane and sparingly soluble in benzene. It was soluble in methylene chloride and gave, in this solvent, a strongly negative P^{31} n.m.r. shift (Table I). The infrared spectrum[5] had a strong band at 6.76 μ, ascribed to the "enolate" carbonyl.[7] The 18 H^1 of the dimethylamino groups gave a doublet, J_{HP} = 10.0 c.p.s., at τ 7.08.

The yellow o-quinone–TA adduct[5] VI, m.p. 101° (benzene–hexane), was insoluble in hexane and in cold benzene. It was obtained unchanged from hot benzene. The P^{31} n.m.r. shift was negative, as shown in Table I. The infrared spectrum[7] had a strong band at 6.78 μ, and the 18 H^1 gave a doublet, J_{HP} = 10.2 c.p.s., at τ 7.42.

It seems clear that the relative stability of compounds with quintuply and quadruply connected phosphorus, derived from the reaction of trivalent phosphorus compounds with polycarbonyl compounds, may vary significantly with the structure of both reagents.[3,8] Therefore, each case must be examined on its own merits until all the factors responsible for the difference are ascertained.

(7) The absence of the infrared bands due to the stretching of normal carbonyl functions is one argument against adducts having a phosphorus–carbon bond. Other arguments are based on chemical reactions to be presented in the final paper of this series.

(8) For reactions of aldehydes with triaminophosphine see: (a) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963); (b) M. S. Newman and S. Blum, *ibid.*, **86**, 5598 (1964).

Fausto Ramirez, A. V. Patwardhan, Curtis P. Smith
State University of New York at Stony Brook
Stony Brook, New York
Received September 3, 1965

Electron Paramagnetic Resonance and Geometry of Perfluoroalkylmethylenes. A Chemiluminescent Reaction with Oxygen

Sir:

We have observed the electron paramagnetic resonance spectra of several ground-state triplet perfluoroalkylmethylenes, R–$\dot{C}$–H, R = CF_3 (I), R = $CF_3CF_2CF_2$ (II), R = $CF_3(CF_2)_6$ (III), and $CF_3\dot{C}CF_3$ (IV), including the fluorine hyperfine structure in IV. This is the first direct physical evidence for alkylmethylenes. I–IV are bent at the divalent carbon, *i.e.*, θ < 180°. As such, they are similar to the aromatic methylenes (*e.g.*, diphenylmethylene) which have θ ≈ 140–150° and which are approximately planar.[1,2] However, the values of θ for the monosubstituted I–III are significantly greater than that of disubstituted IV. Extrapolation to the unsubstituted CH_2 indicates a linear geometry. Thus, although all the substituted methylenes that have been observed by e.p.r. are bent, the observations are compatible with Herzberg's conclusion, from the ultraviolet spectrum, of a "linear or nearly linear" structure for the lowest triplet state of CH_2.[3]

Dilute "solid solutions" of the diazo precursors[4,5] were irradiated at 4°K. and the spectra were obtained and analyzed as described previously.[1,6] The values of the zero-field parameters were D_I = 0.712, E_I = 0.021, D_{II} = 0.723, E_{II} = 0.027, D_{III} = 0.72, E_{III} = 0.024, and D_{IV} = 0.7444, E_{IV} = 0.0437 cm.$^{-1}$. The spectrum of IV in $CFCl_3$ exhibited the hyperfine pattern expected for six equivalent fluorine nuclei. The magnitudes of the splittings along the x, y, and z principal axes were 85.9, 37.6, and 115.6 Mc.p.s., respectively, where x is the bisector of θ and y is perpendicular to the C–C–C-plane.[1] The splittings are probably all positive although the y value could be negative. The magnitudes of the isotropic (average) and anisotropic components indicate ~0.2% s and ~2% p character, respectively, for the unpaired electrons in the fluorine orbitals.[7] These values are similar to those found for β-fluorines in the radical from sodium perfluorosuccinate.[8]

Assuming that $D_{IV} - D_I = D_I - D_{CH_2}$, we obtain D_{CH_2} = 0.69–0.70 cm.$^{-1}$, which (*vide infra*) should be appropriate for the linear molecule. If one of the hydrogens is replaced by an aromatic system the resulting value of D is approximately proportional to the π spin density remaining at the divalent carbon after delocalization, since D is a measure of $1/r^3$ with r the distance between the unpaired electrons. The proportionality of the observed D values with the theoretical spin densities for several aromatic methylenes[2] leads to an extrapolated D_{CH_2} = 0.69–0.72 cm.$^{-1}$, in good agreement with the value obtained above.

E measures the difference of the magnetic dipole interaction along the x and y axes. It would vanish for the 3-fold symmetry of linear structures in I and IV in which these two axes would be equivalent. The nonzero values of E_I and E_{IV} thus indicate bent structures. The angle may be determined from the E/D ratios[1,9] which give θ_I ≈ 160° and θ_{IV} ≈ 140°. The ratios also indicate that θ_I ≈ θ_{II} ≈ θ_{III}.

Empirically, θ_{IV} < θ_I indicates that an attached CF_3 group reduces the angle at a divalent carbon. The same effect may be observed in a comparison of phenylmethylene, D = 0.5150 cm.$^{-1}$, E = 0.0251 cm.$^{-1}$,[1] and phenyltrifluoromethylmethylene, D = 0.5183 cm.$^{-1}$, E = 0.0313 cm.$^{-1}$.[10] If a similar effect occurs in

(1) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).

(2) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 129 (1965).

(3) G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

(4) The monosubstituted diazo compounds were prepared by decomposition of the sodium salts of the corresponding tosylhydrazones.

(5) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965), describe the preparation of the precursor of IV. We are grateful to Drs. Middleton, Krespan, and H. E. Simmons of the Central Research Department, Experimental Station, E. I. du Pont de Nemours, for making available the experimental details for the preparation of the bis(trifluoromethyl)diazomethane.

(6) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964); P. Kottis and R. Lefebvre, *ibid.*, **41**, 379 (1964).

(7) The anisotropic components indicate that the axis of the p orbital on each fluorine is well displaced from any of the principal axes of the electron spin–spin interaction, *i.e.*, the x, y, z system mentioned above.

(8) M. T. Rogers and D. H. Whiffen, *J. Chem. Phys.*, **40**, 2662 (1964).

(9) J. Higuchi, *ibid.*, **39**, 1339 (1963).

(10) In a previous publication (E. Wasserman, *ibid.*, **42**, 3739 (1965)),

I, CH_2 should have an angle larger than 160°. Extrapolating from θ_{IV} to θ_I to θ_{CH_2}, a linear geometry for CH_2 is indicated. Although all the derivatives which have been observed by e.s.r. are bent, nonconjugated alkylmethylenes may be linear as phenylmethylmethylene has an E/D ratio[11] close to that of phenylmethylene.

A white chemiluminescence is observed after irradiation of a solution of bis(trifluoromethyl)diazomethane in perfluorodimethylhexane. At 77°K. the light is emitted for more than 'an hour after irradiation ceases and appears only if the sample contains oxygen or is exposed to oxygen after irradiation. On warming, the emission is sufficiently bright to be observed under ordinary room illumination. The spectrum is identical with the phosphorescence of hexafluoroacetone measured at 77°K. Presumably IV reacts with oxygen and eventually yields the lowest triplet state of hexafluoroacetone.[12]

Acknowledgment. We wish to thank Mr. R. M. R. Cramer for his assistance in obtaining the e.s.r. spectra.

the values for phenyltrifluoromethylmethylene and those of I were said to lead to $D_{CH_2} = 0.74$ cm.$^{-1}$. This conclusion involved a correction of $+0.02$ cm.$^{-1}$ on going from a bent to a linear configuration with I, following the dependence of D on angle predicted in ref. 10. However, such an angular dependence of D, if it is correct, is overshadowed in I and IV by the effect of the CF_3 groups. With I and IV a decrease in angle accompanies an increase in D. In any case, 0.74 cm.$^{-1}$ may be viewed as an upper limit to our extrapolated values, but should be given less weight than the lower values mentioned.

(11) $D = 0.4957$ cm.$^{-1}$, $E = 0.0265$ cm.$^{-1}$ (R. W. Murray, to be published).

(12) The phosphorescence of benzophenone has been observed from the reaction of oxygen with diphenylmethylene [A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4490 (1962)].

E. Wasserman, L. Barash, W. A. Yager

Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey

Correlation of *cis*- and *trans*-3-Methylproline with (Allo) Isoleucine

Sir:

The biosynthesis of actinomycin from *Streptomyces antibioticus* is strongly inhibited by 3-methylproline.[1] As little as 0.1 μg./ml. of the mixture of racemic *cis*- and *trans*-3-methylprolines causes a 50% inhibition. In order to extend and detail these observations the diastereoisomers were separated and their configuration elucidated as follows.

The racemates of *cis*- and *trans*-3-methylproline have recently been synthesized.[2] One isomer, m.p. 218–219°, had a n.m.r. coupling constant $J_{23} = 4.6$ c.p.s. while the other, m.p. 210–211°, had $J_{23} = 7.2$ c.p.s. Although the question of relative configuration was left open, it seemed probable, by analogy with 3-hydroxyproline,[3,4] that the isomer having the larger coupling constant J_{23} would be *cis* (II; R = R' = H: L forms are shown throughout to represent racemates).

The *cis* and *trans* isomers were originally separated by fractional crystallization. For small-scale separations

(1) T. Yoshida, A. B. Mauger, B. Witkop, and E. Katz, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 40C. Also in press.

(2) D. A. Cox, A. W. Johnson, and A. B. Mauger, *J. Chem. Soc.*, 5024 (1964).

(3) F. Irreverre, K. Morita, A. V. Robertson, and B. Witkop, *J. Am. Chem. Soc.*, **86**, 8293 (1964).

(4) J. Blake, C. D. Willson, and H. Rapoport, *ibid.*, **86**, 5293 (1964).
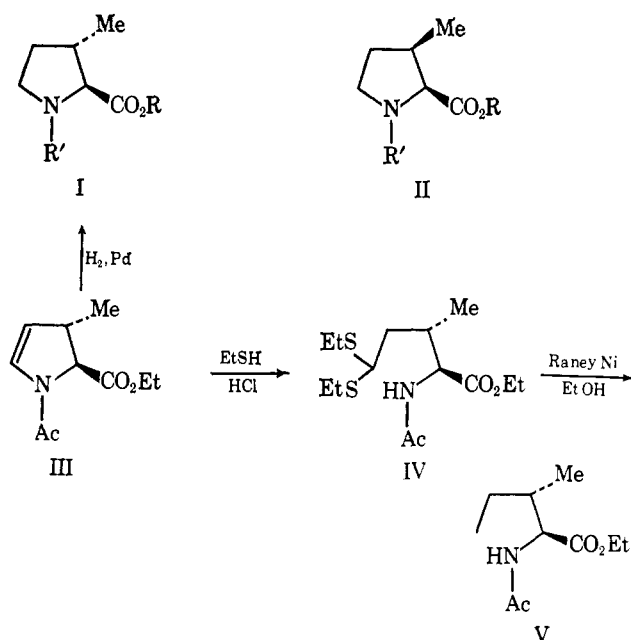
we have found ion-exchange chromatography (Amberlite IR-120) more convenient. For large-scale preparations the method of choice is preferential saponification. A study of the relative rates of saponification (4.5-fold excess of 0.24 N methanolic sodium hydroxide at 32°) of a mixture of I and II (R = Me, R' = Tos) by gas–liquid partition chromatography showed that one of the isomers was saponified to the extent of 96% after 55 min. Only 5% of the other ester had hydrolyzed during this time as shown by g.l.p.c. of the acid fraction after re-esterification. The more resistant ester must be the sterically hindered *cis* form II (R = Me); the saponified acid is therefore the *trans* form I (R = H). This confirms the initial assignments based on n.m.r. data.

Final proof was obtained by correlation of I (R = Et, R' = Ac) with DL-isoleucine *via* III, IV, and V.

N-Acetyl-3-methyl-4,5-dehydro-DL-proline ethyl ester, the synthesis of which will be described elsewhere, was separated into *cis* and *trans* isomers by preferential saponification. The *trans* ester III, m.p. 49–51°,[5] was hydrogenated to N-acetyl-3-methyl-DL-proline ethyl ester, identified by g.l.p.c. (Table I) with the corresponding derivative of I (R = R' = H).

Reaction of III with ethyl mercaptan and hydrogen chloride in dioxane at room temperature gave the mercaptal IV. Desulfurization of IV with Raney nickel in boiling ethanol afforded N-acetyl-DL-isoleucine ethyl ester (V), which was compared and identified with the corresponding derivative of L-isoleucine by g.l.p.c. and n.m.r. (the α-proton in N-acetyl-L- and -D-alloisoleucine ethyl ester appeared as multiplets at δ 4.68 and 4.78 p.p.m., respectively). The other diastereoisomer of III was similarly converted both into N-acetyl-DL-alloisoleucine ethyl ester and into II (R = Et, R' = Ac).

These interconversions establish unambiguously the stereochemistry of the isomeric 3-methylprolines. Additional interest is provided by the recent claim that *cis*-3-methyl-L-proline occurs in the peptide antibiotic

(5) Most of the 3-methylproline derivatives described were low melting solids or liquids. They all gave satisfactory analytical results for C, H, and N and were characterized by n.m.r., infrared, and g.l.p.c. techniques.