Figure 1. Esr spectrum of a malonic acid-d_4 crystal recorded 90 min after a 15-min exposure to X-rays. The magnetic field lies approximately in the C-C-C plane.

^{13}C(II) hyperfine, and (1.9964, 2.0019, 2.0040) for the g value. The similarity of the ^{13}C(I) tensor to those of the radicals CO_2^- [2] and $H\dot{C}=O^{3c,d}$ indicates that the bulk of the unpaired spin density is localized in a σ orbital on carbon. An angle of about 130° between the two bonds to this carbon can be deduced from the tensor.[7] The low g value along one canonical axis corresponds well with the characteristic behavior of $-\dot{C}=O$ σ radicals[2,3,5c,d] suggesting some delocalization of the σ-unpaired electron onto the oxygen of a $C=O$ group.[3a] The presence of the large second carbon-13 splitting eliminates ·COOH as a possibility, and in fact leads to

$$\text{\backslash C-C}\overset{O}{\underset{·}{\diagup}}$$
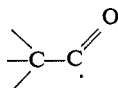
as the most plausible framework.

Further, a pleasing internal consistency is achieved when the above tensors are compared with the malonic acid crystal structure.[8] The major anisotropy axis of the ^{13}C(I) tensor, the major axis of the ^{13}C(II) tensor, and the g-minimum axis are parallel (respectively) to the C—O single bond, the C—C bond, and C=O double bond directions for one of the two carboxyl groups. The inescapable conclusion is that the trapped radical is $RCH_2\dot{C}=O$, and is produced by fission of the C–O single bond in that carboxyl group which is parallel to the C-C-C plane of malonic acid. The lines marked σ' in Figure 1 arise from the complementary σ radical whose carbon-13 and g tensors indicate[9] that it is the species produced by C–O bond fission in the *other* carboxyl group (the one perpendicular to the C-C-C plane).[8]

The size of the ^{13}C(II) splitting is at first very surprising, for it means that about 20% of the spin density is localized in the single bond between carbons. However, this is exactly analogous to the spin density distribution in the formyl radical ($H\dot{C}=O$), whose extraordinarily large (380 MHz) proton splitting is explained by Adrian, *et al.*, on the basis of extensive mixing of a nonbonded structure into the radical ground state.[3a] Application of the same model to $RCH_2\dot{C}=O$ predicts that the ^{13}C(II) tensor should be about one-third the size of the ^{13}C(I) tensor, as observed.

The most important unresolved question concerning acetyl radicals is the size of the hyperfine coupling to

(7) Using the s- and p-orbital parameters collected by J. R. Morton, *Chem. Rev.*, 64, 453 (1964).

(8) J. A. Goedkoop and C. H. MacGillavry, *Acta Cryst.*, 10, 125 (1957).

(9) The anisotropy of these tensors is reduced, apparently by a large amplitude motional averaging. Esr spectral changes observed upon cooling the crystal confirm the existence of a motional effect for the σ' radical and the absence of one for the σ radical.

the protons. Although Figure 1 shows no resolved deuteron splitting, the carbon-13 satellites from the σ radical in protonated crystals do reveal an excellent hyperfine pattern from two protons, as expected. The principal tensor elements for each proton (absolute signs assumed) are $(-)12 \pm 1, (-)16 \pm 1$, and $(+)5 \pm 3$ MHz, with the axial direction in each case being roughly the line between the proton and C(I), the carboxyl carbon. This isotropic hyperfine coupling of $(-)8 \pm 2$ MHz is smaller in absolute value than that obtained from randomly oriented acetyl radicals.[10]

The bright pink color which we associate with RCH_2-$\dot{C}=O$ in these crystals compares nicely with the red coloration imparted to hydrocarbon glasses by acetyl radicals.[5b] This absorption can be attributed to the $\sigma \rightarrow \pi^*$ electronic transition which is also responsible for the low g value when H is parallel to the C=O bond.[3a] Both the color and $RCH_2\dot{C}=O$ esr signal seem to decay at the same rate. The half-life of the latter (at 23°) is about 23 hr in malonic acid-d_4 but is only 1 hr in malonic acid-h_4.

An additional striking isotope effect is apparent in the formation of the radicals themselves. In the limit of short X-irradiation at room temperature, fully 50% of the radicals trapped in malonic acid-d_4 are of the $RCH_2\dot{C}=O$ type whereas 10% is an upper limit in malonic acid-h_4. It is thus possible that $RCH_2\dot{C}=O$ and $R\dot{C}HR$ (the latter is essentially absent in freshly irradiated malonic acid-d_4) are formed in a branching of paths from the same primary damage species, with the rate-determining step being C–O bond fission in the former case and H abstraction in the latter. Similarly the large isotope effect in the aging times hints that a H-abstraction process is rate determining for the decay as well. The observation that disappearance of the σ radical correlates with appearance of $R\dot{C}HR$ in the aging crystals lends support to this interpretation.

(10) The 14-MHz estimate of ref 5a may be passed over, for the g anisotropy, which was not considered, probably accounts for the structure in their spectrum. Tentative values of 14 and 22 MHz (ref 5c and 5d, respectively) for the isotropic component have recently been extracted from line shape studies of matrix-isolated acetyl radicals. Direct comparison of these various isotropic values is complicated by the possibility that part of the proton hyperfine may arise from hyperconjugation and thus depend upon the rotational position of the methyl group. As the C–H bond directions in $RCH_2\dot{C}=O$ are nearly orthogonal to the σ-orbital axis, we expect hyperconjugation to be at a minimum in this radical. To be compatible with the $(+)14$-MHz matrix value,[5c] an average hyperconjugative effect of $+22$ MHz is indicated for the rotating methyl group.

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The Low Barrier to Pyramidal Inversion in Phospholes. A Measure of Aromaticity[1]

Sir:

The rate of pyramidal inversion at phosphorus in acyclic phosphines is remarkably insensitive to variations in structural parameters; expressed as $\Delta G_{130}^{\ddagger}$, the

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

magnitude of the barrier falls into the range of 29–36 kcal/mol for sundry diarylalkyl, dialkylaryl, and tri-alkyl phosphines.[2] However, in cyclic phosphines, angle strain in the transition state introduces a significant *increase* in the barrier height.[3] We now report our finding that the barrier ($\Delta G_{25}{}^{\pm}$) to pyramidal inversion at phosphorus in 1-isopropyl-2-methyl-5-phenylphosphole (**1**) has the extraordinarily low value of 16 kcal/mol, and that the magnitude of this barrier indicates $(3p–2p)\pi$ delocalization and aromaticity in phosphole systems.

1
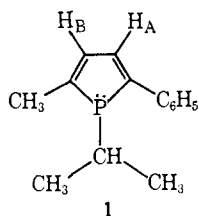
The synthesis of **1** was accomplished through *n*-butyl-lithium catalyzed cyclization[4a] of 1-phenyl-1,3-penta-diyne and phenylphosphine, to give 1,2-diphenyl-5-methylphosphole (**2**), which was subsequently cleaved[5] with lithium (2 equiv) and treated with isopropyl bromide. Separation of **1** from unreacted **2** by rapid distillation (kugelrohr) at reduced pressure, followed by chromatography (Florisil, 30–60° petroleum ether) and final distillation (kugelrohr, *ca.* 85°, 0.04 mm), afforded a sample of **1** which contained a small amount of un-identified material, as judged by nmr. The nmr spectrum of **1**,[6] together with comparable data for other phospholes[4,7] and 2-phospholenes,[8] provides convincing evidence for the assigned monomeric[9] structure: δ 6.9–7.6 (m, C_6H_5), 6.80 (dd, $^3J_{PH}$ = 9.5 Hz, $^3J_{HH}$ = 3.0 Hz, =CH_A), 6.54 (d sextets, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 3.0 Hz, $^4J_{HH}$ = 1.5 Hz, =CH_B), 2.16 (dd,

(2) R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, in press.

(3) 1,2,2,3,4,4-Hexamethylphosphetane [S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Lett.*, 5799 (1968)] and 1,3-dimethylphospholane [K. L. Marsi, *Chem. Commun.*, 846 (1968); *J. Amer. Chem. Soc.*, 91, 4724 (1969)] are reported to show no measurable stereomutation in 4 days at 162°, and in 3 days at 150°, respectively. We find that 3-methyl-1-phenylphospholane (i) suffers stereomutation at 170° in C_6H_6, with $\Delta G \neq$ *ca.* 36 kcal/mol.

i
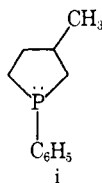
(4) (a) G. Märkl and R. Potthast, *Angew. Chem.*, 79, 58 (1967); (b) G. Märkl and R. Potthast, *Tetrahedron Lett.*, 1755 (1968).

(5) E. H. Braye, U. S. Patent 3,338,941 (1967); *Chem. Abstr.*, 68, 39816z (1968); A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, 31, 112 (1966).

(6) Coupling constants and chemical shifts were assigned by comparison of spectra obtained at 60 and 100 MHz. The line-shape analysis was based on data obtained on a Varian HA-100 spectrometer. The sample was a *ca.* 25 v/v % solution in $CFCl_3$ with *ca.* 5 v/v % TMS (internal lock) and *ca.* 5 v/v % CH_2Cl_2.

(7) L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, 91, 3308 (1969).

(8) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, 33, 1034 (1968).

(9) Consistently, absence of any absorption in the region δ 3–6 excludes the possibility of dimerization of **1** to an adduct analogous to those found[4b,10] for various phosphole oxides.

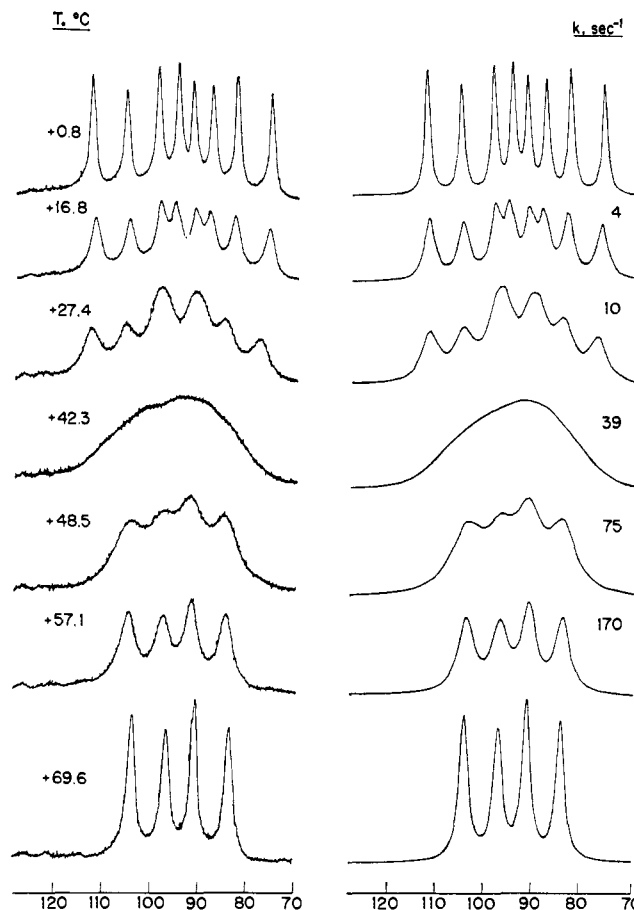(10) R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, 91, 4143 (1969).

Figure 1. Comparison of experimental spectra of **1** at different temperatures (left) and theoretical spectra at various rates (right). The scale is in hertz and is relative to the internal lock signal, TMS. The low-intensity broad signals at *ca.* 110–128 Hz are an unidentified impurity.

$^3J_{PH}$ = 10.0 Hz, $^4J_{HH}$ = 1.5 Hz, =CCH_3), 1.6–2.3 (m, $CH(CH_3)_2$).

Examination of the isopropyl region of the nmr spectrum of **1** at 0.8° gave the expected pattern for a conformationally restricted phosphole: δ 1.02 ($^3J_{PH}$ = 13.9 Hz, $^3J_{HH}$ = 7.1 Hz, $CH_{3(a)}$), 0.85 ($^3J_{PH}$ = 12.2 Hz, $^3J_{HH}$ = 7.1 Hz, $CH_{3(b)}$). Total line-shape analysis of the temperature dependence of these signals (Figure 1), utilizing Binsch's DNMR program,[11] led to values of $\Delta H^{\pm}$ = 17.1 ± 0.4 kcal/mol and $\Delta S^{\pm}$ = 3.1 ± 1.1 eu,[12] which correspond to $\Delta G_{25}{}^{\pm}$ = 16 kcal/mol. Presumably, pyramidal inversion at phosphorus is the rate-determining step which corresponds to the measured barrier.

The dramatic lowering of the inversion barrier by *ca.* 23 kcal/mol[14] may be ascribed to increased delocalization ("aromaticity") of **1** in the transition state of inversion, where, in contrast to the ground state, the orbital

(11) G. Binsch, *ibid.*, 91, 1304 (1969).

(12) The reported values of $\Delta H \neq$ and $\Delta S \neq$ were obtained from a least-squares treatment (correlation coefficient 0.998) of ln (k/T) *vs.* (1/T), using nine data points obtained in the range 12–58°. The error values reported for $\Delta H \neq$ and $\Delta S \neq$ are standard deviations, but the actual errors are most likely greater than statistical.[13]

(13) A. Allerhand, F. Chen, and H. S. Gutowsky, *J. Chem. Phys.*, 42, 3040 (1965); A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, 88, 3185 (1966).

(14) An appropriate comparison system for **1** might be 1-cyclohexyl-3-methylphospholane, for which we estimate a $\Delta G \neq$ of *ca.* 39 kcal/mol (36 kcal/mol for the 1-phenyl analog,[3] plus 3 kcal/mol for substitution of a cyclohexyldialkyl- for a phenyldialkylphosphine system[2]).

axis of the lone pair of electrons on phosphorus is parallel to the $2p\pi$ orbital axes on carbon.[15] It is now recognized that previous evidence adduced for aromaticity in phosphole derivatives, based on thermochemical[16] and spectroscopic (nmr[4,7] and uv[7]) data, must be referred to the pyramidal (*i.e.*, ground state) rather than planar conformation. Data based on chemical reactivity, which have been offered as evidence against aromaticity,[7,17] bear little relevance to considerations affecting the ground state of the molecule.

The effect of substituents on the barrier to inversion in phospholes and cognate systems is currently under investigation.

(15) D. A. Brown, *J. Chem. Soc.*, 929 (1962), has suggested, on the basis of HMO calculations, that phosphole in the planar conformation gains considerable conjugation energy through involvement of the $3p\pi$ orbital of phosphorus.

(16) A. F. Bedford, D. M. Heinekey, I. T. Millar, and C. T. Mortimer, *ibid.*, 2932 (1962).

(17) E. H. Braye and W. Hübel, *Chem. Ind.* (London), 1250 (1959); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *J. Amer. Chem. Soc.*, 82, 5099 (1960); E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, 83, 4406 (1961); A. N. Hughes and S. Uaboonkul, *Tetrahedron*, 24, 3437 (1968).

(18) (a) National Aeronautics and Space Administration Fellow, 1969–1970; (b) National Defense Educational Act Fellow, 1969; Public Health Service Predoctoral Fellow, 1969–1970.

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Stable Radicals by Photooxidation of Nitrones

Sir:

The isomerization of nitrones to oxaziranes by exposure to light has been reported.[1,2] We have observed that ultraviolet irradiation of nitrones in solution at room temperature produces long-lived radicals. They arise apparently by a photochemical oxidation of the nitrones. By means of esr measurements these radicals have been identified as N-benzoylnitroxides.
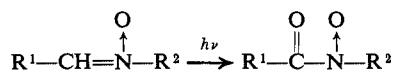
Listed in Table I are the nitroxides and their hfsc's. The esr spectrum of N-benzoyl-N-phenylnitroxide (1)

**Table I.** Splitting Constants of Aroylnitroxides in Benzene[a]

Radical	R^1	R^2	A^N	$A_{o,p}^{H}$[b]	A_m^{H}[b]
1	C_6H_5	C_6H_5	7.53	1.55	0.70
1	C_6H_5	C_6H_5	7.58[c]	1.55[c]	0.70[c]
2	p-$CH_3OC_6H_5$	C_6H_5	7.78	1.62	0.68
3	C_6H_5	p-$CH_3C_6H_5$	7.53	1.63[d]	0.65
4	C_6H_5	t-C_4H_9	7.92		

[a] A Varian 4500 epr spectrometer was used. Measurements were made at room temperature. Sweep rates were calibrated by the spectrum of p-benzosemiquinone in aqueous ethanol according to the procedure of E. W. Stone and A. H. Maki, *J. Chem. Phys.*, 36, 1944 (1962). The splittings are given in gauss. [b] The H splittings are from the N-phenyl group. [c] By NiO_2 oxidation of N-benzoyl-N-phenylhydroxylamine in benzene, Aurich and Baer[3] reported A^N 7.55, $A_{o,p}^{H}$ 1.54, and A_m^{H} 0.64 G. [d] The p-methyl- and o-H's are equivalent and give rise to a sextuplet.

(1) J. Splitter and M. Calvin, *J. Org. Chem.*, 20, 1086 (1955).
(2) K. Shinazawa and I. Tanaka, *J. Phys. Chem.*, 68, 1205 (1964).

was reported by Aurich and Baer[3] who prepared this radical by chemical oxidation of N-benzoylphenylhydroxylamine (5). The radical has also been obtained
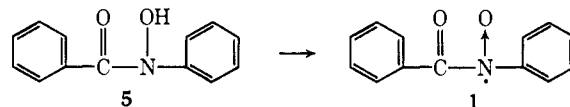

by combination of benzoyl radical and nitrosobenzene.[4]

Janzen and Blackburn[5] have apparently formed N-benzoyl-N-t-butylnitroxide (4) by chemical oxidation of α-phenyl-N-t-butylnitrone. A triplet with A^N = 7.67 G splitting was attributed to 4.

The nitrones have also been reported recently as radical traps for short-lived species,[5–8] in which case the short-lived radicals add to the α-carbon atom of the nitrone to give the stable nitroxide radical. The hfsc's of the nitrogen and α-H atoms vary with the added group. The nitrogen hfsc's observed are characteristically larger than those from aroyl nitroxides.

We prepared nitrone solutions approximately 0.05 M in benzene and deaerated the solutions with a fine stream of argon bubbles. The solutions were prepared, deaerated, and measured in the dark, and were exposed for 10–30 sec only to the light from a Bausch and Lomb SP 200-W super pressure mercury lamp. No esr signals were detected prior to irradiation. Maximum signal strength was obtained 15–30 min after irradiation and the signals lasted for days. We found that a second deaeration after exposure usually improves the intensity and the resolution of the signal. It is quite likely that oxygen is formed during irradiation of the nitrones, for the liberation of oxygen from N-oxides under irradiation has been observed.[9,10]

Benzoyl nitroxides are also detected when the phenylnitrones are irradiated in methylene chloride, but no esr signals are obtained in ethanol solutions. No esr signal is obtained when the α-hydrogen atom is replaced, *e.g.*, from α-cyano-α-phenyl-N-phenylnitrone when irradiated.

α-Phenyl-N-t-butyloxazirane (6), which is a stable compound at room temperature,[11] when irradiated in benzene gives the same triplet with A^N = 7.92 G as the
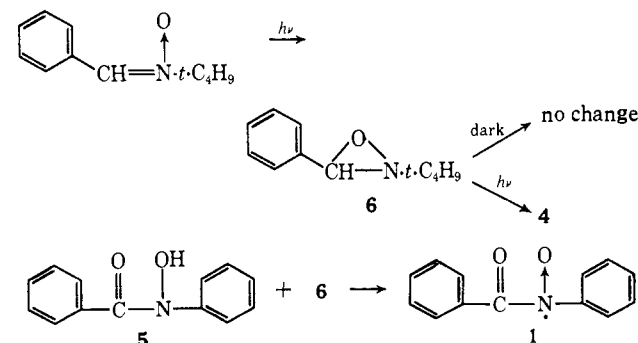
(3) H. G. Aurich and F. Baer, *Tetrahedron Lett.*, 3879 (1965).
(4) A. Mackor, Th. A. J. W. Wajer, and Th. J. deBoer, *Tetrahedron*, 24, 1623 (1968).
(5) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 91, 4481 (1969).
(6) E. G. Janzen and B. J. Blackburn, *ibid.*, 90, 5909 (1968).
(7) E. G. Janzen and B. J. Blackburn, *ibid.*, 91, 3108 (1969).
(8) M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Jap.*, 40, 702 (1967).
(9) N. Hata and I. Tanaka, *J. Chem. Phys.*, 36, 2072 (1962).
(10) A. Alkaitis and M. Calvin, *Chem. Commun.*, 292 (1968).
(11) W. D. Emmons, *J. Amer. Chem. Soc.*, 79, 5739 (1957).