

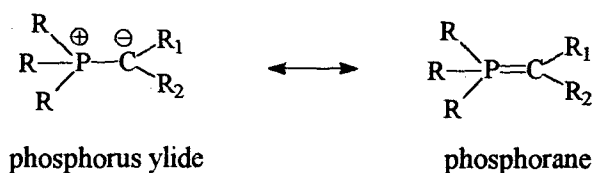
ENDOR Spectra of an X-irradiated Single Crystal of the $R_3P=CH-C(O)CH_3$ Wittig Reagent

T. Berclaz, M. Geoffroy*, G. Rao and Z. Tancic

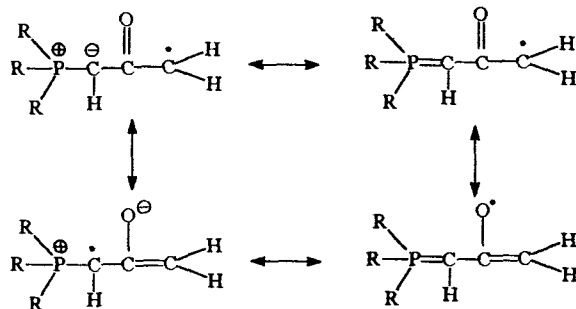
Department of Physical Chemistry, 30 Quai E. Ansermet
1211, Geneva (Switzerland)

1. Introduction

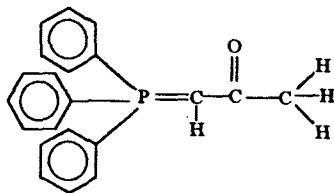
Wittig reagents are hybrid of two canonical forms:



When a radical center is produced on a carbon atom in α -position to a $P=C-C(O)$ group several mesomeric forms are therefore possible¹.

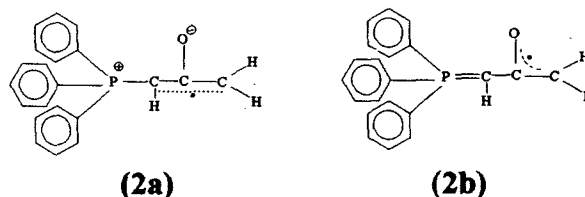


The objective of the present study is to determine, from a single crystal ENDOR study, the real delocalisation of the unpaired electron on a radical derived from the *l*-triphenyl phosphoranylidene-2-propanone (1):



This radical (2), produced by a homolytic scission of a C-H bond of the methyl group, can be written either as an allylic radical

bearing a phosphonium group on a terminal carbon atom (2a) or as a radical delocalized in a π -orbital constructed on the OCC fragment (2b).



2. Experimental

Triphenylphosphoranylidene propanone is a commercial compound (Aldrich). Single crystals were obtained by slow evaporation from a solution in CH_2Cl_2 . These crystals are monoclinic. The ENDOR reference frame was defined as follows: OX, OY, OZ were aligned along c , $-a^*$ and $-b$ respectively

A large single crystal was exposed for 3 hours at room temperature to the radiation of a Philips X-ray tube (30 kV, 30 mA).

The ENDOR spectrometer is a home made cw system². The spectra were recorded at 200 K, the crystal was rotated around the three reference axes in steps of 10° .

The analysis of the spectra was performed by using second order perturbation³ as well as an optimization program which compares the positions of the calculated and experimental lines.

3. Results

The EPR spectrum obtained with an X-irradiated single crystal of (1) is very complex: it exhibits coupling constants with several spin $1/2$ nuclei and, except in the XY plane, it results

from the presence of two magnetically non-equivalent crystallographic sites (two different orientations of the same radical species). Nevertheless, the spectrum obtained with the deuterated species $(C_6D_5)_3PC(H)C(O)CH_3$ is identical to the spectrum obtained with (1), we can therefore rule out the contribution of a radical centered on a phenyl ring (e.g. cyclohexadienyl species) and the most likely trapped radical is indeed the radical (2). It is however impossible to follow the angular variation of the EPR spectrum and to identify, among the various splittings, the coupling which could be due to hyperfine interaction with ^{31}P . An example of ENDOR spectrum obtained at 200 K is shown in Fig. 1.

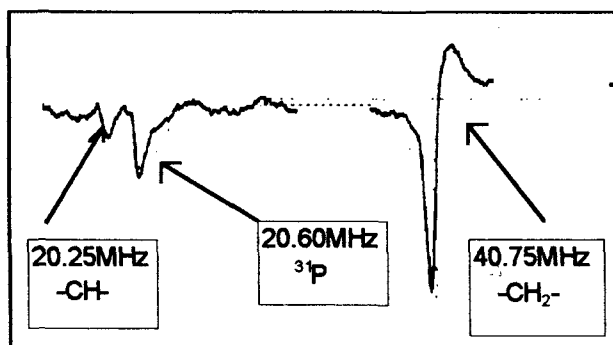


Fig. 1. ENDOR spectrum obtained when the magnetic field lies in the XY plane, 45° from the Y-axis

From these signals, and from their angular dependence in the three perpendicular reference planes it is easy to recognize the lines due to the ^{31}P nucleus. We could thus determine the hyperfine couplings with two protons and one phosphorus atom.

These couplings were compared with the splittings observed on the EPR spectrum and it was possible to simulate some EPR spectra by assuming the presence of an additional spin 1/2 splitting whose signal was not immediately observed by ENDOR. Subsequent measurements showed that additional 1H ENDOR lines were indeed detectable, with difficulty, in the corresponding region of the spectrum.

4. Discussion

The angular variation of the ENDOR lines led to a ^{31}P hyperfine tensor $^{31}P-T$ whose eigenvalues were equal to 29 MHz, 30 MHz

and 33 MHz. One 1H tensor ($^1H-T_1$) was fairly anisotropic (eigenvalues: 46 MHz, 56 MHz and 80 MHz) while the second one ($^1H-T_2$) had smaller eigenvalues: 7 MHz, 11 MHz and 16 MHz. Finally, the third 1H hyperfine tensor, $^1H-T_3$ obtained with a poorer precision since its ENDOR lines were not observed for all the orientations, had eigenvalues approximately equal to 24 MHz, 55 MHz and 83 MHz.

Decomposition of $^{31}P-T$ into isotropic ($A_{iso} = 30.6$ MHz) and anisotropic ($\tau_1 = -1.6$ MHz, $\tau_2 = -0.6$ MHz, $\tau_3 = +2.2$ MHz) coupling constants show, after comparison with the phosphorus atomic coupling constants⁴ ($A^*_{iso} = 13306$ MHz, $2B_o = 734$ MHz) that the delocalisation of the unpaired electron on the phosphorus is very low ($\rho_s = 0.003$, $\rho_p = 0.003$). The hyperfine couplings $^1H-T_1$ and $^1H-T_3$ are rather similar and if we assume that these eigenvalues are all negative the corresponding A_{iso} constants are respectively equal to -60 MHz and -54 MHz. These values are consistent with two protons bound to a hybridized sp^2 carbon atom which contains 80% of the spin in its $2p_z$ orbital. The eigenvectors measured for T_1 and T_3 indicate that the angle between the two C-H bonds is equal to *c.a.* 140° . The last proton tensor $^1H-T_2$ is characterized by a small isotropic coupling constant ($A_{iso} = 11$ MHz) which, on the hypothesis of an α -proton, implies a spin density of *c.a.* 0.16 on the carbon atom. These experimental results show that the most plausible structure for the trapped species 2 is 2a, which in contrast with the non-substituted allyl radical, is largely localized on the terminal carbon. No spin delocalization onto the phosphorus atom is observed; the small ^{31}P coupling is probably due to spin polarization only.

References.

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- ⁴ J.R. Morton and K. F. Preston. *J. Magn. Reson.* **30**, 577 (1978).