removal of the solvent 41 mg (94%) of a *mixture of the two acetates* **15**[8]) *and* **17**[8]) were obtained. The ratio of **15** to **17** (as determined by NMR. see above) was 4:1.

Isomerization Experiments with the Diiodo Compounds 2, 3, and 4. – The experimental details and the results are listed in Table 4.

The elemental analyses were carried out in the Microanalytical Laboratory of the ETH Zürich (Mr. *W. Manser*). Nuclear magnetic resonance spectra were measured in our Instrumental Division (Prof. *W. Simon*). For the mass spectra we are indebted to PD Dr. *J. Seibl.*

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192. ESR. Spectra of the Radical Anion of Dimethyl-phenyl-phosphine

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Herrn Prof. Dr. *Eugen Müller* zum 65. Geburtstag gewidmet

(27. VII. 70)

Summary. ESR. spectra of the radical anion ($I^{\ominus}$) produced from dimethyl-phenyl-phosphine (I) both by electrolysis and reaction with alkali metals have been studied upon variation of temperature. The coupling constant assigned to the ^{31}P nucleus depends strongly on temperature, whereas the coupling constants attributed to protons do not exhibit such a dependence. The π-spin populations at the benzene ring of $I^{\ominus}$ give evidence – in accordance with other experimental data [1] [2] – that the dimethylphosphino substituent is electron-attracting. This effect is thought to be due mainly to $P \leftarrow C_{\pi}$ delocalization, which is analogous to the $Si–C_{\pi}$ interaction in trimethylsilyl-substituted π-systems [3].

The ESR. spectrum previously [4] ascribed to $I^{\ominus}$ is shown to arise from a secondary radical. The formation and structure of this radical are briefly discussed.

A dimethylphosphino group attached to a benzene ring behaves as an electron-attracting substituent, in sharp contrast to the structurally related dimethylamino group. This behaviour has been evidenced by various physico-chemical properties of dimethyl-phenyl-phosphine (I) as compared with those of N,N-dimethylaniline (II). For example, the dipole moments (μ) of the two compounds point in opposite directions [1], and their ionisation potentials (IP) differ by as much as 1.35 eV [2].

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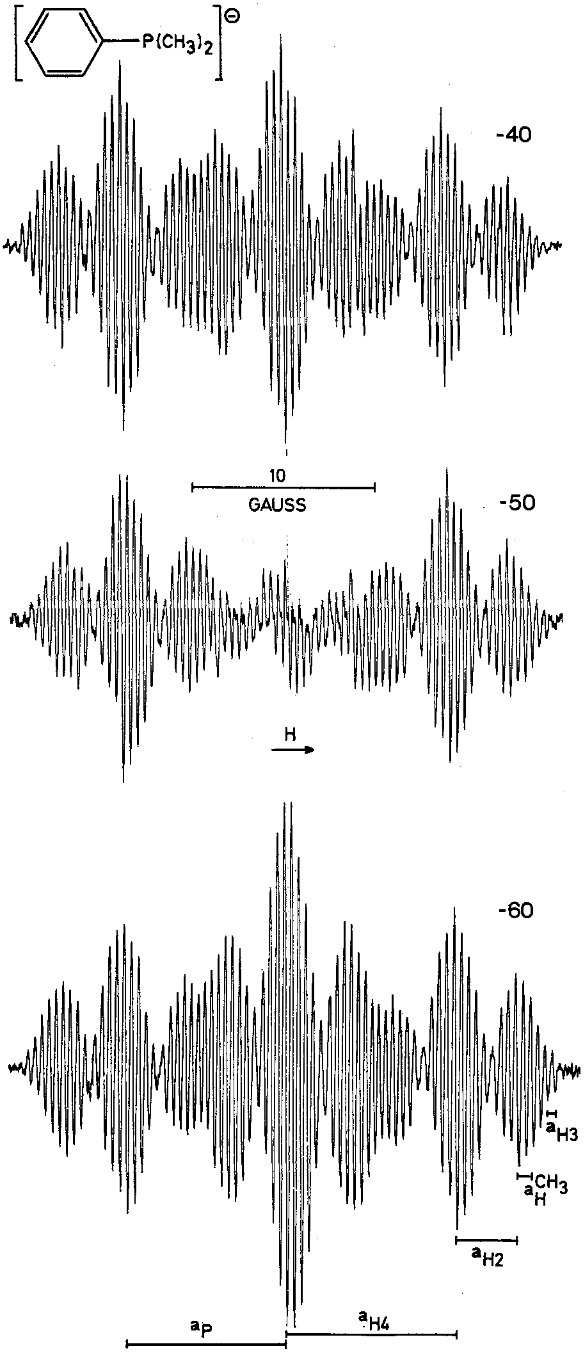
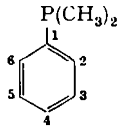


Fig. 1. *ESR. Spectra of dimethyl-phenyl-phosphine radical anion generated by electrolysis*

Solvent: N,N-dimethylformamide; gegenion: $(C_2H_5)_4N^{\oplus}$; temperature (°C) as indicated in the Figure

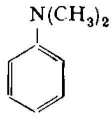


I

$\mu(\mathrm{I}) = 1.31$ debye

$\mathrm{C1}\ {+}\!\!\xrightarrow{\mu}\ \mathrm{P}$

$IP(\mathrm{I}) = 8.13$ eV



II

$\mu(\mathrm{II}) = 1.65$ debye

$\mathrm{C1}\ \xleftarrow{\mu}\!\!{+}\ \mathrm{N}$

$IP(\mathrm{II}) = 6.78$ eV

Two arguments are usually invoked to account for the different substituent effect of the dimethylphosphino and the dimethylamino group:

1. the smaller conjugative power of the phosphorus lone pair relative to the nitrogen lone pair, and
2. the extension of the π-system to vacant phosphorus orbitals of appropriate symmetry (presumably $3d$-character), *i.e.* $\mathrm{P} \leftarrow \mathrm{C}_\pi$ delocalization.

These arguments should be particularly important for radical anions because of their negative charge and the energetic proximity of $3d$-levels to the singly occupied lowest antibonding π-levels.

Whereas N,N-dimethylaniline (II) cannot be reduced to its radical anion by standard methods, the analogous reduction of dimethyl-phenyl-phosphine (I) proceeds quite readily. This fact indicates that I has a much higher electron affinity than II, according to the different effect of the two substituent groups.

In this paper we wish to report on the ESR. studies of the radical anion ($\mathrm{I}^\ominus$) of dimethyl-phenyl-phosphine. An ESR. spectrum ascribed to $\mathrm{I}^\ominus$ has already been published [4], but – as will be shown below – this spectrum does not arise from $\mathrm{I}^\ominus$, but from a secondary radical.

Results. – Dimethyl-phenyl-phosphine (I) (prepared according to *Meisenheimer* [5]) was reduced to its radical anion ($\mathrm{I}^\ominus$) both by electrolysis in N,N-dimethylformamide with tetraethylammonium perchlorate as supporting salt, and by reaction with sodium or potassium in 1,2-dimethoxyethane.

Electrolytical reduction. The ESR. spectra of the electrolytically generated radical anion were analysed in the temperature range of −40 to −60 °C. Above −40°, the radical concentration decreased rapidly, and only weak signals were observed. The spectra taken at −40, −50, and −60° are shown in Figure 1. The striking differences in the spectra are due to a strong temperature dependence of the coupling constant of one single nucleus. This nucleus may be identified with either $^{31}\mathrm{P}$ or the proton in the *para* position of the benzene ring. For reasons to be presented in the 'Discussion', the assignment of the temperature dependent coupling constant to the $^{31}\mathrm{P}$ nucleus is obvious. The values of this coupling constant (a_P) are as follows:

t (°C) =	−40	−50	−60
a_P (gauss) =	8.28	8.50	8.67 ± 0.06.

In the range of −40 to −60 °C, a_P thus increases by 0.02 gauss per degree with decreasing temperature.

The remaining four coupling constants, which do not exhibit an unusual temperature dependence, arise from one set of six equivalent protons, one single proton, and two pairs of equivalent protons. The assignment of the two first values:

$$a_{H}^{CH_3} = 0.78 \pm 0.01 \quad \text{and} \quad a_{H4} = 9.06 \pm 0.07 \text{ gauss}$$

to the six methyl protons and to the *para* proton, respectively, is unequivocal. Comparison with the data of the radical ions of structurally related monosubstituted derivatives of benzene leads to the assignment of the last two values. The larger one must belong to the two equivalent *ortho* protons, leaving the smaller one for the two equivalent *meta* protons:

$$a_{H2} = a_{H6} = 3.31 \pm 0.03 \quad \text{and} \quad a_{H3} = a_{H5} = 0.39 \pm 0.01 \text{ gauss}.$$

The analysis of the spectra shown in Figure 1 has been confirmed by their computer simulation. In particular, the partial cancellation of the line intensities in the center, which was observed at –50 °C, could be satisfactorily reproduced.

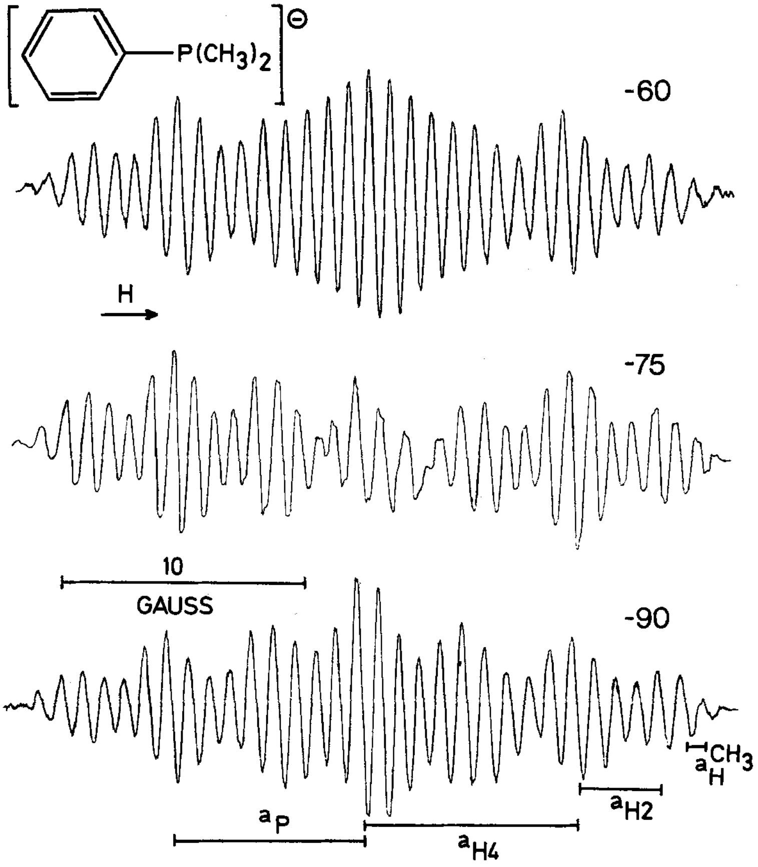


Fig. 2. *ESR. Spectra of dimethyl-phenyl-phosphine radical anion produced with an alkali metal*
Solvent: 1,2-dimethoxyethane; gegenion: Na$^{\oplus}$; temperature (°C) as indicated in the Figure

Reduction with alkali metals. The radical anions ($I^{\ominus}$) produced by the reaction of I with an alkali metal differ in their stability according to the metal (sodium or potassium) used. Whereas the radical anion $I^{\ominus}$ prepared with sodium was almost as stable as that generated by electrolysis, the stability of $I^{\ominus}$ obtained with potassium was very low, even at –90 °C. Consequently, since the use of either alkali metal resulted in the same ESR. spectra, a detailed analysis of the hyperfine structure has been carried out only for the radical anion prepared by the reduction of I with sodium. The spectra were examined at the lowest possible temperatures; they are shown in Figure 2 for –60, –75 and –90° C. Their resolution is inferior to that of the spectra reproduced in Figure 1, the line-widths being 0.40 and 0.15 gauss, respectively.

The coupling constant which is responsible for the changes in the spectra with temperature is again assigned to the ^{31}P nucleus:

t (°C) =	–60	–75	–90
a_P (gauss) =	7.2	7.6	7.9 ± 0.1

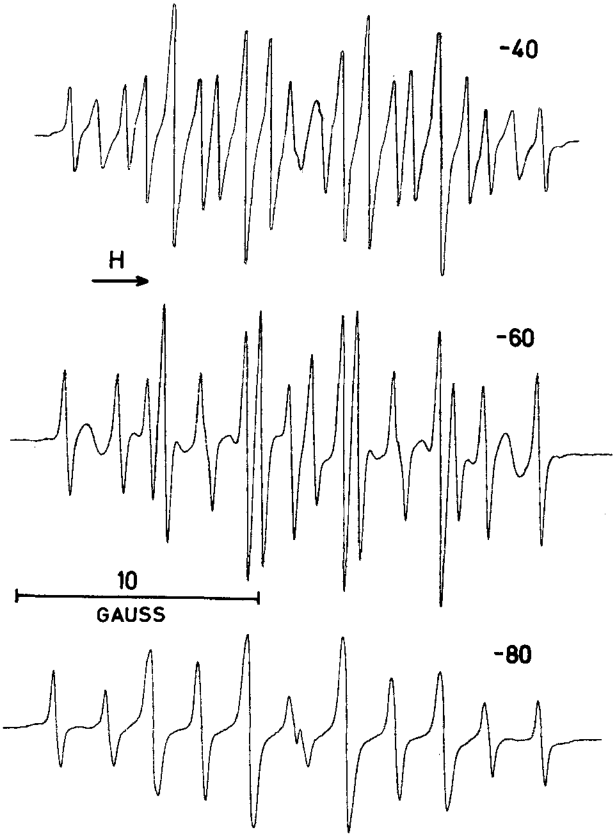


Fig. 3. *ESR. Spectra of the secondary radical produced by the reaction of dimethyl-phenyl-phosphine with an alkali metal*

Solvent: 1,2-dimethoxyethane; temperature (°C) as indicated in the Figure

The a_P value presents a similar temperature dependence as in the spectra of Figure 1. On the other hand, no significant variations in the range of –60 to –90° could be measured for the proton coupling constants which have the following values:

$$a_H^{CH_3} = 0.90 \pm 0.05; \quad a_{H4} = 8.9 \pm 0.1;$$
$$a_{H2} = a_{H6} = 3.5 \pm 0.1 \quad \text{and} \quad a_{H3} = a_{H5} < 0.4 \text{ gauss}.$$

Although these values differ slightly from those quoted above, there is no doubt that they characterize the same radical anion, namely $I^{\ominus}$.

If, after the decay of $I^{\ominus}$, the solution is again brought into contact with an alkali metal, a secondary radical is produced. The ESR. spectra of this radical, which is more stable than $I^{\ominus}$, are shown in Figure 3 for –40, –60 and –80°C. They exhibit not only a strong temperature dependence of the splitting pattern, but also a marked line-width variation.

A provisional analysis of the spectra in Figure 3 yields one coupling constant which may be attributed to a ^{31}P nucleus:

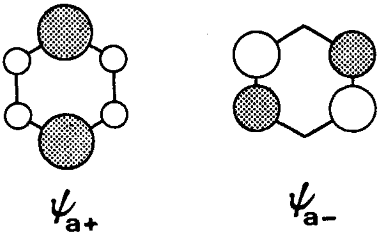
t (°C) =	–20	–40	–60	–80
a_P (gauss) =	2.4	2.9	3.3	3.8 ± 0.1

This coupling constant (a_P) is responsible for the temperature dependence of the splitting pattern in the spectrum. The remaining coupling constants must be due to two pairs of equivalent protons and one single proton. It is tempting to assign these coupling constants to two *ortho* protons, two *meta* protons, and one *para* proton of the benzene ring, respectively:

$$a_{H2} = a_{H6} = 2.9 \pm 0.1; \quad a_{H3} = a_{H5} = 1.10 \pm 0.05; \quad a_{H4} = 7.7 \pm 0.2.$$

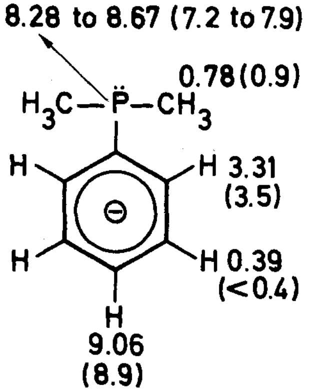
Such an assignment is based on the assumption that the secondary radical also represents a monosubstituted derivative of benzene.

Discussion. – *Substituent effect.* The experimental data for the radical anion ($I^{\ominus}$) of dimethyl-phenyl-phosphine are fully consistent with the electron-attracting substituent effect of the dimethylphosphino group. The odd electron in $I^{\ominus}$ occupies an orbital which strongly resembles the symmetric lowest antibonding MO of benzene, ψ_{a+}, this MO being stabilized by an electron-attracting substituent relative to the corresponding antisymmetric MO, ψ_{a-} [6]. (In the unsubstituted benzene the two MO's, ψ_{a+} and ψ_{a-}, are degenerate.)

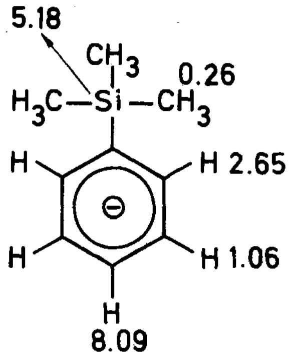


It is informative to compare the coupling constants reported here for $I^{\ominus}$ with those found for the radical anion of trimethylsilyl-benzene (III) [3] [7].

The resemblance of the coupling constants of the ring protons in $I^{\ominus}$ and $III^{\ominus}$ indicates that the dimethylphosphino and trimethylsilyl groups exert a similar influence on the distribution of π-spin population in the benzene ring. This influence in



I$^\ominus$



III$^\ominus$

Coupling constants in gauss[3])

III$^\ominus$ is thought to be due to a $\mathrm{Si} \leftarrow \mathrm{C}_\pi$ delocalization [3] [8], so that an analogous $\mathrm{P} \leftarrow \mathrm{C}_\pi$ electron donation may be postulated as the most important substituent effect in I$^\ominus$.

The differences in the coupling constants of the ring protons in I$^\ominus$ and III$^\ominus$ probably arise from the presence of the phosphorus lone pair in I$^\ominus$ and its interaction with the benzene π-system (rather than from the different electronegativities of P and Si)[4]).

Assignment of ^{31}P coupling constant. Although no information is available on the geometry of the dimethylphosphino group in I$^\ominus$, one would expect it to be sensitive to variations in temperature and to the chemical environment of the phosphorus lone pair. This sensitivity should be primarily shown by the coupling constant of the ^{31}P nucleus and not by that of a ring proton. In fact, a strong temperature dependence was found only for the coupling constant of one single nucleus. The same value also exhibited a large change in going from N,N-dimethylformamide/$(C_2H_5)_4N^\oplus$, as solvent/gegenion (electrolysis), to 1.2-dimethoxyethane/Na$^\oplus$ (alkali metal reduction). On the other hand, the remaining coupling constants were practically unaltered by variations of temperature and only slightly affected by changes of solvent and gegenion. Accordingly, these coupling constants were assigned to protons, whereas the first mentioned value was identified with the coupling constant of the ^{31}P nucleus.

The structure of the secondary radical. The striking similarity of the spectrum shown in Figure 3 for –40°C with that published previously [4] is evidence that they arise from one and the same paramagnetic species. The structure of this species which has been clearly established by our experiments as a secondary product of an alkali metal reduction of dimethylphenyl-phosphine (I) was erroneously ascribed by the authors [4] to the primary radical anion I$^\ominus$. Apparently, the authors have overlooked the ESR. spectrum of the unstable radical anion I$^\ominus$ generated originally by the re-

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[3]) The non-bracketed and bracketed values for I$^\ominus$ refer to the radical anion produced electrolytically and with an alkali metal, respectively (see text). The value of 5.18 gauss for III$^\ominus$ is the coupling constant of a ^{29}Si nucleus in natural abundance (4.7%).

[4]) ESR. studies on model compounds to test the correctness of this statement are in progress.

duction of I with potassium (Figure 2), and examined only the spectrum of the more stable species formed subsequently. The fact that the error remained unrevealed is certainly due to the coupling constants observed for the secondary radical; as pointed out in the 'Results', these values are consistent with those expected for a species containing a monosubstituted benzene ring and a phosphorus atom in the substituent.

Presumably, a reaction takes place between $I^{\ominus}$ and the solvent leading to the displacement of one or both methyl groupings; an addition of new groupings resulting in the increase of the valency of the phosphorus must also be considered. The reaction seems to yield first a diamagnetic product, since the vanishing of the spectrum of $I^{\ominus}$ is not accompanied by the appearance of new signals. A renewed contact with alkali metal must necessarily occur in order that the secondary paramagnetic species, probably the radical anion of the diamagnetic product, can be obtained and its spectrum recorded (see 'Results').

Beside the coupling constants, additional information concerning the structure of the secondary radical is provided by the width of the lines in the spectrum. The selective line broadening and its various appearance at different temperature points to an interconversion between two (or more) equivalent (or nearly equivalent) forms, the interconversional rate being of the order of 10^6 to 10^8 s^{-1} (ESR. time scale). A thorough study of the line-width variation may lead to the identification of these forms and thus to determination of the structure of the secondary radical. At present, one can only suggest that the interconverting forms are those with different conformations of the substituent which – as mentioned above – probably contains different groupings attached to the phosphorus atom.

A comment on the experimental data of the secondary radical is noteworthy, since our results deviate in some respect from those given previously [4]. These deviations are considered below:

a) The temperature of $-70°$, which was specified for the spectrum in [4], seems to be too low. As noted above, a similar spectrum was observed in our experiments at $-40°$, whereas the spectra obtained at lower temperatures differed considerably (cf. Figure 3).

b) The coupling constants listed in [4] exceed our values by ca. 15%. This discrepancy is certainly due to an error in calibration.

c) The larger coupling constant of a single nucleus (ca. 8 gauss) was previously assigned to ^{31}P [4], leaving the smaller one (ca. 3 gauss) to the proton in the *para* position of the benzene ring. The authors [4], however, have examined the ESR. spectrum only at one temperature, in contrast to our studies which were carried out over a range of 60 degrees. If one takes into account the different behaviour of the two coupling constants with varying temperature and applies our arguments stated above, the alternative assignment used in this paper should be preferred.

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