SYNTHESIS AND SOME PROPERTIES OF FREE RADICALS WITH TRIPLE BONDS

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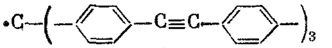
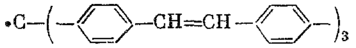
To determine the structures of highly unsaturated polymers, which would possess the greatest electric conductivity, it is necessary to establish which of the bonds – double or triple – more readily transfer an electron along the macromolecule and thus ensure maximum mobility of the current carriers. Since the elucidation of such questions directly on the macromolecule may involve great errors, the source of which might be impurities, inhomogeneities in the structure of the macromolecule, barriers between microcrystals of the sample, etc., these problems should be solved at the level of models.

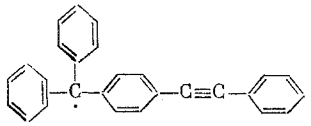
One of the most suitable models for this purpose, in our opinion, is free radicals of the type of triphenylmethyl, containing fragments with double and triple bonds in the molecule. For example:



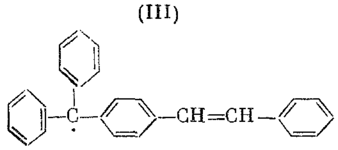
(I)



(III)



(II)



(IV)

This model seems most suitable to us, since the delocalization of the unpaired electron along the molecule in this case will depend upon the ability of the multiple bond to transfer an electron. The distribution of electron density along the aromatic rings, as well as the degree of dissociation of the corresponding substituted ethanes into radicals itself, will also be a quantitative measure of the ability of the multiple bond to transfer an electron.

In the communication [1] the possibility of synthesizing a number of substituted triphenylcarbinols with triple bonds was demonstrated. This communication describes the synthesis of radicals (I) and (II); the possibility of delocalization of an unpaired electron was demonstrated and the degree of delocalization estimated by an analysis of their EPR spectra.

The radicals (I) and (II) were synthesized according to Scheme 1. Condensation of tris-p-iodophenyl)methane (V) with copper phenylacetylide proceeds in boiling pyridine in 6-7 h and gives tris-(p-tolanyl)methane (VI) with 41% yield. As a rule, mono- and bis-(tolanyl)methanes are obtained simultaneously and can be used after separation in the subsequent synthesis of (VI). The initial tris-(p-iodophenyl)-methane (V) was produced by two methods. The first of them was a diazoreaction from tris-(p-aminophenyl)-methane [2], which was also produced by hydrogenation of the corresponding nitroderivative over skeletal nickel with hydrogen under pressure with a yield of ~25%. The second method, direct iodination of triphenylmethane according to the method described for diphenylmethane [3], in the presence of iodic acid in glacial CH_3COOH, gives a better yield (51%). The oxidation of (VI) by MnO_2 in boiling CCl_4 for 30 h produced tris-(p-tolanyl)carbinol (VII) with a yield of 65%. It is interesting to note that oxidation with chromic oxide in glacial CH_3COOH does not give the required product, but leads to decomposition of the initial (V). Upon boiling in anhydrous acetyl chloride for 2 h, tris-(p-tolanyl)chloromethane (VIII) is obtained in 81% yield. Diphenyl-(p-phenylethynyl)phenylcarbinol (IX) was described earlier [1]. After 3 h passage of dry HCl into

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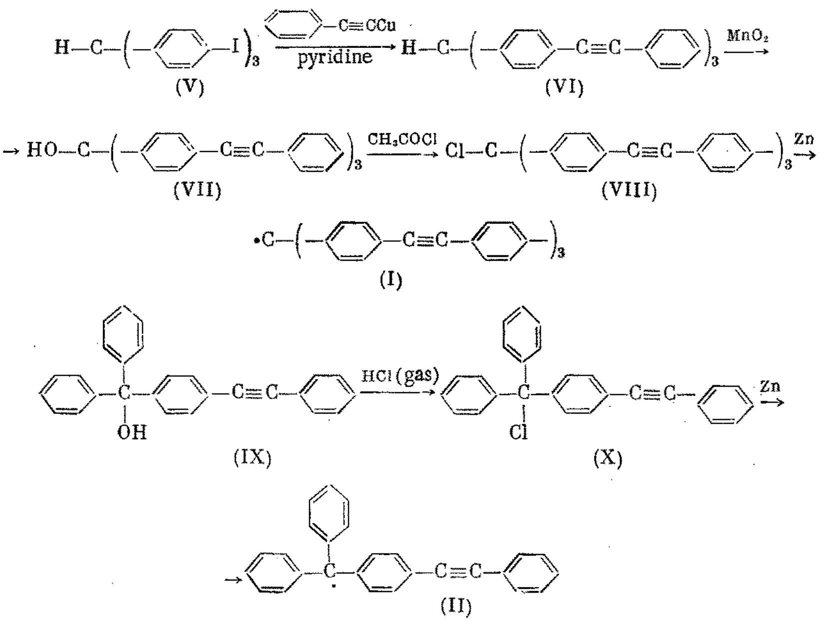

Scheme 1

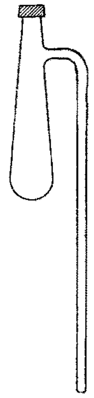

Fig. 1. Ampoule for production of radicals.

a solution of (IX) in acetic anhydride, diphenyl-(p-phenylethynyl)phenylchloromethane (X) precipitates in 52.5% yield.

In the treatment of benzene or toluene solutions of (VIII) and (X) with zinc dust in an atmosphere of dry CO_2, the radicals (I) and (II) are formed; moreover, in the case of (I) the solution is colored an intense blue, while in the case of (II) it is colored claret. The radicals were produced in a specially designed glass ampoule (Fig. 1) with a branch for investigation by the EPR method. The ampoule was tightly stoppered with a cap of oil and gasoline-stable rubber.

The method of preparation of the solution of radicals consists of the following. In an ampoule we placed 0.0298 g (VIII) or 0.0193 g (X) and the corresponding tenfold amount of zinc dust. The ampoule was capped, and connected with a vacuum system through the needle of a syringe inserted into the cap. After 1-1.5 h, the stopcock connecting the ampoule to the vacuum system was switched, and the ampoule was filled with pure dry CO_2 through a second syringe needle. After 15 min, the ampoule was again disconnected from the vacuum system, and the CO_2 passed through for another 2 h. After this, 1 ml of an anhydrous solvent was introduced with a syringe in a stream of CO_2. The needle for introduction of CO_2 was removed, and the opening was rapidly covered with picein and with BF glue. Color appears immediately after addition of the solvent. The contents of the ampoule were mixed until an intense color was obtained (15-20 min); the solution was allowed to stand and cautiously poured over into the branch.

The concentration of (VIII) and (X) is 0.5 M. Precisely this value proved to be the most suitable for obtaining good EPR spectra. The spectra were recorded on a Varian E-3 spectrometer. The measurements were conducted both at room temperature and at temperatures below 0°. As can be seen from Figs. 2 and 3, the resolution of the spectra increases significantly when the temperature is lowered. For comparison, Fig. 4 depicts the spectrum of the triphenylmethyl radical (XI), taken under conditions of low resolution (room temperature). The distance between components of this spectrum is 1.28 Gs. The spectrum of the triphenylmethyl radical, obtained at high resolution, entirely coincides in shape and values of the splittings ($a_0=2.53$ $a_\mathrm{m}=1.11$, $a_\mathrm{p}=2.77$ Gs) with the literature data [4].

On the spectrum of the radical (I) (Fig. 2a), 15 lines with splitting between them of 1.21 ± 0.04 Gs are visible. The reduction of the number of observable lines in comparison with triphenylmethyl (15 instead of 19) indicates that the protons of the substituents in the para-position do not give any significant splittings in the spectrum. Since the ratio of the ortho- and meta-constants in (XI) is close to two, it may be assumed that the ratio $a_0=2a_\mathrm{m}$ is approximately fulfilled for (I) as well. The ratio of the intensities calculated on

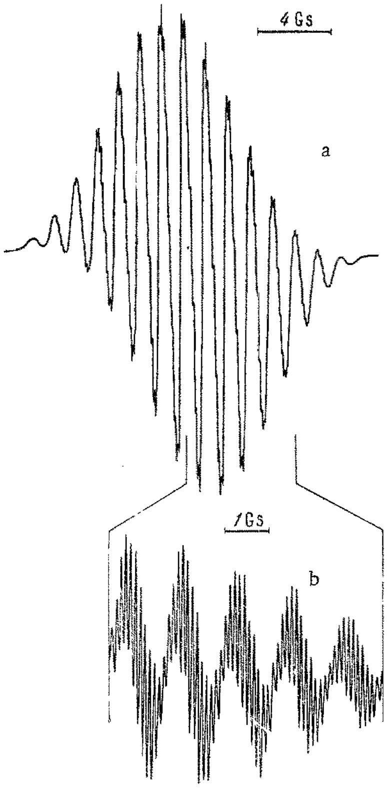

Fig. 2

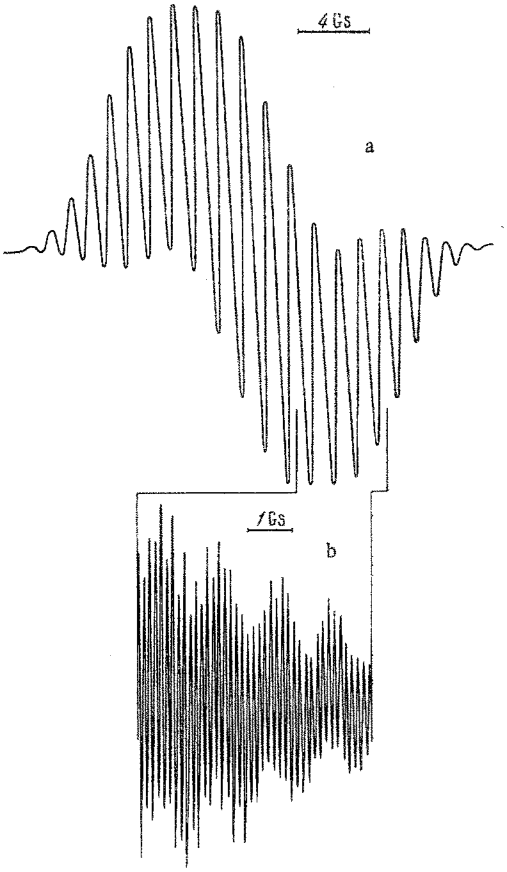

Fig. 3

Fig. 2. Spectrum of radical (I), taken in toluene: a) at room temperature; b) at −30°.

Fig. 3. Spectrum of radical (II), taken in toluene: a) at room temperature; b) at −30°.

this assumption is in good agreement with the experimental value (Table 1). Thus the basic splitting in the spectrum of the radical (I) is due to interaction with the protons of the triphenylmethyl portion of the radical; moreover, $a_0 \approx 2.4$; $a_m \approx 1.2$ Gs.

The lines of a hyperfine structure are visible on a fragment of the resolved spectrum of the radical (I) (Fig. 2b); they can be explained exclusively by interaction of the unpaired electron with the protons of the far phenyl rings. If there were no such interaction, then the entire spectrum would consist of only $7 \times 7 = 49$ lines, which is substantially less than the observed number of lines. The value of the splitting between lines of the hyperfine structure is 0.1 Gs. Assuming that the distribution of spin density for the benzene rings is analogous to the distribution in triphenylmethyl, the value of the splitting 0.1 Gs can be related to the splitting constant on the far meta-protons. Since the splitting on the near metaprotons of the radical (I) is ≈ 1.2 Gs, it may be concluded that only ~ 10% of the spin density is delocalized from the near rings to the far rings. The spectrum of the radical (II) (Fig. 3a) consists of a larger number of lines. By analogy with the spectra of radicals (I) and (XI), it may be assumed that the distance between the lines (1.25 ± 0.04 Gs) approximately corresponds to the constant of splitting on the meta-protons. Since the splittings in the spectra of the radicals (XI), (I), and (II) are approximately equal, we might have assumed the same multiplicity of the constants for (II) as for the radicals (XI) and (I), i.e., $a_p \approx a_0 \approx 2a_m$. The theoretical spectrum constructed on this assumption, however, does not agree with the observed intensity distribution (see Table 1). It might have been assumed that the cause of this lack of agreement is the poorer resolution of the spectrum (a) of radical (II) in comparison with the spectra of the radicals (I) and (XI). The deterioration of the resolution, however, should have led to a decrease in the intensity of the extreme components of the

TABLE 1

Radical	Ratio of constants	Distribution of intensities	Number of lines
I	Calculation $a_o = 2a_m$; $a_p = 0$	1 : 6 : 21 : 56 : 120 : 216 : 336 : 456 : 546 : 580	19
	Experiment	11:44 :115 : 220 : 350 : 465 : 550 : 580	15
II	Calculation $a_o = 3a_m$: (substituted) $a_p = 3a_m$ $a_o = 2a_m$ (unsubstituted ring)	1 : 6 : 19 : 48 : 105 : 198 : 337 : 538 : 757 : 1030 : 1263 : 1472 : 1604 : 1664	27
	Experiment	28 : 100 : 245 : 455 : 670 : 830 : 930 : 1060 : 1310 : 1550 : 1660	21
II	Calculation $a_p = a_o = 2a_m$	1 : 6 : 23 : 68 : 163 : 334 : 597 : 944 : 1336 : 1708 : 1974 : 2072	23
	Experiment	34 : 120 : 300 : 565 : 840 : 1030 : 1150 : 1320 : 1630 : 1920 : 2070	21
XI	Calculation $a_p = a_o = 2a_m$	1 : 6 : 24 : 74 : 186 : 402 : 760 : 1278 : 1935 : 2652 : 3312 : 3780 : 3948	25
	Experiment	80 : 270 : 460 : 1010 : 1530 : 2260 : 2970 : 3420 : 4040 : 3950	19

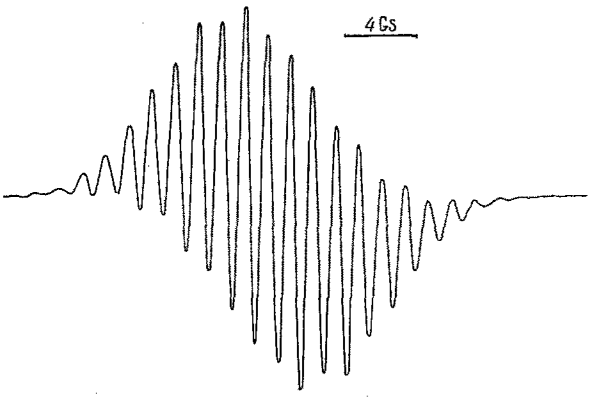

Fig. 4. Spectrum of radical (XI), taken in benzene at room temperature.

spectrum, whereas actually the intensities of the extreme components in the spectrum of the radical (II) are greatly increased.

Probably these peculiarities of the spectrum of the nonsymmetrical radical (II) are due to a difference in the constants of hyperfine interaction with the protons of the substituted and unsubstituted phenyl rings. Actually, by varying the ratio of the ortho-, meta- and para- constants, one can obtain the theoretical spectrum of the radical (II), which is in good agreement with the experimental data (see Table 1). This, however, cannot serve as unambiguous evidence that the ratio of the constants was correctly selected, since, as has already been noted, the basic lines of the radical (II) are insufficiently well resolved. The resolved spectrum of the radical (II) (Fig. 3b) consists of a large number of components with different distances between them, ~0.12 Gs. These splittings are probably associated both with the influence of the protons of the substituent and with the inaccurate multiplicity of the constants in the substituted and unsubstituted rings.

EXPERIMENTAL

Tris-(p-iodophenyl)methane (V). A 12.2-g portion of triphenylmethane was dissolved with heating in 300 ml CH_3COOH, then 21 ml water and 4 ml of conc. H_2SO_4, 19.2 g finely pulverized I_2, 8.2 g HIO_3, and 16 ml CCl_4 were added. The mixture was heated for 9 h at a bath temperature of 90°, poured out into a mixture of ether with water, placed in a 1-liter separatory funnel. The ether extracts were washed several times with a solution of $Na_2S_2O_3$, with water, and with $NaHCO_3$ and dried over $MgSO_4$. A substantial portion of the product precipitated at the end of the reaction in the form of a dense resin. It could be separated from the solution by treatment with ether, preliminarily neutralizing the excess acid. The ether solutions were evaporated to dryness and chromatographed on Al_2O_3 (activity II), eluent benzene:petroleum ether (high boiling), 1:2. After evaporation of the eluate, the substance was recrystallized from alcohol. The only individual reaction product was (V), yield up to 51%.

Tris-(p-tolanyl)methane (VI). A 4.0-g portion of (V) was condensed with 4.75 g phenylacetylene in 35 ml boiling pyridine in a stream of dry N_2 according to the method of [5]. Then it was poured into a mixture of ether and water, the ether layer repeatedly washed with dilute HCl, with water, with a solution of $NaHCO_3$, and dried over $CaCl_2$. The ether was evaporated and chromatographed on Al_2O_3 (activity II), eluent benzene:petroleum ether, 1:2. The following were eluted successively: fraction I) diphenyldiacetylene 0.33 g; fraction II) a mixture of mono-, di-, and tris-(p-tolanyl)methanes, 0.94 g. From fraction III we isolated 1.44 g (41%) (VI), mp 166-168° (alcohol). Found: C 94.68; H 5.30%. $C_{43}H_{28}$. Calculated: C 94.82; H 5.18%. IR spectrum (ν, cm^{-1}): 2230 s ($C\equiv C$).

Tris-(p-tolanyl)carbinol (VII). A mixture of 1.19 g (VI) and 17 g freshly prepared MnO_2 [6] was boiled in 70 ml anhydrous CCl_4 for 30 h, cooled, filtered to remove MnO_2, evaporated to a minimal volume, and chromatographed on Al_2O_3 (activity II). The following were eluted successively: fraction I) eluent benzene: petroleum ether, 1:1, (VI) – 0,20 g. From fraction II, eluent benzene, we obtained 0.80 g (VIII), yield 65%, mp 95-96° (alcohol). Found: C 91.62; H 4.83%. $C_{43}H_{28}O$. Calculated: C 92.11; H 5.03%. IR spectrum (ν, cm^{-1}): 2230 s ($C\equiv C$), 3620 m (OH).

Tris-(p-tolanyl)chloromethane (VIII). A 0.31-g portion of (VII) was boiled for 2 h in 20 ml of acetyl chloride. The bright blue solution was evaporated to a minimum volume and left in a refrigerator for several days. The crystals that precipitated were filtered off, washed with petroleum ether, and dried under vacuum. We obtained 0.26 g (VIII), yield 81%, mp 127-129° (in a sealed capillary). Found: Cl 6.07%. $C_{43}H_{27}Cl$. Calculated Cl 6.12%.

Diphenyl-(p-phenylethynyl)phenylchloromethane (X). A 3-g portion of (IX), described earlier [1], was dissolved in a minimum amount of Ac_2O, and dry HCl passed through for 3 h with cooling with ice-water. The precipitate, which separated out first in the form of an oil, was crystallized. It was filtered, washed with Ac_2O, with petroleum ether, and dried under vacuum. We obtained 1.58 g (X), yield 52.5%, mp 105° (in a sealed capillary). Found: Cl 9.28%. $C_{27}H_{19}Cl$. Calculated Cl 9.36%.

CONCLUSIONS

1. Free radicals containing triple bonds in the substituents, tris-(p-tolanyl)methyl (I) and diphenyl-(p-phenylethynyl)phenylmethyl (II), were produced.

2. The EPR spectra of the radicals (I) and (II) were taken and analyzed. A weak hyperfine (0.1 Gs) interaction of the unpaired electron with the protons of the far phenyl rings was detected.

3. Approximately 10% of the spin density of the unpaired electron is transmitted from the triphenylmethyl rings through the triple bond.

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