establish if this effect is sufficient to help distinguish between diastereoisomeric structures (three of which are found in the case of (cyclo-C₆H₅)₃C⁺, for instance).

6. Substitution of the “isolated” phosphoryl oxygen on phosphorus by sulphur causes either shielding or deshielding of the H—(P) proton, as seen in the following examples,

\[
\begin{align*}
\delta & \quad \Delta \delta \\
(cyclo-C₆H₅)_3PH(O) & \quad 6.40 \quad -0.44 \\
(cyclo-C₆H₅)_3PH(S) & \quad 7.96 \quad +0.87
\end{align*}
\]

The above data and remarks may help to determine the main factors which influence \( \delta \) H—(P) values: coordination number of the phosphorus atom, nature of the atoms directly bonded to phosphorus, ring current anisotropy, etc. and, we hope, will be useful in structure determination, particularly in stereochemical problems and comparison with results obtained on other X—H groups.

Observations on the Thermochromism of Triphenylchloromethane

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Es wurde die Thermochromie von Lösungen des Triphenylchloromethane in Dekalin im Temperaturbereich von 25° bis 150° C untersucht. Polarisationmessungen zeigen keine Veränderung bis 110° C. Der Thermochromie ist die Bildung des Triphenylmethyl-Radikals, das sich in Anwesenheit von Luft zersetzt, zuzuschreiben. Die Reaktionsprodukte wurden identifiziert und das Reaktions-Schema angegeben.

It was noted for a long time that benzonitrile solutions of triphenylchloromethane are thermochromic: the phenomenon was attributed to the formation of triphenylmethyl ions, \((C₆H₅)₃C^+\).

On the contrary, the bibliography did not show that the possibility of obtaining the triphenylmethyl radical \((C₆H₅)₃C^−\), by analogous heating of the triphenylchloromethane in apolar solvents, had ever been verified, although our purely qualitative observation had shown that also decalin solutions of triphenylchloromethane are thermochromic. The formation of the triphenylmethyl radical by direct heating of triphenylchloromethane at not very high temperatures would be extremely interesting also for some eventual applications such as, for example, the studies on auto-oxidation processes.

Recently, in fact, it has been shown by various authors that the auto-oxidations proceed by means of chain mechanisms in which the triphenylmethyl and polyarilmethyl radicals in general can easily intervene as inhibitors.

In this work, we intend to verify the possibility of obtaining the radical directly and to study its behaviour at not very high temperatures.

We have therefore examined decalin solutions of triphenylchloromethane in the temperature range 25° — 150° C.

Experimental Part

The following determinations were carried out:

1) Dielectric polarisations, utilizing a Kipp and Zonen resonance apparatus, functioning at the frequency constant 1504.1 kHz, for measuring the dielectric constants; and a Pulfrich refractometer for measuring the index of refraction.


Conclusion

The following conclusions can be drawn:

- The phenomenon was attributed to the formation of triphenylmethyl ions, \((C₆H₅)₃C^+\).
- Polarisation measurements showed no change up to 110° C. The thermochromism is due to the formation of the triphenylmethyl radical, which decomposes in the presence of air.
- The reactions were identified and the reaction scheme was established.
- It was noted for a long time that benzonitrile solutions of triphenylchloromethane are thermochromic.
- On the contrary, the bibliography did not show that the possibility of obtaining the triphenylmethyl radical \((C₆H₅)₃C^−\), by analogous heating of the triphenylchloromethane in apolar solvents, had ever been verified.
- Our purely qualitative observation had shown that also decalin solutions of triphenylchloromethane are thermochromic.
- The formation of the triphenylmethyl radical by direct heating of triphenylchloromethane at not very high temperatures would be extremely interesting also for some eventual applications such as, for example, the studies on auto-oxidation processes.
- Recently, in fact, it has been shown by various authors that the auto-oxidations proceed by means of chain mechanisms in which the triphenylmethyl and polyarilmethyl radicals in general can easily intervene as inhibitors.

In this work, we intend to verify the possibility of obtaining the radical directly and to study its behaviour at not very high temperatures.
2) E.P.R. spectra, recorded with a Varian 4502 spectrometer having frequency of 9000 Mc/s and field modulation of 100 kc/s.

3) U.V. spectra, obtained by means of a Beckman DU spectrophotometer.

4) I.R. spectra, recorded by means of an Infrascan.

5) Thin layer chromatography for the analysis of the products of reaction, using as absorbent silica G gel and as eluent benzene and hexane; the identification of the products was carried out by means of U.V. spectra of the substances removed from the chromatograms (by benzophenone, phenol, 9-phenylfluorene, triphenylchloromethane and triphenylmethane) and using chromatographic revealers: 5% formic aldehyde in concentrated H₂SO₄ and successive heating for the phenol and triphenylmethane; saturated 2 N HCl solution of dinitrophenylhydrazine for the benzophenone; 25% antimonium pentachloride in CCl₄ for the triphenylchloromethane, and reagent containing potassium iodide and starch for the peroxide.

All the solvents were Carlo Erba products purified for analysis, which was furtherly purified by means of repeated crystallizations with petroleum ether.

**Results**

In tables I — III are reported the results relative to the dielectric polarization measurements: in them, \( c_1 \) represents the concentration in moles/l, \( N_1 \) the concentration in molar fractions, \( \epsilon_s \) the dielectric constant, \( n_D \) the index of refraction for line D of the sodium, \( d_4 \) the density of the solutions at diverse temperatures, \( P_{A+O} \) the atomic and orientation polarization, \( P_{A+O}^\infty \) the same polarization extrapolated with infinite dilution, \( P_1 \) and \( P_1^\infty \) the total dielectric polarizations at the diverse concentrations and with infinite dilution, respectively.

In Figs. 1 — 3 are reported the results relative to the U.V. and E.P.R. spectra.

**Discussion of the Results**

The decalin solutions of triphenylchloromethane, heated for about 4 hours at 150°C in a nitrogen current, assume an intense yellow color that, for successive cooling, fades and disappears; these solutions are besides very sensitive to the presence of oxygen that decolors them rapidly, provoking the precipitation of a white, crystalline com-

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4 The E.P.R. spectra were obtained and interpreted by Dott. Giovanna Bettoli to whom we wish to extend our appreciation.

THERMOCHROMISM OF TRIPHENYLCHLOROMETHANE

It resulted therefore that such radical can be obtained by simple decomposition of the triphenylchloromethane at 150 °C.

If the heating is carried out at the same temperature and for the same length of time in the presence of air, the solutions assume a stable, brownish-yellow color, do not form any precipitate, the E.P.R. spectrum does not reveal any presence of radicals and the U.V. spectra present a maximum at 340 nm, while they do not have any band at wavelengths over 400 nm (Fig. 3).

Since it is presumable that the heating always provokes the same type of decomposition, it can be thought that, also in this case, the triphenylmethyl radical is formed and that, in presence of air, it enters into a successive reaction.

The most immediate hypothesis is that the peroxide is formed and that from this, with heat, proceeds the decomposition.

We separated the final products by means of thin layer chromatography and these were found to be: benzophenone, phenol, 9-phenyl fluorene, triphenylmethane and triphenylmethylperoxide.

The identification was accomplished both with specific coloring reactions and with U.V. spectra (see experimental part).

The presence of benzophenone was also confirmed by the I.R. spectra carried out directly on the heated solution (bands at 935, 1275, 1665 cm⁻¹).

The formation of hydrochloric acid was also evidenced (reaction with HNO₃ and AgNO₃ on the vapors of the heated solution).

On basis of these results, it can be admitted that the reaction proceeds according to the following scheme:

\[(\text{C}_6\text{H}_5)_3\text{C}Cl \rightarrow (\text{C}_6\text{H}_5)_3\text{C}^\cdot + \text{Cl}^\cdot \quad (1)\]
\[2(\text{C}_6\text{H}_5)_3\text{C}^\cdot + \text{O}_2 \rightarrow (\text{C}_6\text{H}_5)_3\text{COOC}(\text{C}_6\text{H}_5)_3 \quad (2)\]
\[(\text{C}_6\text{H}_5)_3\text{C}^\cdot \text{COOC}(\text{C}_6\text{H}_5)_3 \rightarrow 2(\text{C}_6\text{H}_5)_3\text{CO}^\cdot \quad (3)\]
\[(\text{C}_6\text{H}_5)_3\text{C}^\cdot + \text{O}_2 \rightarrow (\text{C}_6\text{H}_5)_3\text{CO} + \text{C}_6\text{H}_5^\cdot \quad (4)\]
\[\text{C}_6\text{H}_5^\cdot + \text{O}_2 \rightarrow (\text{C}_6\text{H}_5\text{O}_2)^\cdot \rightarrow \text{C}_6\text{H}_5\text{OH} \quad (5)\]
\[2(\text{C}_6\text{H}_5)_3\text{C}^\cdot \rightarrow (\text{C}_6\text{H}_5)_3\text{CH} + (\text{C}_6\text{H}_4)_2\text{CHC}_6\text{H}_5 \quad (6)\]
\[(\text{C}_6\text{H}_5)_3\text{C}^\cdot + \text{Cl}^\cdot \rightarrow (\text{C}_6\text{H}_5)_2\text{CHC}_6\text{H}_5 + \text{HCl} \quad (7)\]

This scheme was confirmed by means of a verification which we carried out on a sample of triphenylmethylperoxide.

\[4 \text{ M. Gomberg, Chem. Reviews} 24, 115 [1924].\]
nylmethylperoxide whose decomposition into benzophenone and phenol is also reported in the bibliography; the mechanism of phenol formation has not however been interpreted until now and scheme 5 is therefore entirely general and qualitative.

It can be excluded the intervention of the solvent in the reaction in as much on heating a sample of solid triphenylchloromethane, are obtained exactly the same products.

In order to establish the temperature at which the phenomenon of decomposition becomes noteworthy, we carried out determinations of dielectric polarization in function of temperature; it resulted that the graph of the polarizations as function of $1/T$ presents a discontinuity at $110 \, ^\circ\text{C}$.

For temperatures under $110 \, ^\circ\text{C}$ (Table I), the function is represented by a straight line from whose angular coefficient it is possible to derive an electric moment equal to 1.91 D.u. and a polarization of distorsion of 86.0 cc.

Both these values are predicted for the triphenylchloromethane molecule.

The moment coincides with the one we calculated with other means at $25 \, ^\circ\text{C}$ in decalin (Table III) and with those reported by the bibliography in other ambients; the polarization of distorsion is in agreement both with the molecular refraction calculated directly (83.9 cc.) and with that determined experimentally from measurements of density and index of refraction (84.2 cc.).

At temperatures over $110 \, ^\circ\text{C}$ (Table II), abnormally high values of dielectric constant are obtained and the course of the polarizations in function of the temperature is not regular any longer.

Therefore, it can be concluded that the thermochromism of the decalin solutions of triphenylchloromethane is due to formation of triphenylmethyl radical and that the temperature at which the phenomenon becomes evident is localized around $110 \, ^\circ\text{C}$.

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