

252. *Tropylium Salts. Part II.*¹ *Valid and Invalid Preparations of Tropylium Chloride: An Unusual Tropylium-Phosphorus Chloride Complex.*

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Tropylium chloride is a rather unstable colourless deliquescent solid, m. p. 102° (decomp.). Several preparative procedures are described. Some previously reported procedures which give products having different properties have been investigated. In particular, Kursanov and Volpin's preparation² from cycloheptatriene and phosphorus pentachloride has given a product, C₁₄H₁₄Cl₇P, m. p. 170° (decomp.), which has also been obtained by reaction of tropylium chloride with phosphorus pentachloride; its structure is discussed.

TROPYLIUM CHLORIDE was required in connection with another problem, but was found to have been very variously described in the literature. Doering and Knox³ first reported this substance as pale yellow needles, m. p. 101° (decomp.), formed by the action of hydrogen chloride on alcoholic tropylium bromide. Dewar and Pettit⁴ obtained a product by reaction of norcaradienyl isocyanate with hydrogen chloride which in one place was stated to be "identical" with Doering and Knox's material, but was described elsewhere in the same paper as "white needles, . . . m. p. 189° (decomp.)." Professor Dewar has unfortunately

¹ Bryce-Smith and Perkins, *J.*, 1961, 2320, is regarded as Part I; cf. *idem*, *Chem. and Ind.*, 1959, 1022.

² Kursanov and Volpin, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 339.

³ Doering and Knox, *J. Amer. Chem. Soc.*, 1954, **76**, 3203.

⁴ Dewar and Pettit, *J.*, 1956, 2021.

been unable to clarify this discrepancy for us.⁵ Kursanov and Volpin² reported that tropylium chloride, m. p. 96—97°, was obtained in 98% yield (estimated indirectly) by the action of phosphorus pentachloride on cycloheptatriene, and the method has since been referred to as the best available.⁶ No analysis or mixed melting point has been given for tropylium chloride prepared in this manner.

In the present work Doering and Knox's preparation³ from tropylium bromide and hydrogen chloride was first examined. Yellow products having melting points in the range 84—87° were obtained in repeated experiments. These contained bromine and chlorine, and were undoubtedly mixtures of tropylium bromide (yellow) and tropylium chloride (colourless). Prolonged re-treatment of one such product in ethanol with a current of hydrogen chloride gave purer material, m. p. 95°, but this was still pale yellow and contained a little bromine as well as chlorine. Although it is possible that even more prolonged treatment with hydrogen chloride would have given a purer product, the procedure cannot be recommended.

An obvious route to tropylium chloride lay in the reaction of di(cycloheptatrienyl) ether with hydrogen chloride. Reaction of this ether with ethereal hydrogen chloride gave a precipitate of tropylium chloride (94% yield) as colourless deliquescent crystals, which were recrystallised from dry acetonitrile to constant m. p. 101—102° (decomp.). Since di(cycloheptatrienyl) ether can be readily prepared by mild alkaline hydrolysis of tropylium salts,^{1,3} this is probably the procedure of choice for the preparation of tropylium chloride.

In Part I of this series,¹ tropylium chloride had been prepared by Kursanov and Volpin's method² from cycloheptatriene and phosphorus pentachloride. At first, there was no suspicion regarding the authenticity of the product as it behaved chemically much as expected. The m. p. of the initial product was consistently 170° (decomp.) and recrystallised products had m. p.s which varied from 95° to 155°, depending on the conditions. Since figures of 189° (decomp.) and 101° (decomp.) for the melting point of tropylium chloride had been reported,^{4,3} it appeared at first that dimorphic forms were involved. Further investigation of Kursanov and Volpin's product was hampered by considerable analytical difficulties, but consistent analyses were eventually obtained corresponding to the formula $C_{14}H_{14}Cl_7P$.*

This substance had the following properties. Hydrolysis at 20° gave an acidic solution which showed the ultraviolet absorption spectrum of the tropylium ion and contained chloride and phosphate ions. The absence of phosphite ions or other species capable of reducing potassium permanganate or mercuric chloride excludes the formulation as a derivative of phosphorus(III). Thus the structure $C_7H_7^+PCl_4^-$ is excluded, although it fitted some early analytical data fairly well. Hydrolysis with sodium hydrogen carbonate solution gave di(cycloheptatrienyl) ether (this is a useful source of the ether, and thence of tropylium chloride into which the ether can conveniently be converted without the need for prior isolation either of it or of the phosphorus complex: thus cycloheptatriene can be converted into tropylium chloride in virtually a single stage). The phosphorus complex gave a dark brown solution in ethanol with evolution of heat. Addition of ether precipitated slightly impure tropylium chloride, and reprecipitation gave the pure compound as a colourless deliquescent solid (17% yield). The use of nitromethane (cf. Kursanov and Volpin²) in place of ethanol also gave tropylium chloride, but in even lower yield and the final product was not wholly free from phosphorus. At 85°/0.7 mm., the complex slowly dissociated to tropylium chloride and phosphorus trichloride. Presumably, phosphorus pentachloride was first produced and then dissociated further: there was,

* The reactions attributed in Part I¹ to tropylium chloride which actually involved this complex have now been shown to occur with authentic tropylium chloride.

⁵ Dewar, personal communication.

⁶ Kursanov, Volpin, and Parnes, *Khim. Nauka i Prom.*, 1958, **3**, 159; Volpin, *Uspekhi Khim.*, 1960, **29**, 298.

however, no direct proof of this. The complex appears to be stable indefinitely in dry nitrogen at room temperature, whereas tropylium chloride cannot be kept for more than a few days under these conditions.

The infrared spectrum of the solid complex showed all the characteristic peaks due to tropylium ions, but differed appreciably from that of cycloheptatriene. The complex was not sufficiently stable in any solvent yet examined to enable spectra of solutions to be obtained.

Structure of the Complex.—No final structural proposals are yet justified pending a detailed analysis by X-ray techniques; * but the analytical, chemical, and spectroscopic evidence permit some preliminary conclusions. Thus, from the infrared spectrum, the complex is undoubtedly a tropylium salt. The formation of Cl^- and PO_4^{3-} on hydrolysis suggests that phosphorus is present as a complex chlorophosphate. A number of stable tropylium complex halide salts of other elements have recently been described.¹ The empirical formula $\text{C}_{14}\text{H}_{14}\text{Cl}_7\text{P}$ may in principle be written (i) $(\text{C}_7\text{H}_7^+\text{Cl}^-)_2\text{PCl}_5$, (ii) $\text{C}_7\text{H}_7^+\text{PCl}_6^-$, $\text{C}_7\text{H}_7^+\text{Cl}^-$, or (iii) $(\text{C}_7\text{H}_7)_2^{2+}\text{PCl}_6^{2-}$. The mode of formation makes it feasible that the complex should contain PCl_6^- ions. Thus, a likely first step † is



Phosphorus trichloride and hydrogen chloride were indeed shown to be formed. This reaction would involve hydride abstraction by PCl_4^+ . Beattie and Webster have recently provided evidence that "phosphorus pentachloride" can exhibit acceptor properties.⁷ Structure (iii) does not seem attractive at first sight since it would involve the previously unknown heptachlorophosphate ion in which phosphorus has an outer shell of fourteen electrons. It is worth noting, however, that compounds which might contain heptacoordinate phosphorus, e.g., PCl_5Br_4 , have been known for over sixty years⁸ and that their existence has more recently been confirmed in Russian work.⁹ Further, a cryoscopic investigation of phosphorus trichloride and bromine in nitrobenzene by Harris and Payne has shown the existence of PX_5 and PX_7 species.¹⁰ Thus no overwhelming steric objections to (iii) are apparent. Nevertheless, the double-salt structure (ii) seems rather more attractive, and it could be pictured as involving weak interaction between PCl_6^- and Cl^- which falls short of the formation of a normal P-Cl covalency. A somewhat similar type of bonding appears to occur in the salt $\text{K}^+\text{Sb}_4\text{F}_{13}^-$, the anion of which is believed to contain fluoride loosely co-ordinated with four molecules of antimony trifluoride.¹¹ The bonding in certain solvates of some Group V trihalides also seems to be of related character.¹²

Certain other relevant observations have been made. Addition of t-butyl chloride in the preparation of the complex led to no improvement in yield or other discernible effect. This contrasts with the related preparations of tropylium chlorostannates, etc., described in Part I,¹ but conforms with the mechanism proposed above in which PCl_4^+ acts as the hydride-acceptor.

The complex was also prepared by prolonged reaction between tropylium chloride and an excess of phosphorus pentachloride in nitromethane. The first step here may be pictured essentially as metathesis between $\text{PCl}_4^+\text{PCl}_6^-$ and $\text{C}_7\text{H}_7^+\text{Cl}^-$. In Part I,¹ phosphorus trichloride was reported not to produce tropylium ions from cycloheptatriene under nitrogen in the presence of t-butyl chloride. Further investigation has now shown

* Dr. I. R. Beattie is engaged on this.

† This might be preceded by some form of addition to the triene, and a transient initial yellow coloration is indeed observed.

⁷ Beattie and Webster, *J.*, 1961, 1730.

⁸ Michaelis, *Annalen*, 1872, 164, 9; 1900, 310, 45; 1901, 315, 58.

⁹ Kialkov and Kuz'menko, *Zhur. obshchei Khim.*, 1951, 21, 33; 1952, 22, 1290, 1335.

¹⁰ Harris and Payne, *J.*, 1956, 4613.

¹¹ Byström and Wilhemi, *Arkiv Kemi*, 1951, 3, 17.

¹² Agerman, Andersson, Lindquist, and Zackrisson, *Acta Chem. Scand.*, 1958, 12, 477; Kolditz, *Z. anorg. Chem.*, 1957, 289, 118.

the formation of 0.02% of tropylium ion under more forced conditions, and omission of t-butyl chloride led to a similar result. Although in neither case could a definite complex salt be isolated, the result appears to provide the first indication that phosphorus trichloride can exhibit feeble acceptor properties. Such properties have not yet been established even for phosphorus trifluoride,¹³ and this seems to underline the great sensitivity of the test with cycloheptatriene (cf. Part I¹). It is significant in this connexion that evidence was obtained for the formation of a phosphorus-containing tropylium salt by interaction of phosphorus trichloride and tropylium chloride in nitromethane, although no pure compound was isolated. Phosphorus pentabromide which of course differs structurally from the pentachloride also reacted differently with cycloheptatriene. The main organic products of the reaction have not been investigated, but only a trace of an orange solid tropylium complex bromide was obtained.

Reaction of cycloheptatriene with sulphur monochloride or dichloride gave no isolable amounts of solid tropylium salts, although tropylium ion yields of 0.2% and 0.1%, respectively, were determined spectroscopically, and these were increased to 1.2 and 0.3%, respectively, when the reactions were performed in the presence of t-butyl chloride.

Since several independent procedures for the preparation of tropylium chloride have given products having melting points at or close to 102° (decomp.), it is felt that the value 189° quoted by Dewar and Pettit⁴ should be treated with reserve. It is now clear that the pure compound is colourless.

Preliminary Attempts to Obtain Salts of C₈H₈²⁺.—It was hoped that reaction of cyclo-octatetraene, stannic bromide, and bromine might produce a salt C₈H₈²⁺SnBr₆²⁻. An infusible black solid was obtained from such a reaction, and contained carbon, hydrogen, bromine, and tin; but consistent analyses could not be obtained. Reaction of the bicyclic isomer of cyclo-octatetraene dichloride with stannic chloride gave a black solid, m. p. 177°. This was insoluble in hydrocarbons and carbon tetrachloride, but gave purple solutions in nitromethane or methylene dichloride (λ_{max} 540 m μ). Again, consistent analytical data could not be obtained, although the substance was shown to contain carbon, hydrogen, chlorine, and tin. Numerous attempts to abstract two hydride ions from cyclo-octa-1,3,5-triene by the procedures described in Part I¹ for cycloheptatriene gave largely polymeric material, and no trace of salt-like products.

EXPERIMENTAL

Tropylium ion was estimated spectroscopically.¹

Reaction of Tropylium Bromide with Hydrogen Chloride.—Repetition of the previous procedure³ with tropylium bromide (3.3 g.) in ethanol (125 ml.) at 10° gave a pale yellow solid (1.2 g.), m. p. 84—87° (Found: C₇H₇⁺, 57.2. Calc. for C₇H₇Cl: C₇H₇⁺, 71.95%). Qualitative tests showed that chlorine and bromine were present. The product was redissolved in ethanol (25 ml.) and a brisk current of dry hydrogen chloride was passed through the solution for 4½ hr. at 10°. Sufficient ether was then added to produce a faint turbidity. Cooling to -50° gave a pale yellow solid (0.8 g.), m. p. 95° (decomp.) (Found: C₇H₇⁺, 64.2%). This also was not wholly free from bromine.

In a further experiment, the passage of hydrogen chloride was continued for 22 hr. The pale yellow product, m. p. 95° (decomp.), still contained a little bromine.

Reaction of Cycloheptatriene with Phosphorus Pentachloride (cf. ref. 2).—(a) A solution of cycloheptatriene (0.91 g.) in carbon tetrachloride (10 ml.) was added in 10 min. with stirring under nitrogen (anhydrous conditions) to a solution of phosphorus pentachloride (4.1 g.) in carbon tetrachloride (40 ml.). A marked yellow colour appeared transiently after each addition of the cycloheptatriene solution. Hydrogen chloride was evolved. Stirring was continued for a further 2½ hr., and the resulting gelatinous suspension was set aside overnight. Filtration, washing with carbon tetrachloride (100 ml.), and drying *in vacuo* at room temperature gave a colourless, deliquescent product (1.63 g., 130%, calc. as C₇H₇⁺Cl⁻), m. p. 170° (decomp.)

¹³ Woolf, J., 1955, 279.

(Found: C, 36.95, 37.05, 36.0; H, 3.35, 3.55, 3.1; Cl, 54.8, 53.85, 54.05, 53.55; P, 7.0, 6.75, 6.6. $C_{14}H_{14}Cl_7P$ requires C, 36.45; H, 3.05; Cl, 53.8; P, 6.7%) (yield, 72%; calc. as $C_{14}H_{14}Cl_7P$). Spectroscopic determination of $C_7H_7^+$ gave the value 36%, which agrees poorly with the calculated value of 39.5%. This determination is based on the value $\log \epsilon_{\max} = 3.63$ (λ_{\max} , 277 m μ), and is very sensitive to any error in $\log \epsilon$. A value of 3.58 would give the calculated figure for $C_7H_7^+$. Doering and Knox³ give $\log \epsilon_{\max} = 3.6$.

The infrared spectrum of the solid complex (hexachlorobutadiene mull) showed the following principal maxima over the range 600—4000 cm^{-1} : 630w, 664w, 996w, 1043vw, 1104w, 1307m, 1475vs, 1894w, 2077w, 2415vw, 2500w, 2556w, 2698w, 2765vw, 2869w, 2944w, 3017s, 3048w, 3070m, 3083w, 3128w.

A preparation performed on fifteen times the above scale gave an 84% yield of the complex.

(b) Experiment (a) was repeated, except that the mixture after addition of the cycloheptatriene solution was stirred for 1 hr. and then heated under reflux for 15 min. The yield of the complex, m. p. 170° (decomp.), was 82%. The presence of phosphorus trichloride in the carbon tetrachloride solution after filtration of the complex was demonstrated by the formation of phosphorous acid on hydrolysis.

Reaction of Tropylium Chloride with Phosphorus Pentachloride.—A solution of tropylium chloride (0.32 g.) and phosphorus pentachloride (1.0 g.) in dry nitromethane (50 ml.) was left at room temperature in the dark for 7 days. Addition of a 5% solution of phosphorus pentachloride in carbon tetrachloride, filtration, and washing with carbon tetrachloride gave the above tropylium-phosphorus chloride complex (0.38 g.), m. p. and mixed m. p. 169° (decomp.).

Reaction of Tropylium Chloride with Phosphorus Trichloride.—A solution of tropylium chloride (1.15 g.; m. p. 101°) and phosphorus trichloride (5.0 g.) in dry nitromethane (15 ml.) was left at room temperature for 24 hr. The solution was poured into dry ether (100 ml.). The colourless precipitate (0.18 g.), when filtered off and washed with dry ether, had m. p. 91—93° (Found: $C_7H_7^+$, 61.3; Cl, 36.85. Calc. for C_7H_7Cl : $C_7H_7^+$, 71.95; Cl, 28.05. Calc. for $C_7H_7Cl_4P$: $C_7H_7^+$, 34.55; Cl, 53.7%). The presence of phosphorus was detected qualitatively. These results suggest that reaction was far from complete and that the product may have been a mixture of unchanged tropylium chloride with (say) tropylium tetrachlorophosphate. No method of separation has yet been devised.

Reaction of Cycloheptatriene with Phosphorus Pentabromide.—A solution of cycloheptatriene (1.84 g.) and phosphorus pentabromide (8.62 g.) in dry ether (250 ml.) was kept at room temperature for 20 hr. Filtration and washing with dry ether gave an orange solid (0.050 g.) containing phosphorus and bromine and 0.7% of the cycloheptatriene as tropylium ion.

Use of carbon tetrachloride in place of ether led to a similar result.

Chemical Properties of the Tropylium-Phosphorus Chloride Complex, $C_{14}H_{14}Cl_7P$.—(a) *Thermal decomposition.* The complex (1.0 g.) was heated at 83—88°/0.7 mm. for 4 hr. in a sublimation apparatus. Tropylium chloride (0.07 g.), m. p. 102° (decomp.), collected as a glass on the cold finger (Found: $C_7H_7^+$, 72.35; Cl, 27.8%). Phosphorus trichloride (0.02 g.), b. p. 70—73°, was collected in a trap at -75°. Any free chlorine formed would not have been detected.

(b) *Reaction with ethanol.* Dissolution of the complex (6.7 g.) in dry ethanol (40 ml.) at room temperature gave a brown solution, and the temperature rose to 45°. After 2 min. at 60°, the solution was cooled and poured into dry ether (300 ml.) to give a colourless solid, m. p. 94—95°, which after two similar reprecipitations gave tropylium chloride (0.63 g.), m. p. 98° (decomp.). This gave no reaction for phosphorus (Found: $C_7H_7^+$, 71.4; Cl, 28.65%).

(c) *Reaction with nitromethane.* Repetition of experiment (b) with nitromethane in place of ethanol gave crude tropylium chloride, m. p. 70° (unsharp); this contained phosphorus.

(d) *Neutral hydrolysis.* The complex (0.5 g.) was dissolved in water (20 ml.) and shaken with ether (20 ml.). A portion of the aqueous solution gave a positive test for tropylium ion when tested with sodium tetraphenylborate. The unseparated aqueous layer was brought to pH 7 with sodium hydroxide solution and again shaken with the ether. The separated aqueous layer was boiled to remove volatile organic material and shown to contain phosphate but no phosphite by the usual qualitative tests. Phosphate was confirmed through precipitation of the silver salts by addition of silver nitrate solution and separation from silver chloride (Found: Ag, 76.55. Calc. for Ag_3PO_4 : Ag, 77.3%).

(e) *Alkaline hydrolysis: preparation of di(cycloheptatrienyl) ether.* A solution of the complex (13.9 g.) in water (100 ml.) was added to a solution of sodium hydrogen carbonate (84 g.) in water (500 ml.) in the presence of pentane (75 ml.). The mixture was stirred for 2 hr., and the

separated aqueous layer was further extracted with pentane (4×50 ml.). The combined pentane extracts were washed with water, and dried (MgSO_4). Fractional distillation gave di(cycloheptatrienyl) ether (2.13 g.), b. p. $107\text{--}110^\circ/0.7$ mm., having the correct infrared spectrum. The absence of cycloheptatrienone was demonstrated by the absence of the characteristic peak at 6.3μ .¹

Preparation of Tropylium Chloride from Di(cycloheptatrienyl) Ether.—Dry hydrogen chloride was passed for 20 min. just above the surface of a solution of di(cycloheptatrienyl) ether (3.08 g.) in dry ether (40 ml.). Filtration and washing with dry ether gave colourless tropylium chloride (3.69 g., 94%), m. p. 98° (decomp.) (Found: C_7H_7^+ , 71.5; Cl, 27.9%).

Stability of Tropylium Chloride.—Although tropylium bromide seems to be stable indefinitely, decomposition of the chloride is apparent within 3 days at room temperature under dry nitrogen in the dark. Solutions of the chloride in ethanol or nitromethane are likewise unstable. The solid chloride can be kept for several weeks in the dark at 0° . The highest m. p. observed in the present work was 102° , but the substance is very deliquescent, and satisfactory products have often been found to melt a few degrees below this.

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