70. *Free Radicals and Radical Stability. Part V. The Thermal Stability of Chloroformates and Carbonates.*

By Sydney T. Bowden.

Attempts to prepare triphenylmethyl carbonate, $(CPh_3)_2CO_3$, by interaction of a metal triphenylmethoxide with carbonyl chloride, gave a nearly theoretical yield of triphenylmethyl chloride. This is due to the thermal instability of the intermediate triphenylmethyl chloroformate, $Cl\cdot CO_2CPh_3$, which decomposes with evolution of carbon dioxide. The behaviour of other phenylated derivatives towards carbonyl chloride has been examined in order to establish the connexion between the radical

stability of the ester group and the thermal stability of the chloroformate. The simple alkyl chloroformates are comparatively stable, but benzyl chloroformate is unstable, and the benzhydryl ester is unknown.

The stability of the substituted alkyl carbonates has been studied from the same standpoint, and both for these and for the simple phenylated derivatives the thermal behaviour conforms to the following rule: The greater the radical stability of the ester group in chloroformates and carbonates, the lower will be the thermal stability of the compound.

IN the course of an investigation of the properties of certain triarylmethoxides we attempted to prepare triphenylmethyl carbonate by the action of carbonyl chloride on the corresponding methoxide. On no occasion, however, were we able to obtain the anticipated product, or indeed, the intermediate chloroformate, and we were led accordingly to examine in greater detail the factors governing the thermal stability of the esters of chloroformic and carbonic acids.

When potassium triphenylmethoxide is treated with a toluene solution of carbonyl chloride, precipitation of colloidal potassium chloride and evolution of carbon dioxide rapidly occur with evolution of heat. When the solution is concentrated in the absence of moisture, pure triphenylmethyl chloride is obtained in nearly theoretical yield. Experiments conducted at different temperatures showed that the first product of the interaction is triphenylmethyl chloroformate, which, however, is thermally unstable and spontaneously decomposes into triphenylmethyl chloride and carbon dioxide: $CPh_3{\cdot}OK + COCl_2 \longrightarrow KCl + CPh_3{\cdot}O{\cdot}COCl \longrightarrow CPh_3Cl + CO_2$.

This interpretation assumes a further significance in the light of Roberts and Bowden's hypothesis (*Rec. Trav. chim.*, 1930, **49**, 665) advanced to account for the reduction of triarylcarbinols by formic acid. In this case the triarylmethyl formate is thermally unstable and decomposes on heating, with formation of the corresponding methane and carbon dioxide: $H{\cdot}CO_2CPh_3 \longrightarrow CHPh_3 + CO_2$. These apparently dissimilar processes are thus brought into line, although the thermal stability of the chloroformate is considerably lower than that of the formate, which may be isolated in the crystalline condition at room temperature.

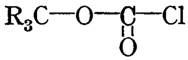
In view of the above reactions of the potassium derivative, the behaviour of triphenylcarbinol itself towards carbonyl chloride is of interest. When a cold benzene solution of the carbinol is treated with carbonyl chloride, carbon dioxide is evolved and triphenylmethyl chloride and water are produced. If the reaction is carried out in the presence of anhydrous calcium chloride, triphenylmethyl chloride may be isolated in good yield. The three main reactions involved may be expressed as follows: $CPh_3{\cdot}OH + COCl_2 \longrightarrow Cl{\cdot}CO_2CPh_3 + HCl$; $Cl{\cdot}CO_2CPh_3 \longrightarrow CPh_3Cl + CO_2$; $CPh_3{\cdot}OH + HCl \rightleftharpoons CPh_3Cl + H_2O$. The presence of calcium chloride largely inhibits the hydrolysis of the triarylmethyl chloroformate and chloride. These interpretations may be compared with Gomberg and Davies's observation (*Ber.*, 1903, **36**, 3924) that triphenylmethyl chloride is produced from the carbinol and acetyl chloride through the intermediate formation of the acetate: $CPh_3{\cdot}OH + CH_3{\cdot}COCl \longrightarrow CH_3{\cdot}CO_2CPh_3 + HCl$. There is, however, a fundamental difference in the subsequent behaviour of the chloroformate and the acetate under ordinary conditions: whereas the former gives rise to triphenylmethyl chloride directly, the latter, being more stable, is converted into the chloride through further interaction with acetyl chloride: $CH_3{\cdot}CO_2CPh_3 + CH_3{\cdot}COCl \longrightarrow CPh_3Cl + (CH_3{\cdot}CO)_2O$.

Benzyl carbonate may be prepared by the action of carbonyl chloride on potassium benzyloxide in virtue of the comparatively high stability of the intermediate chloroformate. In fact, Thiele and Dent (*Annalen*, 1898, **302**, 257) isolated the chloroformate as an oil by the action of carbonyl chloride on benzyl alcohol at a low temperature. In this connexion, the diphenylated derivative may be expected to be more similar to the benzyl than to the triphenylmethyl compound. This anticipation is fully realised, and although benzhydryl chloroformate has not been isolated, we have prepared the carbonate as a white crystalline solid through the action of carbonyl chloride on potassium benzhydryloxide. Phenyl carbonate is easily prepared by an analogous reaction; the intermediate phenyl chloroformate is a fairly stable liquid, but it decomposes at 180° into phenyl carbonate and carbonyl chloride. The influence of the ester radical on the properties of chloroformates is shown in the following table :

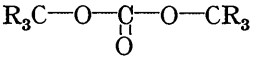
Chloroformate.	B. p.	Action on methoxide.
Methyl	71°	Forms carbonate
Phenyl	90°/20 mm.	" "
Benzyl	103°/20 mm.	" "
Benzhydryl (unknown)	—	" "
Triphenylmethyl (unknown)	—	Does not form carbonate

The chloroformate structure (I) is much less stable than the carbonate structure (II), and Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 200) was able to prepare triphenylmethyl

(I.)



$R_3C{-}O{-}C({=}O){-}Cl$



$R_3C{-}O{-}C({=}O){-}O{-}CR_3$

(II.)

carbonate by the interaction of triphenylmethyl chloride and silver carbonate. The substance, however, melts at 208° with evolution of carbon dioxide and formation of triphenylmethyl oxide, and the reaction may be catalysed at 130—140° by means of copper powder (Halford, *ibid.*, 1929, **51**, 2157). Since methyl carbonate is thermally very stable, it seemed probable that the thermal stability of carbonates is likewise connected with the unimolecular stability of the ester radical, although the course of the reaction may be different in the various cases. In fact, Ritchie (J., 1935, 1056) has shown that methyl carbonate decomposes at 600° to produce olefinic as well as other products, $Me_2CO_3 \longrightarrow Me{\cdot}OH + CO_2 + CH_2{:}$, whereas the primary pyrolysis of phenyl carbonate occurs thus : $Ph_2CO_3 \longrightarrow Ph_2O + CO_2$.

Benzhydryl carbonate melts without decomposition, but the liquid begins to decompose at 260° with evolution of carbon dioxide. Benzyl and methyl carbonates, however, exhibit much greater stability, as indicated in the following table :

Carbonate.	M. p.	Decomp. temp.	Carbonate.	M. p.	Decomp. temp.
Methyl	5°	$> 500°$	Benzhydryl	123°	260°
Benzyl	29	> 350	Triphenylmethyl	208	208

Within the limits of the simple phenylated series the results conform to the rule : The greater the unimolecular stability of the ester radical, the lower will be the thermal stability of the compound. This influence is doubtless of quite general character and is likewise operative in the case of other esters, but must perforce be modified by polar and steric factors, and particularly, by the presence of other functional groups.

EXPERIMENTAL.

Action of Carbonyl Chloride on Potassium Triphenylmethoxide.—(a) Potassium triphenylmethoxide, prepared from triphenylcarbinol (10 g.) by Blicke's method (*J. Amer. Chem. Soc.*, 1923, **45**, 1965), was cooled to 0° and slowly treated with an ice-cooled solution of carbonyl chloride (3·8 g.) in toluene (30 g.). The strongly exothermic reaction was accompanied by considerable effervescence and the precipitation of gelatinous potassium chloride. The clear, supernatant liquid was decanted through the side-tube of the reaction flask, the residual mass washed with benzene, and the washings combined with the main solution. The solution was concentrated under reduced pressure, and the triphenylmethyl chloride recrystallised from benzene–light petroleum. All the operations were carried out in an atmosphere of nitrogen with rigorous exclusion of moisture. The substance was thus obtained in large, cubic crystals, m. p. 112° (Found : Cl, 12·4. Calc. for $C_{19}H_{15}Cl$: Cl, 12·75%) ; it gave the yellow halochromic derivative with an ethereal solution of anhydrous ferric chloride, and was converted into triphenylmethyl ethyl ether, m. p. 84°, on dissolution in warm ethyl alcohol.

(b) In order to estimate the amount of triphenylmethyl chloride produced in the reaction, the experiment was conducted as described above, and a known volume of the resulting solution removed and treated with a current of dry nitrogen to expel traces of carbonyl chloride. The solution was diluted with sodium-dried benzene and shaken with excess of mercury in a sealed vessel for several hours. The yellow solution of the free radical was carefully separated from the finely divided mercurous chloride, and air passed through the solution until the colour was discharged. Triphenylmethyl peroxide was deposited as a pale yellow, crystalline precipitate, which, after being washed with ether, had m. p. 177—180°. The yield of peroxide attained in a control experiment with pure triphenylmethyl chloride was 70%, and that in the present experiment was 69·5%. The formation of triphenylmethyl chloride from the methoxide and carbonyl chloride is therefore practically quantitative.

(c) In order to estimate the amount of carbon dioxide, the reaction was carried out while nitrogen was slowly led through the apparatus, and the issuing gases passed through 100 c.c. of N-potassium hydroxide. This was found to contain 0·600 g. of potassium chloride and 2·436 g. of the carbonate. If the carbonate were produced merely from the carbonyl chloride carried over, its amount would be 0·554 g. The difference, 1·882 g., was therefore due to the carbon dioxide evolved in the reaction, and corresponds to 100% evolution of the gas.

Action of Carbonyl Chloride on Triphenylcarbinol.—(*a*) Carbonyl chloride was passed through a cold, nearly saturated solution of triphenylcarbinol in benzene. After a few minutes the solution became turbid and there was visible separation of water. The presence of triphenylmethyl chloride in the dried benzene layer was shown by the formation of the addition derivative with anhydrous ferric chloride, and by the formation of free triphenylmethyl on reduction with metallic mercury.

(*b*) Carbonyl chloride was led into a solution of the carbinol (2·6 g.) in benzene (25 g.) in the presence of a few lumps of freshly dehydrated calcium chloride. After saturation, the solution was decanted from the drying agent, and the excess of carbonyl chloride removed by passage of dry air. The resulting solution was shaken in a sealed vessel with excess of metallic mercury for 4 hours, siphoned from the mercurous chloride, and oxidised by a stream of air until the precipitation of triphenylmethyl peroxide was complete. The peroxide (m. p. 177°) weighed 1·84 g., corresponding to the formation of 76% of the theoretical amount of triphenylmethyl chloride in the above reaction.

Action of Carbonyl Chloride on Potassium Benzhydryloxide.—(*a*) The potassium derivative was prepared by heating a solution of pure benzhydrol (9·2 g.) in dry xylene (50 c.c.) with metallic potassium (1·95 g.) in an atmosphere of oxygen-free nitrogen. The reaction commenced in the cold, but was still incomplete after 4½ hours' boiling. When the solution was cooled, blue streamers of the ketylic derivative issued from the surface of the metal, but potassium benzhydryloxide was subsequently precipitated as a white crystalline solid. When this was slowly treated at room temperature with a solution of carbonyl chloride (2·48 g.) in toluene (15 c.c.), the exothermic reaction was accompanied by slight effervescence. The solution, filtered from potassium chloride and concentrated under reduced pressure, slowly deposited white crystals (3 g.) of *benzhydryl carbonate*; after three crystallisations from ligroin, this had m. p. 123° (Found: C, 81·9; H, 5·9. $C_{27}H_{22}O_3$ requires C, 82·2; H, 5·6%). When the same reaction was carried out at 0°, there was no evolution of carbon dioxide, and the yield was slightly better.

(*b*) The benzhydryloxide was cooled in an ice–salt bath to —16° and treated with a cold solution of carbonyl chloride (3·7 g.) in toluene (25 c.c.). The reaction took place without visible evolution of carbon dioxide. After standing for 12 hours, the solution was filtered in a dry atmosphere and concentrated by warming under reduced pressure. The solid deposited from the cold solution melted at 85—95°, and by fractional crystallisation from light petroleum was shown to be a mixture of benzhydryl carbonate and unchanged benzhydrol. Benzhydryl chloroformate could not be isolated by concentrating the mother-liquor. However, its presence as an intermediate is indicated by the fact that carbon dioxide was evolved when the original reaction mixture was warmed gently on the water-bath.

Action of Carbonyl Chloride on Potassium Benzyloxide.—A solution of freshly distilled benzyl alcohol (10 g.) in potassium-dried xylene (50 c.c.) was boiled with potassium (3·9 g.) in an atmosphere of dry nitrogen for 4·5 hours. In every case, some of the metal could be recovered unchanged, although Bischoff (*Ber.*, 1903, **36**, 159) states that there is practically complete interaction between sodium and benzyl alcohol at 70°. The precipitated benzyloxide was treated with carbonyl chloride (4·9 g.) in toluene (25 c.c.), and after a few hours the solution was filtered, the solvent evaporated, and the residue distilled under reduced pressure. The carbonate was obtained as a colourless liquid, b. p. 200—201°/13·5 mm., which slowly crystallised in large plates, m. p. 29°.

Decomposition Temperatures of Carbonates.—The thermal stability of benzyl carbonate was examined by passing the liquid from a small dropping-funnel into a glass coil immersed in a metal bath, while nitrogen was slowly passed through the apparatus into a vessel containing lime-water. Although the carbonate was maintained at 350° for an hour, no carbon dioxide was evolved and the liquid could be recovered unchanged. Benzhydryl carbonate, however, was placed in a glass U-tube and heated in a current of nitrogen as described above. Decomposition occurred at 260° and the liquid suffered fairly rapid pyrolysis at 270°.

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