170. *Free Radicals and Radical Stability. Part VIII. The Stability of Formates and the Reduction of Triarylcarbinols.*

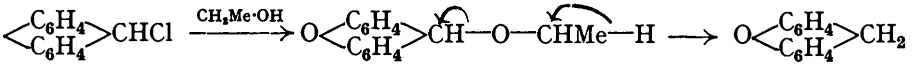
By Sydney T. Bowden, D. Leslie Clarke, and William E. Harris.

The general problem of the reducibility of triarylcarbinols has been examined with particular reference to the thermal stability of formates. The order of resistance to the thermal decomposition $H{\cdot}CO_2R \longrightarrow RH + CO_2$ may be represented (R =) : methyl > benzyl > benzhydryl > triphenylmethyl < diphenyldiphenylylmethyl < diphenylnaphthylmethyl. The radical stability increases throughout this series, and the inversion of the stability relationships at the triphenylmethyl member shows clearly that two fundamentally different mechanisms are involved, *viz.*, intramolecular change in the colourless homopolar formates, and ionic interaction in the coloured polar formates.

The influence of substituents has been further examined by comparing the rates of decomposition at 77°. The most easily reduced carbinols are those containing *o*-methoxyl groups, and the influence of *p*-methoxyl is also strongly favourable. Although *m*-methoxyl exerts a very slight favourable influence in the early stages of the reaction, the over-all effect is strongly inhibitory and the yield of *m*-methoxytriphenylmethane is relatively low. These features are also apparent in the behaviour of dimethoxy- and trimethoxy-triphenylmethyl derivatives. Replacement of one of the phenyl groups by a diphenylyl, naphthyl, or acenaphthyl group raises the decomposition temperature and lowers the rate of reduction. This is attributed to normal electronic influences and to steric factors.

It is shown on experimental and theoretical grounds that no simple connexion obtains between the basicity of a carbinol and its reducibility as indicated by the formic acid method.

Although little direct evidence is available, it appears that the course of reduction of certain highly arylated derivatives is intimately connected with the unimolecular stability and other properties of the radical complex. The reduction of triphenylmethane dyes and related carbinols by vanadous chloride has been studied by Conant and Bigelow (*J. Amer. Chem. Soc.*, 1931, **53**, 676), who found that the first product of the reaction is the free radical, which may be isolated under certain conditions but usually suffers further rearrangement to form a Tschitschibabin type of compound or undergoes partial reduction in the presence of acids to produce the corresponding methane : $2R + H^+ = RH + R^+$. According to Kny-Jones and Ward (J., 1930, 536), the reduction of xanthydrol and xanthydryl chloride by alcoholic hydrochloric acid and alcohol, respectively, proceeds *via* the ethyl ether :



$$<\!\!{}^{C_6H_4}_{C_6H_4}\!\!>CHCl \xrightarrow{CH_2Me\cdot OH} O<\!\!{}^{C_6H_4}_{C_6H_4}\!\!>CH{-}O{-}CHMe{-}H \longrightarrow O<\!\!{}^{C_6H_4}_{C_6H_4}\!\!>CH_2$$

The development and subsequent disappearance of a yellow-green colour in these experiments is taken as evidence of the presence of the xanthyl ion corresponding to the free xanthyl radical, which Conant and Sloan (*J. Amer. Chem. Soc.*, 1923, **45**, 2468) were able to isolate in the impure state.

A few general observations on the reducibility of triarylcarbinols were made by Baeyer and Villiger (*Ber.*, 1902, **35**, 3013), who found that zinc and acetic acid effect reduction of 4 : 4′ : 4″-trimethoxytriphenylcarbinol more rapidly than the unsubstituted derivative. The reduction of triarylcarbinols by hot formic acid has been examined by Kauffmann and Panwitz (*ibid.*, 1912, **45**, 766), who obtained rough estimates of the speed of reduction from the time required for the decolorisation of the boiling solution. Failing to observe any simple relationship between the so-called reducibility of the carbinol and the basicity, they suggested that a connexion may exist between the former and the halochromic properties as reflected in the colour of the triarylmethyl salts. The formation of triarylmethanes by the action of formic acid on carbinols has been investigated from the preparative standpoint by Guyot and Kovache (*Compt. rend.*, 1912, **154**, 120; 1912, **155**, 883), who showed that the reaction may be used for the estimation of carbinols.

In order to trace the connexion between the stability of the radical complex and the thermal stability of the formate we have determined the decomposition temperatures of the following series :

Formate.	Colour.	Decompn. temp.	Radical stability.*
Methyl	Colourless	>440°	Very small
Benzyl	Colourless	320	Very small
Benzhydryl	Colourless	206	Very small
Triphenylmethyl	Yellow	49	3—5%
Diphenyl-*p*-diphenylylmethyl	Light red	56	15%
Diphenyl-α-naphthylmethyl	Bluish-green	68	60%

* The radical stability refers to a 2% benzene solution at the freezing point.

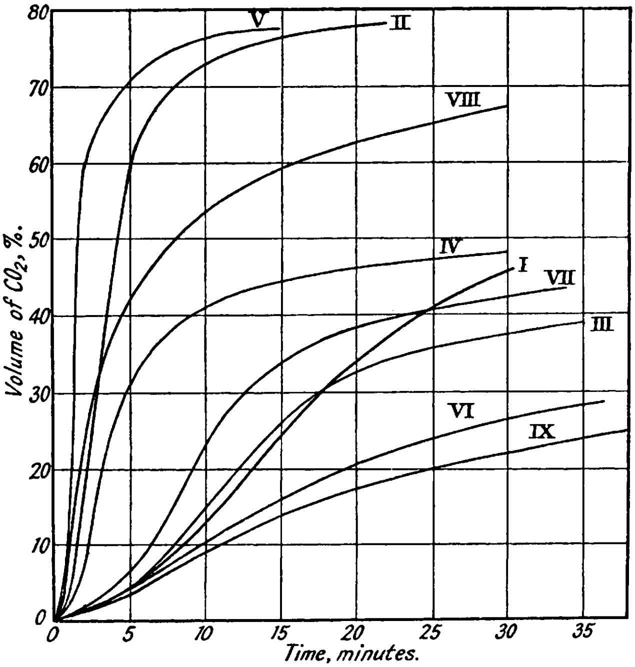
The colourless formates are typical esters, and the thermal stability falls with increasing stability of the radical in accordance with the rule previously noted for chloroformates and carbonates (Bowden, J., 1939, 310). The coloured formates, however, are salts, and here the thermal stability of the formate increases with the unimolecular stability of the radical. There is therefore an inversion of the stability relationships as we pass from derivatives composed of short-lived to those containing long-lived radicals. In this connexion, Ingold (*J. Soc. Chem. Ind.*, 1939, **58**, 81) has pointed out that the decomposition of chloroformates, $Cl{\cdot}CO_2R$, is an intramolecular rearrangement promoted by electron-release from R, and that the facility of the change increases with the stability of R^+, decreasing again only when the rearranging molecule begins to be replaced by the pair of ions R^+ and $(O{\cdot}COCl)^-$.

The influence of the methoxyl group on the basicity of triphenylcarbinol was investigated by Baeyer and Villiger (*Ber.*, 1902, **35**, 1189), who found that the basicity was increased by an amount depending on the number and orientation of the substituents. The methoxytriphenylmethyl formates are stable at ordinary temperature, but decompose on being warmed. The introduction of methoxyl groups in *o*-positions causes a fairly marked lowering in the decomposition temperature; *e.g.*, triphenylmethyl formate begins to decompose in formic acid solution at 49°, but the 2 : 2′-dimethoxy- and 2 : 2′ : 3″-trimethoxy-derivatives decompose at 31° and 33°, respectively. In general, however, triphenylmethyl formates corresponding to carbinols of widely different basic and halochromic properties have decomposition points which lie within a comparatively narrow temperature range. Apart from the above cases, the influence of constitutional differences is not disclosed by this method, but is prominently reflected in the velocity of reduction at higher temperatures.

These experiments involved the measurement of the rate of evolution of carbon dioxide from solutions of the carbinols in formic acid at 77°. A few representative examples of the curves obtained by plotting the percentage of carbon dioxide against the time are shown in Fig. 1. In view of the initial complications arising from the heterogeneous character of the system and the presence of water owing to salt formation, it is not surprising that the rate of evolution seldom conforms with any of the simple reaction formulæ. Apart from the reactions of the *o*-substituted derivatives which conform with the unimolecular formula over a fairly wide range, there is an early drift in all other cases and especially with *m*-substituted compounds. In these circumstances, therefore, the rates may be indicated by the times for 20% conversion as shown in the last column of Table I.

The most striking feature is the powerful influence of *o*-methoxyl in promoting decomposition of the formate, as shown by the high rate of decomposition and the high yield of triarylmethane from *o*-methoxy- and 2 : 2′-dimethoxy-triphenylmethyl formates. *p*-Methoxyl also exerts a fairly strong favourable influence in the triphenylmethyl series of derivatives, but the effect is less marked in more complex compounds such as phenyl-*p*-anisyldiphenylylmethyl formate. *m*-Methoxyl appears to exert a slightly favourable influence in the early stages of the reaction, but this is rapidly offset by a subsequent inhibiting effect which leads to a low yield of corresponding methane. The latter effect is very marked with all compounds containing *m*-methoxyl, and is doubtless connected with the fact that 3 : 3′ : 3″-trimethoxytriphenylmethyl formate does not evolve carbon dioxide at 77°. Replacement of two methoxyl groups by a methylenedioxy-group, as in the diphenylpiperonylmethyl derivative, lowers the rate of decomposition, but a similar difference is found in the corresponding radical stabilities. The influence of a methyl substituent is revealed in the behaviour of 2-methoxy-4′-methyltriphenylmethyl formate,

Fig. 1.



Formate: I, *Triphenylmethyl.* II, o-*Methoxytriphenylmethyl.* III, m-*Methoxytriphenylmethyl.* IV, p-*Methoxytriphenylmethyl.* V, 2 : 2′-*Dimethoxytriphenylmethyl.* VI, 3 : 4-*Dimethoxytriphenylmethyl.* VII, 3 : 4 : 5-*Trimethoxytriphenylmethyl.* VIII, 2-*Methoxy*-4′-*methyltriphenylmethyl.* IX, *Diphenyl*-p-*diphenylylmethyl.*

Table I.

Radical.	Radical stability, %.	Basicity of carbinol.	Colour of formate.*	Time (mins.) for 20% conversion.
Triphenylmethyl	3—5	1	Yellow	13·0
o-Methoxytriphenylmethyl	27	1·9	Red	2·0
m-Methoxytriphenylmethyl	12	1·2	Brownish-red	12·0
p-Methoxytriphenylmethyl	24	6·5	Orange	3·2
2 : 2′-Dimethoxytriphenylmethyl	40	—	Purple-brown	1·0
2 : 4′-Dimethoxytriphenylmethyl	28	11·8	Blood red	2·4
3 : 4-Dimethoxytriphenylmethyl	22	5·9	Red	21·2
Diphenylpiperonylmethyl	9	4·0	Carmine red	4·2
2-Methoxy-4′-methyltriphenylmethyl	—	2·1	Deep reddish-brown	2·1
3 : 4 : 5-Trimethoxytriphenylmethyl	24	3·6	Crimson	8·9
2 : 4 : 2′-Trimethoxytriphenylmethyl	—	19·0	Dark reddish-brown	5·2
2 : 2′ : 3″-Trimethoxytriphenylmethyl	—	—	Brownish-purple	0·9
3 : 3′ : 3″-Trimethoxytriphenylmethyl	—	1·4	Red	∞
Diphenyl-*p*-diphenylylmethyl	15	1·7	Light red	27·0
Phenyl-*p*-anisyldiphenylylmethyl	—	9·6	Light red	24·2
Diphenyl-3-acenaphthylmethyl	—	2·0	Bluish-green	∞

* The colours refer to M/100-solutions of the carbinols in formic acid.

and it is evident that *p*-methyl has a much weaker influence than the corresponding methoxyl group. The operation of the characteristic electronic effects associated with these groups is evident in all the above reactions. The introduction of heavier aromatic nuclei for a phenyl group in triphenylmethyl formate leads to higher decomposition temperatures and lower rates of reduction. The inhibiting effect of these groups, as observed in the formates of diphenyl-*p*-diphenylylmethyl, diphenyl-α-naphthylmethyl, and diphenyl-3-acenaphthylmethyl, is probably to be referred, not only to normal electronic influences, but also to steric factors arising from the large size of the groups. It is noteworthy that 4 : 4′ : 4″-trinitrotriphenylcarbinol, with a corresponding radical stability of 100%, dissolves in formic acid to form a colourless solution, which does not evolve carbon dioxide at 100°. With regard to a possible relationship between the reducibility and the halochromic properties of the carbinols, which was suggested by Kauffmann and Panwitz (*loc. cit.*), it is evident from Table I that no simple connexion exists between the colour of the triarylmethyl cation and the rate of reduction.

The present work brings into prominence the fundamental difference between the homopolar and the polar formates. The former, containing short-lived radicals covalently linked to the formate radical, decompose at high temperatures in virtue of a process involving intramolecular rearrangement :

$$\mathrm{Ph_2H\overset{\curvearrowleft}{C{-}O{-}CO{-}}H} \longrightarrow \mathrm{Ph_2HCH + CO_2}$$

The polar formates, in which long-lived ionised radicals are associated with the formate ion, decompose at comparatively low temperatures through ionic interaction :

$$\mathrm{Ph_3C^+ + (OOCH)^-} \longrightarrow \mathrm{Ph_3CH + CO_2}$$

In the case of the methoxytriphenylmethyl formates, no simple connexion is discernible between the facility of the interaction and the corresponding radical stability, but this is intelligible, since the factors determining the non-polar scission of a hexa-arylethane would be expected to be entirely different from those involved in the interaction of a triarylmethyl cation and the formate anion. The present work also shows conclusively that no simple connexion exists between the basicity of a carbinol and its rate of reduction in formic acid solution. The reason for this is clear, since the reducibility of the carbinols, as measured by the formic acid method, bears no direct relation to the reactivity of the hydroxyl group, and in this connexion, it is to be noted that the reaction is fundamentally different from that involved when the reduction to triarylmethane is effected by zinc and acetic acid. Indeed, no simple relationship between basicity and reducibility is to be anticipated, since the former is a measure of the stability of the triarylmethyl salt towards hydrolysis, while the reducibility, as measured by the present method, is determined by the thermal stability of the salt.

EXPERIMENTAL.

Preparation of Materials.—The majority of the carbinols were prepared by known methods, and were purified by repeated crystallisation from the appropriate solvent, and finally from ligroin. The finely-powdered material was freed from solvent by standing over activated silica gel and concentrated sulphuric acid before use.

2-*Methoxy*-4′-*methyltriphenylcarbinol.*—The preparation of *p*-methylbenzophenone (Meyer, *Monatsh.*, 1907, **28**, 1223) was rendered more convenient by the following procedure. A solution of toluene (100 g.), benzoyl chloride (90 g.), and carbon disulphide (200 c.c.) was treated with aluminium chloride (90 g.) in small quantities, and the mixture heated under reflux for 4 hours. On hydrolysis in the usual manner, the ketone separated as a solid which is, however, appreciably soluble in carbon disulphide. After removal of the solvent, steam was passed through the residue to complete the hydrolysis of the dichloride. The ethereal solution of the ketone was washed with dilute alkali, dried over calcium chloride, and fractionated. The ketone was collected at 280° and solidified to a greasy solid, which hardened readily on trituration with light petroleum; m. p. 59°, yield 65 g.

o-Iodoanisole (58 g.), prepared by diazotising *o*-anisidine and treatment with potassium iodide, was converted into the Grignard derivative, and the filtered solution was treated with an ethereal solution of *p*-methylbenzophenone (42·7 g.). After being boiled under reflux for 2 hours, the mixture was decomposed with water and sulphuric acid. The precipitated *carbinol* was filtered off, combined with that obtained from the ethereal solution, and washed with sodium hydroxide. After recrystallisation from alcohol, it had m. p. 126°; yield 43 g. (Found : C, 82·5; H, 6·7. $C_{21}H_{20}O_2$ requires C, 82·8; H, 6·6%).

The halochromic salts are reddish-brown and the basicity of the carbinol, as determined experimentally, is 2·1. On the basis of Baeyer's " product rule " the calculated value of the basicity is 3·1, and it appears therefore that the presence of a methyl group in a methoxytriphenylcarbinol renders the rule inapplicable.

2 : 4 : 2'-*Trimethoxytriphenylcarbinol.*—Kauffmann and Panwitz (*loc. cit.*) do not give experimental details for the preparation of this compound, but the best method is as follows. Resorcinol dimethyl ether, obtained in 78% yield from resorcin and methyl sulphate (cf. Perkin, J., 1906, **89**, 1653), was readily converted into 2 : 4-dimethoxybenzophenone by the method of Kauffmann and Grombach (*Annalen*, 1905, **344**, 46); m. p. 83° after recrystallisation from ligroin.

The carbinol was prepared by treating a filtered solution of *o*-anisylmagnesium iodide (from 52 g. of iodoanisole) with a suspension of the ketone (45 g.) in ether (100 c.c.). The mixture was vigorously shaken during the addition of the ketone, and finally heated on the steam-bath for 2 hours. Hydrolysis was effected in the usual manner, and the carbinol was deposited on evaporating the ethereal solution. After being washed with dilute alkali, the material was recrystallised from alcohol and then from ligroin; m. p. 119—120°, yield 51 g. The carbinol forms a deep brownish-red sulphate and perchlorate.

2 : 4 : 2'-*Trimethoxytriphenylmethane.*—Kauffmann and Panwitz (*loc. cit.*) prepared this compound by heating a formic acid solution of the carbinol, but we employed the following methods. (*a*) The carbinol (2 g.) in glacial acetic acid (20 c.c.) was heated with zinc dust on a steam-bath for 2 hours. The almost colourless solution was filtered hot, and the deposited methane recrystallised from alcohol; m. p. 118°, yield 65%. (*b*) The carbinol (2 g.) was dissolved in boiling alcohol (100 c.c.) and treated with concentrated hydrochloric acid (10 c.c.). The dark red solution was heated on the steam-bath until it became pale yellow. The methane crystallised on concentrating the solution, and was purified as described above; yield 70%.

*Diphenyl-*p*-diphenylylcarbinol.*—This carbinol, first obtained by Schlenk and Weickel (*Annalen*, 1909, **368**, 295), was prepared by a modified procedure through the interaction of benzophenone and *p*-diphenylylmagnesium bromide (Bowden, J., 1931, 1111). The product obtained after hydrolysing the reaction mixture was dissolved in benzene and dried over calcium chloride. The residue obtained on removal of the solvent was triturated with light petroleum, and melted at 136° after two crystallisations from ligroin. The identity of the material was further established by its conversion into the corresponding methane (m. p. 112°), chloride (m. p. 146°), and peroxide (m. p. 180°). The carbinol dissolves readily in liquid sulphur dioxide to form a pink solution.

Diphenyl-α-naphthylcarbinol.—The method was based on that of Acree (*Ber.*, 1904, **37**, 2755), who isolated the carbinol by distillation. The latter process was avoided by recourse to the following procedure. The reaction product of phenylmagnesium bromide and α-naphthyl phenyl ketone was decomposed with ice and sulphuric acid, and the ethereal layer washed and dried in the usual way. The thick yellowish oil obtained on concentrating the solution was easily solidified by trituration with cold light petroleum. After recrystallisation from ligroin the carbinol melted at 135° (Found: C, 88·8; H, 6·0. Calc. for $C_{23}H_{18}O$: C, 89·1; H, 6·0%).

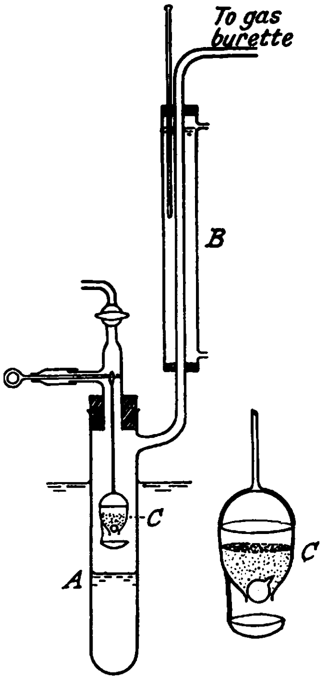
The sulphate, perchlorate, and phosphate are green, and the carbinol dissolves in liquid sulphur dioxide to form a yellowish-green solution.

Decomposition Temperatures of Formates.—The decomposition temperatures of the colourless formates were roughly estimated as follows. Methyl and benzyl formates were examined by passing the vapour (generated by dropping the liquid into a flask maintained at 10° above the b. p.) through a 50-cm. glass coil immersed in baths of potassium nitrate–sodium nitrate and sulphuric acid–potassium sulphate, respectively. The gaseous products were led into a trap maintained at 0°, and finally into lime water. The temperature at which carbon dioxide began to form was taken as the decomposition temperature. That of benzhydryl formate was ascertained by dropping the liquid into a heated flask while the vapours were carried into lime-water by a stream of nitrogen. These temperatures are merely indicative of the general order of stability, but the corresponding values for the coloured formates can be determined with much greater accuracy by the method described below.

At the ordinary temperature in the absence of light and moisture the highly coloured triarylmethyl formates are stable, and the carbinols can be completely recovered by the hydrolysis of formate solutions which have stood for several months in the dark. When, however, the solution is heated, the salt decomposes with evolution of carbon dioxide and formation of triarylmethane. In the case of formates decomposing below 60°, the temperature at which decomposition sets in was determined by slowly heating the solution and noting the volume of the solution–gas system at different temperatures. By plotting the expansion against the temperature, we obtain a curve with a point of inflexion corresponding to the temperature at which carbon dioxide begins to be evolved from the solution. Preliminary experiments revealed that the solubility of carbon dioxide in pure formic acid is negligible at the higher temperatures, and the point of inflexion therefore corresponds fairly closely to the actual temperature at which the formate breaks down. The point of inflexion was easily found by comparison with the curve obtained by heating formic acid alone in the same apparatus.

The apparatus consisted of a small, thin-walled flask (bulb capacity 5 c.c.) with a ground neck for attaching it to the recording unit, which comprised a mercury slug in a stout capillary tube (100 cm. long; 2 mm. bore) set accurately in a horizontal position by means of a spirit-level. The vessel, charged with a known weight of the dry, finely-powdered carbinol and 1·5 c.c. of pure formic acid, was immersed in a well-lagged bath provided with a motor-driven stirrer, and the temperature was raised at a rate of 1°/min. by means of a burner controlled by a needle valve. The position of the mercury slug was read on a millimetre scale, and sticking of the mercury was avoided by a mechanical tapper operating at a rate of 5 taps per second. With this standard procedure reproducible results were obtained without difficulty.

FIG. 2.



This method was not applicable to triarylmethyl formates with higher decomposition temperatures. The diphenyl-*p*-diphenylyl and diphenyl-α-naphthyl derivatives were examined by heating the formic acid solution in a stream of nitrogen and leading the issuing gases through a vertical condenser and trap into lime water. Since the decomposition temperatures of 3 : 3′ : 3″-trimethoxytriphenylmethyl and diphenyl-3-acenaphthylmethyl formates lie above the b. p. of the acid, rough estimates of the decomposition temperature were obtained by preparing the triarylmethyl formate in xylene, and heating the solution as described above. Some of the results have been given in the table on p. 875, and the others are in Table II.

Rate of Decomposition of Formates.—The formates were compared at 77° by measuring the rate of evolution of carbon dioxide. The method employed is superior to previous semi-quantitative methods since it furnishes information as to the course of the reaction in the early stages before the complicating influences arising from side reactions and the precipitation of triarylmethane become apparent. The apparatus (Fig. 2) consisted of a reaction tube *A* with a side tube communicating with a gas burette *via* a short vertical condenser *B*. The reaction tube was closed by a stopper carrying a device for precipitating a glass basket *C* containing the finely powdered carbinol into the formic acid. The basket was provided with a movable bottom consisting of a light, hollow glass sphere, which floated out of the basket on contact with the liquid. This ensured rapid dissolution of the carbinol and avoided the formation of " pockets " in the solution. A subsidiary tray was fused to the basket as an

TABLE II.

Decomposition temperatures of formates.

Formate.	Decompn. temp.	Formate.	Decompn. temp.
o-Methoxytriphenylmethyl	48°	2-Methyl-4′-methyltriphenylmethyl	38°
m-Methoxytriphenylmethyl	49	3 : 4 : 5-Trimethoxytriphenylmethyl	49
p-Methoxytriphenylmethyl	48	2 : 4 : 2′-Trimethoxytriphenylmethyl	44
2 : 2′-Dimethoxytriphenylmethyl	31	2 : 2′ : 3″-Trimethoxytriphenylmethyl	33
2 : 4′-Dimethoxytriphenylmethyl	42	3 : 3′ : 3″-Trimethoxytriphenylmethyl	120
3 : 4-Dimethoxytriphenylmethyl	47	Phenyl-*p*-anisylphenylmethyl	50
Diphenylpiperonylmethyl	48	Diphenyl-3-acenaphthylmethyl	120

additional precaution against the accidental spilling of the fine powder into the liquid before the initial adjustments were complete.

A known amount of pure formic acid was placed in the reaction tube which was immersed in a thermostat at 77° ± 0·01°, and after attainment of thermal equilibrium, the basket was precipitated into the liquid. The volume of carbon dioxide evolved was read at definite intervals in a water-jacketted gas burette charged with mercury. The volume was reduced to standard conditions, and a correction applied for the vapour pressure of formic acid. For brevity, the results have been summarised in the curves shown in Fig. 1 and the values recorded in Table I.

From the standpoint of the preparation of triarylmethanes, it is evident that the formic acid method may be advantageously employed if the carbinol contains an *o*-methoxyl group. If, however, the substituent is in the *m*-position, the yield of reduction product is relatively low, and other methods of reduction are therefore to be preferred. The presence of large aryl groups, such as diphenylyl, naphthyl, and acenaphthyl, also leads to a low yield of triarylmethane, and in these cases, the reduction of the carbinol by zinc and acetic acid or by alcoholic hydrochloric acid furnishes a higher yield and a purer product.

TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF. [*Received, May 4th,* 1940.]