138. *Tritylation and Detritylation of Active Methylene Compounds. Part II.*[1] *Tritylations by Triphenylmethyl Chloride.*

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The reaction of triphenylmethyl chloride with malonic acid, malonic ester, malonamide, malononitrile, and cyanoacetamide has been studied. The reaction is promoted by media which favour the formation of carbonium ions and is general acid-catalysed. The products of *C*-tritylation, $Ph_3CCl + CH_2XY \longrightarrow Ph_3C{\cdot}CHXY$, could be obtained in relatively mild conditions and satisfactory yields, generally without the incursion of side reactions.

IT was previously reported that *C*-tritylation of active methylene compounds by triphenylmethyl chloride or bromide can be carried out by the action of the halide on sodium derivatives of the methylene compounds[2] or on the corresponding ethoxymagnesium[3,4] or chloromagnesium compounds.[5] However, direct tritylation of an active methylene compound itself by triphenylmethyl chloride is not reported in the literature. The only similar case reported is the benzylation of ethyl acetoacetate by benzyl chloride in the presence of boron trifluoride.[6]

The present paper describes direct tritylation of active methylene compounds under mild and simple conditions, and in some cases in relatively good yields.

RESULTS

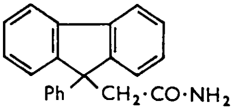
The results of the reactions carried out between triphenylmethyl chloride and some active methylene compounds, with various solvents and catalysts, are summarised in Table 1.

As with the reactions of triphenylmethanol[1] two products were obtained with malonamide (see Table 1). The first was the "normal" condensation product, *C*-tritylmalonamide (I);

$Ph_3C{\cdot}CHX{\cdot}CO{\cdot}NH_2$

(I) $X = CO{\cdot}NH_2$

(III) $X = CN$



(II)

the second was 9-phenylfluoren-9-ylacetamide (II), probably formed by attack of the acid-catalysed cyclisation product of the trityl ion[1,7] on malonamide and subsequent hydrolysis

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[1] Part I, preceding paper.

[2] Henderson, *J.*, 1887, **51**, 227; Hellerman, *J. Amer. Chem. Soc.*, 1927, **49**, 1735.

[3] Lund, Hansen, and Voigt, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, 1933, **12**, No. 9; Lund, *Ber.*, 1934, **67**, 936.

[4] Holmberg, *Acta Acad. Aboensis, Math. Phys.*, 1949, **16**, No. 6.

[5] Nesmeyanov, Lutsenko, and Tamanova, *Izvest. Acad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, 601; Curtin and Hurwitz, *J. Amer. Chem. Soc.*, 1952, **74**, 5381; Curtin and Kauer, *J. Org. Chem.*, 1960, **25**, 880.

[6] Breslow and Hauser, *J. Amer. Chem. Soc.*, 1940, **62**, 2388.

[7] Benkeser and Schroeder, *J. Org. Chem.*, 1958, **23**, 1058.

and decarboxylation, or in some cases possibly by transamidation followed by decarboxylation (see below).

From cyanoacetamide and triphenylmethyl chloride (see Exp. 22—24 of Table), the first product was the " normal " condensation product, α-cyano-βββ-triphenylpropionamide (III). The second was identical with the " normal " product obtained from triphenylmethyl chloride and malonamide, *i.e.*, α-tritylmalonamide (I), and was formed by partial hydrolysis of the cyano-group. Somewhat surprisingly, the third product proved to be βββ-triphenylpropionitrile. Here the cyano-group of the active methylene compound remained unattacked while the amido-group underwent hydrolysis and decarboxylation.

No *N*-trityl derivative was isolated when the active methylene compound was either malononitrile or cyanoacetamide.

Discussion

It was shown in the preceding paper that acid-catalysed *C*-tritylation of active methylene compounds probably occurs by attack of the carbonium ion on the methylene compound. A similar conclusion may be drawn from the present results. As the carbon–chlorine bond in triphenylmethyl chloride is more polar than the carbon–oxygen bond in the corresponding alcohol, the dissociation of the former to give carbonium ions takes place more easily and in relatively milder conditions. It is well known that triphenylmethyl chloride dissociates in inert solvents, *e.g.*, in nitromethane [8] and other nitroalkanes,[9]

Reactions of triphenylmethyl chloride [a] with active methylene compounds, CH_2XY.

Exp. no.	CH_2XY X	CH_2XY Y	g.	Solvent (ml.)	Catalyst (g.)	Hr.	Temp.	Products [b]	Yield (%)
1	CO_2Et	CO_2Et	50	None	None	12	B. p.	$Ph_3C{\cdot}CH(CO_2Et)_2$ [c]	22
2	CO_2H	CO_2H	2	None	None	1	150°	$Ph_3C{\cdot}CH_2{\cdot}CO_2H$	13
3	,,	,,	2	AcOH (40)	None	2·5	B. p.	,,	Trace
4	,,	,,	2	$MeNO_2$ (30)	None	2	B. p.	,,	54
5	,,	,,	2	$PhNO_2$ (30)	None	2	B. p.	,,	Trace
6 [d]	,,	,,	1	Toluene (100)	$HgCl_2$ (2 g.)	7	B. p.	,,	7·5
7	$CO{\cdot}NH_2$	$CO{\cdot}NH_2$	2	None	None	1	170—180°	I	7·5
8	,,	,,	2	$MeNO_2$ (50)	None	9	B. p.	II I	40 2·5
9	,,	,,	2	,,	$CH_2Cl{\cdot}CO_2H$ (0·5)	5	B. p.	II I	35 14
10	,,	,,	2	,,	$CHCl_2{\cdot}CO_2H$ (0·4)	5	B. p.	II	54
11	,,	,,	2	,,	,, (8)	5	B. p.	II	88
12	,,	,,	2	,,	$CCl_3{\cdot}CO_2H$ (0·5)	5	B. p.	II I	12 2
13	,,	,,	2	$PhNO_2$ (50)	None	2	150°	II I	24 10
14	,,	,,	2	AcOH (50)	None	5	B. p.	II I	61 5
15	,,	,,	2	Toluene (50)	$HgCl_2$ (4)	9	B. p.	II I	4 17
16	CN	CN	1	None	None	1	200°	$Ph_3C{\cdot}CH(CN)_2$	72
17	,,	,,	1	$MeNO_2$ (50)	None	13	B. p.	,,	58
18	,,	,,	1	,,	$CH_2Cl{\cdot}CO_2H$ (0·5)	5	B. p.	,,	27
19	,,	,,	1	,,	$CHCl_2{\cdot}CO_2H$ (8)	5	B. p.	,,	68
20	,,	,,	1	AcOH (50)	None	5	B. p.	,,	75
21	,,	,,	1	Toluene (50)	$HgCl_2$ (4)	8	B. p.	,,	45
22	CN	$CO{\cdot}NH_2$	1	$MeNO_2$ (50)	$CHCl_2{\cdot}CO_2H$ (8)	6	B. p.	III	10
23	,,	,,	1	AcOH (50)	None	6	B. p.	I $Ph_3C{\cdot}CH_2{\cdot}CN$	28 7
24	,,	,,	1	Toluene (50)	$HgCl_2$ (4)	6	B. p.	III	4

[a] Two grams of triphenylmethyl chloride were used in each experiment. [b] Methods of identification, analyses, and properties of the products were given in Part I.[1] [c] Cryst. from dioxan; m. p. 132° (lit.,[3] 133°). [d] One gram of triphenylmethyl chloride was used.

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[8] Pocker, *J.*, 1958, 240.

[9] Bentley and Evans, *J.*, 1952, 3468.

nitrobenzene,[10] and chlorinated ethanes.[11] This ionisation is promoted by the presence of Lewis acids [12,13] in solvents of low dielectric constants.

Positive results for the condensation were obtained in solvents in which the chloride is known to undergo ionisation to the carbonium ion, *i.e.*, in nitromethane, nitrobenzene, or toluene in the presence of mercuric chloride as the Lewis acid. On the other hand, in solvents in which the chloride does not dissociate appreciably (as shown by the lack of colour of the solutions), no condensation was observed, *i.e.*, in acetonitrile, toluene, or ethylene carbonate. No condensation could be detected in the presence of triethylamine, even in ionising solvents. This is probably due to the binding of the carbonium ion by the amine, with the possible formation of a quaternary salt.[14]

Much milder conditions are required for condensation of active methylene compounds with triphenylmethyl chloride than with the alcohol, so that the extent of side reactions and the amount of by-products are reduced considerably. This is probably the reason why a condensation product was obtained from diethyl malonate and triphenylmethyl chloride, while from the corresponding alcohol only " abnormal " products were obtained, *i.e.*, ethyl trityl ether by transethoxylation and triphenylmethane by hydride transfer.[1]

An interesting phenomenon was observed in the effect of the addition of mono-, di-, and tri-chloroacetic acid to the reaction mixtures in nitromethane. The addition of Lewis acids to solutions of triphenylmethyl chloride increases its ionisation to free (or ion-paired) carbonium ions to an extent parallel to the increasing acidities of the added acids.[13] Hence, in our case the amount of carbonium ions available and also the yields of reaction in nitromethane should increase in the order of the acidities of the substituted acetic acids added, *i.e.*, $CCl_3{\cdot}CO_2H > CHCl_2{\cdot}CO_2H > CH_2Cl{\cdot}CO_2H$. However, Table 1 (*e.g.*, experiments 9—12) shows that there is a marked decrease in the yields when the catalyst is changed from dichloro- to trichloro-acetic acid. The explanation of this discrepancy probably lies in the effect of the added acid on the active methylene compounds. Trichloroacetic acid is probably strong enough to protonate considerably the basic functions of the methylene compounds. The positive charge on the ions so formed inhibits the electrophilic attack by the similarly charged carbonium ion, and thus the yield of the reaction decreases.

[It was pointed out by a Referee, that in the presence of organic acids (in experiments 9, 10, 11, 12, and 14) the formation of a substituted acetamide could be explained by transamidation followed by decarboxylation, *i.e.*, $Ar{\cdot}CH(CO{\cdot}NH_2)_2 + R{\cdot}CO_2H \longrightarrow Ar{\cdot}CH(CO_2H){\cdot}CO{\cdot}NH_2 + R{\cdot}CO{\cdot}NH_2 \longrightarrow CO_2 + Ar{\cdot}CH_2{\cdot}CO{\cdot}NH_2$. This explanation cannot hold for the reactions in which no organic acid is present (experiments 8, 13, 15, and 24). If we take into account the difficulties of obtaining absolutely dry organic solvents and the comparatively small amounts of water required for hydrolysis, possibly either or both of these reaction sequences (*i.e.*, transamidation and decarboxylation, or hydrolysis and decarboxylation) may be responsible for the occurrence of such acetamides. We found that when the same solvent batch was used in control experiments, the chloride or the alcohol, or a mixture of the two, was recovered fortuitously (see Experimental, " Unsuccessful Experiments "). With malononitrile as the active methylene compound, only the normal product $Ph_3C{\cdot}CH(CN)_2$ was isolated (experiments 16—21), with recovery of some of the starting material or the corresponding alcohol.]

Although no quantitative conclusions can be drawn from yields as to relative reactivities, the results show that active methylene compounds with a high enol content,

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[10] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1954, **50**, 568; Price and Lichtin, *Tetrahedron Letters*, 1960, No. 18, 10.

[11] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1956, **52**, 332.

[12] Fairbrother, *J.*, 1945, 503; Fairbrother and Wright, *J.*, 1949, 1058; Bayles, Evans, and Jones, *J.*, 1955, 206; 1957, 1020; Bayles, Cotter, and Evans, *J.*, 1955, 3104.

[13] Cotter and Evans, *J.*, 1959, 2988.

[14] Hughes, Ingold, Mok, Patai, and Pocker, *J.*, 1957, 1220.

the enol-forms of which are stabilised by intramolecular hydrogen bonding (*e.g.*, acetylacetone and ethyl acetoacetate), do not react. Similar results were obtained in reaction of the same methylene compounds with triphenylmethanol.

EXPERIMENTAL

Materials.—Triphenylmethyl chloride,[15] malonamide,[16] malononitrile[17] and cyanoacetamide,[18] were prepared according to known procedures. Other reactants, solvents, and catalysts were commercial products, carefully dried before the reaction.

Synthetic Methods.—From the reaction mixtures prepared according to the conditions listed in Table 1, the products were usually separated by removal of most of the solvent *in vacuo*, washing of the residue with water (if this contained an excess of water-soluble reactants, solvents or catalysts), and then filtration and crystallisation of the solid. When the product was acidic (*e.g.*, βββ-triphenylpropionic acid), it was separated by extracting the reaction mixture with dilute aqueous alkali, followed by precipitation with dilute acid.

Most of the products were identified as described in the preceding paper.[1] Diethyl tritylmalonate was identified by a mixed m. p. with an authentic sample[3] and by its ethoxyl analysis (Found: OEt, 21·0. Calc. for $C_{26}H_{26}O_4$: OEt, 22·5%) and by alkaline hydrolysis to βββ-triphenylpropionic acid.

Unsuccessful Experiments.—The chloride, or the corresponding alcohol, was recovered quantitatively or almost quantitatively, from the following experiments: Refluxing of the chloride with diethyl malonate in acetic acid; in nitromethane alone or in the presence of mono-, di-, or tri-chloroacetic acid; in toluene in the presence of mercuric chloride; and with acetylacetone or ethyl acetoacetate in various solvents, with or without catalysts. The chloride did not react with malonic acid in acetonitrile, ethylene carbonate, or toluene, or with cyanoacetamide in nitromethane alone or in the presence of mono- or tri-chloroacetic acid. No reaction took place in the presence of triethylamine between triphenylmethyl chloride and any of the active methylene compounds tried.

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[15] Bachmann, *Org. Synth.*, 1943, **23**, 100.
[16] Röhrs and Lang, *J. prakt. Chem.*, 1941, **158**, 112.
[17] Corson, Scott, and Vose, *Org. Synth.*, 1943, Coll. Vol. II, 379.
[18] Corson, Scott, and Vose, *Org. Synth.*, 1941, Coll. Vol. I, 179.