

137. *Tritylation and Detritylation of Active Methylene Compounds.*
Part I. Tritylation by Various Triarylmethanols.

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The reactions of various triarylmethanols with malonic acid, ethyl malonate, ethyl acetoacetate, malonamide, malononitrile, and cyanoacetamide in different media have been studied. The reaction $\text{Ar}_3\text{C}\cdot\text{OH} + \text{CH}_2\text{XY} \longrightarrow \text{Ar}_3\text{C}\cdot\text{CHXY}$ is catalysed by acid and inhibited by base. Various by-products were obtained and identified, as well as the normal products of tritylation.

MANY reactions of active methylene compounds take place through carbanions and are favoured by basic catalysts. On the other hand, the reactions of triarylmethanols, which show a marked tendency to form carbonium ions, are promoted by acid. The question

therefore arises whether in the tritylation of active methylene compounds the formation of carbanions or of carbonium ions is the governing factor.

Tritylation of active methylene compounds was accomplished as early as 1887 by Henderson¹ and repeated by Hellerman,² who used the usual methods of alkylation of active methylene compounds, involving, *e.g.*, the reaction of triphenylmethyl bromide and the sodium salt of the methylene compound, which gave yields of only 5–10%. Higher yields of tritylmalonates were obtained by the action of triarylmethyl chlorides on ethoxymagnesium malonates.^{3,4} Direct tritylation of active methylene compounds by triphenylmethanol was reported by Fosse:⁵ he heated the alcohol with the methylene compound (malonic and cyanoacetic acid, ethyl and methyl malonate). Malonic acid has also been tritylated in acetic acid in the presence of acetic anhydride.⁶

A single case of triarylmethylation of a methylene compound, which is activated only by one strong electron-attracting group was reported by Burton and Cheeseman,⁷ who obtained 1,1,1-tri-*p*-methoxyphenyl-2-nitroethane by reaction of the triarylmethanol with nitromethane in strong acidic media, though triphenylmethanol failed to react.

The present work was carried out in order to determine the optimal conditions and the scope of the reaction, for various triarylmethanols and active methylene compounds. The results of the representative experiments are given in Table 1.

Discussion.—The substances were found to react in conditions which favour the formation of the carbonium ions, Ar_3C^+ , from the alcohols. The reactions were carried out in acidic media, either by adding a strong acid to the reaction mixture, or, when the active methylene compound was a fairly strong acid (malonic or cyanoacetic), by using an excess of it. Attempts to carry out the reaction in neutral or in basic media failed. We did not succeed in condensing triphenylmethanol with malonic esters without a catalyst, which, according to Fosse^{5c} should give the desired products (in unspecified yields).

The yields and the constitutions of the products were found to be strongly dependent on the nature of the methylene compounds and of the alcohols, as well as on the solvents and catalysts used. Both the methylene compound and the alcohol may undergo side reactions. For instance, methylene compounds which are activated by alkoxy-carbonyl groups (*e.g.*, malonic and acetoacetic esters) undergo transfer of the alkoxy-group from the ester to the alcohol, affording an alkyl triarylmethyl ether. Cyano-groups in strongly acidic media may lead to *N*-trityl-amides; or cyano-groups, as well as amides, may undergo hydrolysis to afford the carboxylic acids; this hydrolysis may occur before or after the condensation and the carboxyl groups formed in positions adjacent to strong electron-attracting groups may undergo decarboxylation. Methylene compounds which are activated by carboxyl groups may also undergo decarboxylation before or after the condensation: in condensations with malonic acid, the product is almost exclusively the propionic acid, and only in one case could tritylmalonic acid be isolated (when the reaction temperature was kept relatively low and the reaction time was relatively short, exp. 11, Table 1; and after longer reaction times only the propionic acid was obtained). Tritylmalonic acid was decarboxylated much faster than malonic acid itself in comparable conditions—the first-order rate coefficients at 110° for $7 \times 10^{-4}\text{M}$ - to 0.1M-solutions in glacial acetic acid were $2.5 \times 10^{-5} \text{ sec.}^{-1}$ for malonic acid and $7.5 \times 10^{-4} \text{ sec.}^{-1}$ for tritylmalonic acid.

The tendency of the alcohols to undergo the reaction depends on the nature of the substituents on the aryl groups. Nitro-substituted triarylmethanols have little tendency

¹ Henderson, *J.*, 1887, **51**, 227.

² 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 Fosse, (a) *Bull. Soc. chim. France*, 1906, **35**, 1016; *Compt. rend.*, 1907, **145**, (b) 196, (c) 1290.

⁶ Moureu, Dufraisse, and Dean, *Bull. Soc. chim. France*, 1928, **43**, 1367.

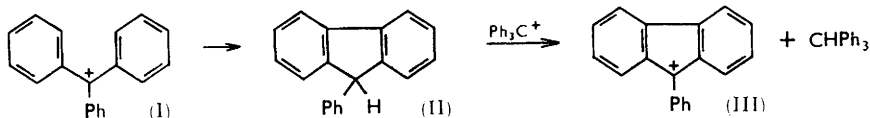
⁷ Burton and Cheeseman, *J.*, 1953, 836.

TABLE I.
 Reactions of various triarylmethanols (ROH) with active methylene compounds (CH₂XY).

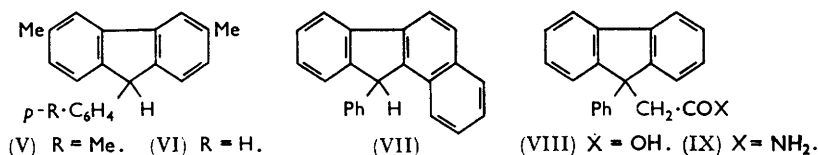
Exp. no.	CH ₂ XY			ROH		Catalyst* (ml.)	Solvent (ml.)	Hr.	Temp.	Product*	Yield (%)	M. p.	Solvent for cryst.	Required (%)			Found (%)		
	X	Y	R*	g.	g.									C	H	N	C	H	N
1	CO ₂ Et	CO ₂ Et	Ph ₂ C	10	5	None	None	2	B. p.	ROEt	84	83 ^a	EtOH	72.5	5.5	71.8	5.9		
2	"	"	"	10	5	H ₂ SO ₄ (0.1)	None	45	40°	RH	80	94 ^b	MeOH	84.0	5.3	84.4	5.5		
3	"	"	"	5	5	H ₂ SO ₄ (5)	AcOH (30)	2-5	B. p.	RH	75	94	MeOH	90.6	6.4	89.9	6.3		
4	"	"	"	20	5	None	None	3	170	ROEt	87	113 ^c	CHCl ₃	83.5	6.3	83.5	6.2		
5	CO ₂ Et	CO ₂ Me	Ph ₂ C	5	5	None	None	2	B. p.	ROEt	92	83	EtOH	81.0	5.5	80.9	5.5		
6	CO ₂ H	CO ₂ H	"	8	2	None	None	0-6	170	R-CH ₂ -CO ₂ H	92	182 ^d	EtOH	76.7	5.8	76.4	5.6		
7	"	"	"	3	5	Ac ₂ O (5)	AcOH (45)	2	B. p.	"	80	182	EtOH	85.7	5.2	85.7	5.2		
8	"	"	"	3	5	Ac ₂ O (5)	AcOH (50)	2	B. p.	"	45	182	EtOH	82.9	5.8	83.0	5.9		
9	"	"	"	5	5	MeNO ₂ (50)	MeNO ₂ (50)	4	B. p.	"	1.4	182	EtOH	82.9	5.8	83.0	5.9		
10	"	"	"	5	5	(C ₂ H ₅) ₂ CO	(C ₂ H ₅) ₂ CO	9	B. p.	"	1.4	182	EtOH	82.9	5.8	83.0	5.9		
11	"	"	"	15	3	None	(40 g.)	18	98	R-CH(CO ₂ H) ₂	21	164 [†]	EtOH	72.5	5.5	71.8	5.9		
12	"	"	"	15	3	None	AcOH (50)	10	110	R-CH ₂ -CO ₂ H	69	182	EtOH	84.0	5.3	84.4	5.5		
13	"	"	"	6	5	None	"	10	110	VIII	17	230-231	AcOH or C ₆ H ₆	90.6	6.4	89.9	6.3		
14	"	"	"	10	3	None	H ₂ SO ₄ (1)	0-33	170-180	{R ₂ O {R-CH ₂ -CO ₂ H	97	135-175	Ligroin	83.5	6.3	83.5	6.2		
15	"	"	"	10	2	None	None	4	B. p.	{R-CH ₂ -CO ₂ H	88	135-175	Ligroin	83.5	6.3	83.5	6.2		
16	"	"	"	8	2	None	AcOH (150)	3	105	{R-CH ₂ -CO ₂ H	6	197	EtOH	84.0	5.3	84.4	5.5		
17	"	"	"	6	2	None	Ac ₂ O (10)	3	105	{R-CH ₂ -CO ₂ H	34	197	EtOH	84.0	5.3	84.4	5.5		
18	"	"	"	10	2	None	None	0-33	160-180	VI	99	212	Ligroin	93.3	6.7	92.9	7.1		
19	"	"	"	10	2	None	AcOH (150)	4	B. p.	VI	98	212	Ligroin	83.6	6.7	83.5	6.6		
20	"	"	"	10	5	None	Ac ₂ O (10)	3-5	105	{R-CH ₂ -CO ₂ H	30	212	Ligroin	83.6	6.7	83.5	6.6		
21	"	"	"	10	3	None	None	0-33	160-170	V	58	178	EtOH	92.9	7.1	92.0	7.6		
22	"	"	"	4	2	None	None	1	B. p.	V	100	220-230	Ligroin	92.9	7.1	92.0	7.6		
23	"	"	"	5	2	None	None	3	B. p.	V	100	220-230	Ligroin	92.9	7.1	92.0	7.6		
24	"	"	"	10	3	None	None	8	B. p.	{VI {R-CH ₂ -CO ₂ H	90	200 ^g	AcOH	94.5	5.5	95.0	5.4		
25	"	"	"	15	3	None	None	1	150	{G {R-CH ₂ -CO ₂ H	90	206 [†]	EtOH	79.5	6.0	79.6	6.3		
26	"	"	"	5	1	None	None	0-33	200	X	93	234 ^g	(Crude)	84.3	5.7	84.4	5.8		
27	"	"	"	10	3	None	Ac ₂ O (10)	8	98	{X {R-CH ₂ -CO ₂ H	85	206 [†]	EtOH	76.7	5.8	76.3	6.1		
28	"	"	"	5	2	None	2.75 AcOH (100)	4	160-170	{X {R-CH ₂ -CO ₂ H	98	230-231	AcOH or Ligroin	84.3	5.7	84.4	5.8		
29	"	"	"	5	2	None	None	4	B. p.	{X {R-CH ₂ -CO ₂ H	35	234 ^g	EtOH	84.3	5.7	84.4	5.8		
30	"	"	"	30	2	None	AcOH (50)	1	B. p.	Ph ₂ C:CH ₂	88	206 [†]	EtOH	84.3	5.7	84.4	5.8		
31	CO ₂ NH ₂	CO ₂ NH ₂	Ph ₂ C	5	5	None	None	0-75	160-170	IX	85	206 [†]	EtOH	84.3	5.7	84.4	5.8		
32	"	"	"	5	2	None	None	2	200	IX	38	206 [†]	EtOH	84.3	5.7	84.4	5.8		
33	"	"	"	8	4	None	H ₂ SO ₄ (8)	120	Room	{R-CH(CO ₂ NH ₂) ₂	85	306-307	AcOH	91.6	5.2	90.6	5.8		
34	"	"	"	2	4	None	H (50 g.)	120	Room	{R-CH(CO ₂ NH ₂) ₂	1	306-307	AcOH	91.6	5.2	90.6	5.8		
35	CO ₂ NH ₂	CN	"	1-5	2	None	H ₂ SO ₄ (10-50)	24	Room	{R-CH(CO ₂ NH ₂) ₂	52	328-331	CCl ₄ -ligroin	81.0	5.5	80.9	5.5		
36	CO ₂ NH ₂	CN	"	2-1	Ph ₂ C	None	I (5 g.)	30	B. p.	{R-CH(CO ₂ NH ₂) ₂	40	239-241	Aq. COMe ₂	76.7	5.8	76.4	5.6		
37	"	"	"	6-5	"	None	None	2	180	K	25	278-279	EtOH	81.0	5.5	80.9	5.5		
38	CN	CN	"	6-5	AcOH (35)	None	H ₂ SO ₄ (1)	3	98	{XIV	10	206-207	Dioxan	85.7	5.2	85.7	5.2		
39	"	"	"	8	None	None	None	0-33	180-220	{R-CH(CN) ₂	63	278	EtOH	82.9	5.8	83.0	5.9		
40	"	"	"	10	AcOH (30)	None	H ₂ SO ₄ (2)	4	98	{XIV	8	302	AcOH	82.9	5.8	83.0	5.9		

^a Nixon and Branch (*J. Amer. Chem. Soc.*, 1936, **58**, 492) give 83%. ^b Schmidlin and Garcia-Banus (*Ber.*, 1912, **45**, 3186) give 92%. ^c Kliegl (*Ber.*, 1902, **35**, 289) gives 113%. ^d Lit., ^e 179-180°. ^f Lit., ^g 155-166 or 141-142° (Witt and Finnelly, *J. Org. Chem.*, 1961, **26**, 2176); sodium salt (from water), m. p. 283°. ^h Bergmann and Wolf (*Ber.*, 1930, **63**, 1178) give 195°. ⁱ Lit., ^j 236-237°. ^k Baeyer and Villiger (*Ber.*, 1904, **37**, 3198) give 192°. ^l B. p. 148-150°/25 mm. Schlenk and Bergmann (*Annalen*, 1928, **465**, 26) give b. p. 135-136°/13 mm. ^m Identical with the unknown product of Kliegl (*Ber.*, 1905, **38**, 291; 1910, **43**, 2490) and of Kovache [*Ann. Chim. (France)*, 1918, **10**, 206], m. p. 320-360°. ⁿ Comberg (*J. Amer. Chem. Soc.*, 1913, **35**, 206) gives 232-233°. ^o A, 9-Phenyl-9-fluorenyl. B, *p*-C₆H₄Me-CPH₂. C, *p*-C₆H₄Me-CPH₂. D, *p*-MeO-C₆H₄-CPH₂. E, 1-C₁₀H₇-CPH₂. F, *o*-NH₂-C₆H₄-CPH₂. G, *o*-NHAc-C₆H₄-C(OH)Ph₂. H, *p*-C₆H₄Me-CPH₂. I, CHCl₃-CO₂H. K, NC-CHR-CO₂NH₂. L, (*p*-C₆H₄Me)₂CPH₂. With decomp.

to give carbonium ions and fail to react. On the other hand, carbonium ions formed from more active alcohols, *i.e.*, those containing electron-donating substituents, may undergo intramolecular cyclisations to form the corresponding fluorene derivatives (cf. Benkeser and Schroeder⁸). The reaction may stop at compound (II) or continue to form



the ion (III), which itself may condense with the active methylene compounds. When the aryl groups in the carbonium ion contain substituents which promote electrophilic substitution, such as methyl groups, the reaction generally stops at (II), *e.g.*, tri-*p*-tolyl- and phenyldi-*p*-tolyl-methanol give in acidic media 3,6-dimethyl-9-*p*-tolyl- (V) and -9-phenyl-fluorene (VI), respectively. Analogously, 1-naphthyldiphenylmethanol gives 9-phenyl-1,2-benzofluorene (VII).



In the reaction of triphenylmethanol and malonic acid, addition of small amounts of concentrated sulphuric acid causes the formation of 9-phenylfluorene-9-ylacetic acid (VIII), *i.e.*, the reaction probably involves condensation of malonic acid with the carbonium ion (III). Similarly, with malonamide we obtained tritylmalonamide and 9-phenylfluorene-9-ylacetamide (IX). These compounds (VIII) and (IX) were also obtained by condensation of 9-phenylfluorene-9-ol with malonic acid and malonamide, respectively.

Attempts to obtain condensation products by the reaction of active methylene compounds with 1,1-diphenylethanol and 9-methylfluorene-9-ol failed, only dehydration products of the alcohols (ethylenes or their polymers) being isolated.

Structure Determinations and Some Secondary Reactions of the Products.—Some of the products were known and could be identified by melting points and mixed melting points. In other cases, chemical and physical methods were used for their identification.

Tritylmalonic acid underwent quantitative thermal decomposition to the known $\beta\beta$ -triphenylpropionic acid.

The acid formed from triphenylmethanol and malonic acid in the presence of sulphuric acid was proved to be the fluorene derivative (VIII), since the same substance was obtained from 9-phenylfluorene-9-ol and malonic acid.

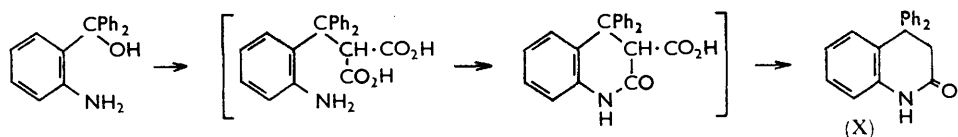
The neutral substance obtained from diphenyl-*p*-tolylmethanol and malonic acid has a different melting range (135—175°) from that reported⁹ for the bis(diphenyl-*p*-tolylmethyl) ether (205—207°) although its elementary analysis and molecular weight [Found (Rast), 525—615. Calc. 530] were correct. However, it was reported⁹ that this ether tends to form low-melting mixtures with traces of contaminants. An impure ether with m. p. 180—185° was isolated by Halford,⁹ who could not purify it completely by crystallisation. Hence, we assume our substance to be this ether.

The two fluorene derivatives (V and VI) were also formed from the alcohols alone in acidic media. The latter might have been the 3,4'-dimethyl compound; however, it has an infrared absorption band at 700 cm.⁻¹, specific for monosubstituted benzene rings, wherefore we decided in favour of structure (VI) since the alternative contains only di- and tri-substituted benzene rings.

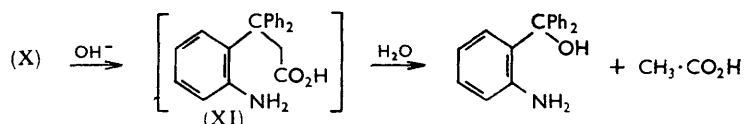
⁸ Benkeser and Schroeder, *J. Org. Chem.*, 1958, **23**, 1058.

⁹ Halford, *J. Amer. Chem. Soc.*, 1929, **51**, 2159.

The fluorene derivative (V) was identical with the product obtained by Schmidlin and Hodgson¹⁰ by heating tri-*p*-tolylmethyl chloride at 250°. We obtained it also, in quantitative yield, by refluxing the alcohol in acetic acid or by the action of chloroacetic acid in acetic acid on the alcohol at room temperature.

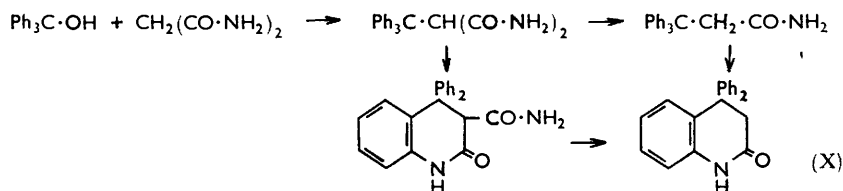


The product obtained from *o*-aminotriphenylmethanol with malonic acid gave the correct analysis for the lactam structure (X) and had an infrared peak characteristic for δ -lactams at 1650 cm^{-1} . The reaction sequence is probably as shown. Alkaline hydrolysis did not yield the corresponding amino-acid, but only *o*-aminotriphenylmethanol probably as indicated by way of (XI).

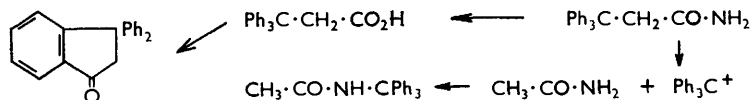


Two products were obtained from triphenylmethanol and malonamide. One was identified as the normal condensation product, $\text{Ph}_3\text{C}\cdot\text{CH}(\text{CO}\cdot\text{NH}_2)_2$. Alkaline hydrolysis converted it into tritylmalonic acid, and it was dehydrated by phosphorus oxychloride to the dinitrile. Concentrated sulphuric acid hydrolysed the central carbon-carbon bond of the diamide, forming triphenylmethyl ions which gave triphenylmethanol on dilution with water or ethers on dilution with alcohols. Attempts to obtain the diamide by ammonolysis of the known diethyl or dimethyl ester failed. The difficulty of ammonolysis of sterically hindered malonic esters is described in the literature.¹¹

Two structures could be suggested for the second, high-melting product (Exp. nos. 24 and 26, Table 1). One is the δ -lactam (X). Attempts to obtain this by heating $\beta\beta$ -triphenylpropionamide with or without traces of strong acid gave, instead, the two



known products indicated by the annexed reaction scheme. As the lactam (X) was synthesised independently from *o*-aminotriphenylmethanol and malonic acid, it was assumed that the high-melting substance is the product (IX) of primary cyclisation to the ion (III) according to Benkeser and Schroeder's scheme⁸ and subsequent condensation with malonamide. Final proof for this structure was obtained by synthesising compound (IX) independently by the action of 9-phenylfluoren-9-ol on malonamide.

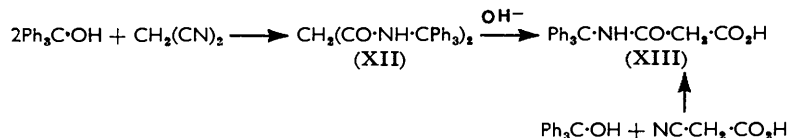


Four substances were obtained on reaction of triphenylmethanol and malononitrile, two of them in strongly acidic media, and two by fusing the reactants alone. Of the

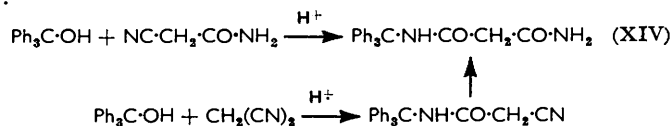
¹⁰ Schmidlin and Hodgson, *Ber.*, 1908, **41**, 436.

¹¹ Fischer and Dilthey, *Ber.*, 1902, **35**, 844; Dox and Yoder, *J. Amer. Chem. Soc.*, 1922, **44**, 1564.

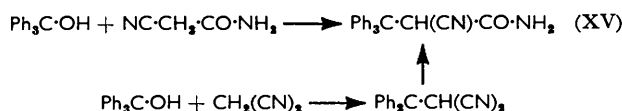
former pair one was the adduct (XII) of two molecules of alcohol to the two cyano-groups and, by alkaline cleavage of one amido-group, formed the amic acid (XIII), a known substance which was also formed by fusion of cyanoacetic acid with triphenylmethanol:¹²



The second was identical with the substance (XIV) obtained from triphenylmethanol and cyanoacetamide:



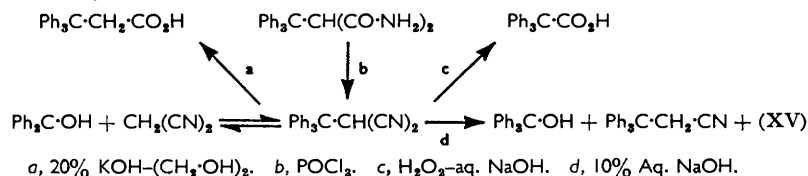
Of the second pair one was identical with that (XV) formed by fusion of the alcohol with cyanoacetamide and is the normal condensation product of the latter reaction:



Alkaline hydrolysis of the amide (XV) gave, somewhat surprisingly, the same C-substituted malonamic acid as was obtained by alkaline hydrolysis of α -tritylmalonamide:



The second member of the second pair had the correct analysis for the normal condensation product, $\text{Ph}_3\text{C}\cdot\text{CH}(\text{CN})_2$. But, as its infrared absorption spectrum did not show clearly the specific peak for cyano-groups (2250 or $2280 \pm 10 \text{ cm.}^{-1}$) we proved its structure by a series of reactions, which are summarised in the annexed scheme that affords sufficient proof of the identity.



EXPERIMENTAL

Materials.—The following compounds were prepared and purified by the methods given in the references: triphenylmethanol;¹³ diphenyl-*p*-tolylmethanol;^{14,15} phenyldi-*p*-tolylmethanol;^{15,16} tri-*p*-tolylmethanol;¹⁷ *p*-methoxytriphenylmethanol;¹⁸ 1-naphthyldiphenylmethanol;¹⁹ tri-(*p*-nitrophenyl)methanol;²⁰ 9-phenylfluoren-9-ol;²¹ 1,1-diphenylethanol;²²

¹² Fosse, *Bull. Soc. chim. France*, 1931, **49**, 159.
¹³ Bachmann and Hetzner, *Org. Synth.*, 1943, **23**, 98; Vogel, "Practical Organic Chemistry," Wiley & Sons Inc., New York, 1959, p. 816.

¹⁴ Bistrzycki and Gyr, *Ber.*, 1904, **37**, 663; Hatt, *J.*, 1929, 1630.

¹⁵ Patai and Dayagi, *J.*, 1958, 3058.

¹⁶ Kliegl, *Ber.*, 1905, **38**, 86; Kovache, *Ann. Chim. (France)*, 1918, **10**, 198.

¹⁷ Tousley and Gomberg, *J. Amer. Chem. Soc.*, 1901, **26**, 1517.

¹⁸ Baeyer and Villiger, *Ber.*, 1902, **35**, 3027.

¹⁹ Acree, *Ber.*, 1904, **37**, 627, 2756.

²⁰ Fischer and Fischer, *Annalen*, 1878, **194**, 256.

²¹ Ullmann and Wursterberger, *Ber.*, 1904, **37**, 73.

²² Klages, *Ber.*, 1902, **35**, 2646.

9-methylfluoren-9-ol;²³ malonamide;²⁴ malononitrile;²⁵ and cyanoacetamide.²⁶ On attempted preparation of *o*-aminotriphenylmethanol by the reported procedure,²⁷ only the *N*-acetyl derivative, m. p. 206° (from ethanol) (lit., 192°) (Found: C, 79.5; H, 6.0; N, 4.4. Calc. for C₂₁H₁₉NO₂: C, 79.6; H, 6.3; N, 4.2%), was obtained. The amino-alcohol was obtained by hydrolysis (20% alcoholic potassium hydroxide) of the acetyl derivative and, crystallised from ligroin, had m. p. 123.5° (lit.,²⁷ 121.5°) (Found: C, 82.3; H, 6.1; N, 4.8. Calc. for C₁₉H₁₇NO: C, 82.9; H, 6.2; N, 5.1%).

Synthetic Methods and Products.—The reaction mixtures, obtained in the conditions listed in Table 1, were usually poured into, or washed with, water to free the products from the excess of reactants or solvents, and then crystallised from appropriate solvents. Acidic products, including tritylmalononitrile, were purified before crystallisation by precipitation by dilute acid from solution in dilute alkali. Identification of known products was by mixed m. p. determinations and comparison of infrared and ultraviolet absorption spectra with those obtained by the methods described in the literature.

Hydrolyses.— α -Tritylmalonamide in a 5% solution of potassium hydroxide in 85% ethanol gave α -tritylmalonamic acid, m. p. 178° (decomp.) (from methanol) (Found: C, 76.6; H, 5.4; N, 4.3. C₂₂H₁₉NO₃ requires C, 76.5; H, 5.5; N, 4.1%).

Tritylmalononitrile in 10% aqueous sodium hydroxide gave triphenylmethanol and $\beta\beta\beta$ -triphenylpropionitrile, m. p. 142° (from ethanol) (lit.,¹² 140°) (Found: C, 88.8; H, 5.7; N, 4.7. Calc. for C₂₁H₁₇N: C, 89.05; H, 6.0; N, 4.9%), and α -cyano- $\beta\beta\beta$ -triphenylpropionamide.

Hydrolysis of the dinitrile in a 20% solution of potassium hydroxide in ethylene glycol gave $\beta\beta\beta$ -triphenylpropionic acid.

α -Cyano- $\beta\beta\beta$ -triphenylpropionamide in 10% aqueous potassium hydroxide gave α -tritylmalonamic acid.

NN'-Ditritylmalonamide (XII) in 10% aqueous potassium hydroxide gave *N*-tritylmalonamic acid, m. p. 173° (decomp.) (from chloroform) [lit.,¹² 175° (decomp.)].

1,2,3,4-Tetrahydro-2-oxo-4,4-diphenylquinoline (X) in 10% alcoholic potassium hydroxide gave *o*-aminotriphenylmethanol.

Other Products of Reactions.—The following reactions were carried out according to the usual methods: Oxidation of α -tritylmalononitrile by 5% hydrogen peroxide in 5% aqueous sodium hydroxide gave triphenylacetic acid, m. p. 275° (from acetic acid) (lit.,²⁸ 267°) (Found: C, 83.2; H, 5.7. Calc. for C₂₀H₁₆O₂: C, 83.3; H, 5.6%); dehydration of α -tritylmalonamide by phosphorus oxychloride in benzene gave the corresponding dinitrile; α -tritylmalonamic acid with diazomethane in ether gave the *methyl ester*, m. p. 178° (from methanol) (Found: C, 77.2; H, 6.05; N, 3.6. C₂₃H₂₁NO₃ requires C, 76.9; H, 5.85; N, 3.9%); decomposition of 1 g. of $\beta\beta\beta$ -triphenylpropionamide by heating it with 0.2 ml. of sulphuric acid at 200° gave *N*-tritylacetamide (10%), m. p. 218–219° (from ethanol) (lit.,¹² 211°) (Found: C, 84.2; H, 6.7; N, 4.6. Calc. for C₂₁H₁₉NO: C, 83.8; H, 6.3; N, 4.65%), and 3,3-diphenylindan-1-one (41%), m. p. 133° (from ethanol) (lit.,²⁹ 131–132°) (Found: C, 89.1; H, 5.6. Calc. for C₂₁H₁₆O: C, 88.7; H, 5.6%).

Unsuccessful Experiments.—The alcohols were recovered quantitatively or almost quantitatively from the following experiments: Azeotropic distillation of mixtures of diethyl malonate and triphenylmethanol and of malonic acid and tri-*p*-tolylmethanol, in toluene; refluxing malonic acid and triphenylmethanol in dimethylformamide or in pyridine; refluxing alone or in presence of acids, an excess of acetylacetone with triphenylmethanol; from solutions of malonamide with triphenylmethanol in acetic-trichloroacetic acid after some days at room temperature; and from fusion of tri-(*p*-nitrophenyl)methanol with malonic acid, or refluxing the same in acetic acid alone or with the addition of sulphuric acid.

Decarboxylation.—Measurements were carried out at 110° \pm 0.2° in glacial acetic acid by measuring gasometrically the amount of carbon dioxide developed at different times. The first-order rate coefficient for the decarboxylation of malonic acid was calculated from the initial rate of the reaction, according to the equation $k_1 = \Delta x / \Delta t C_0$, when x is the amount

²³ Ullmann and Wurstemberger, *Ber.*, 1905, **38**, 4107.

²⁴ Röhrs and Lang, *J. prakt. Chem.*, 1941, **158**, 112.

²⁵ Corson, Scott, and Vose, *Org. Synth.*, 1943, Coll. Vol. II, 379.

²⁶ Corson, Scott, and Vose, *Org. Synth.*, 1941, Coll. Vol. I, 179.

²⁷ Baeyer and Villiger, *Ber.*, 1904, **37**, 3192.

²⁸ Schlenk and Marcus, *Ber.*, 1914, **47**, 1666.

²⁹ Gagnon, *Ann. Chim. (France)*, 1929, **12**, 301.

(calculated for normal temperature and pressure) of the carbon dioxide which was developed after the time, t , C_0 is the initial concentration of the malonic acid, and $\Delta x/\Delta t$ is the slope of the initial straight portion of the line.

The first-order rate coefficient k_1 for decarboxylation of tritylmalonic acid was calculated from the slope of the straight line obtained by plotting $\log(C_0 - x)$ against t ; the slope equals $-k_1/2.303$.

The rate coefficients obtained in seven runs for each substance at different initial concentrations did not differ from the average by more than $\pm 5\%$.

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