The Reactions of Ester with Acyl Chloride in the Presence of Aluminum Chloride. IV. Formation of Tribenzoylmethane

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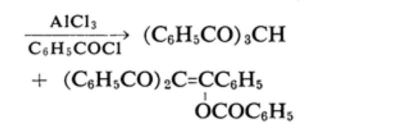
The previous paper[1] reported that monoacylated compounds were obtained when diethyl malonate was acylated with equimolecular amounts of benzoyl chloride or *p*-substituted benzoyl chlorides in the presence of equimolecular amounts of aluminum chloride, while a large quantity of catalyst led to decarbethoxylated diacyl compounds.

In this paper, the results of analysis of products obtained by the reactions of diethyl malonate with more than two molecular equivalents of acid chloride in the presence of three molecular amounts of aluminum chloride are reported on.

Acylation of Diethyl Malonate with Benzoyl Chloride.—Ethyl dibenzoylacetate (I), dibenzoylmethane (II), tribenzoylmethane (III) and tribenzoylmethane-*O*-benzoate (IV) were obtained by this reaction. The high-melting substance mentioned in the previous paper was also obtained; it was confirmed by analysis that this substance was aluminum chelate of dibenzoylmethane (IIa). The reaction conditions and the products of these acylation reactions are given in Table I. What differs from the experimental results of the previous paper[1] is the formation of III, IV and II in good yields. From these differences, it can be seen that benzoylation and decarbethoxylation reactions have proceeded further in this case.



$$(C_6H_5CO)_2CHCOOC_2H_5 \text{ or } (C_6H_5CO)_2CH_2 \xrightarrow[C_6H_5COCl]{AlCl_3} (C_6H_5CO)_3CH + (C_6H_5CO)_2C{=}\underset{\displaystyle OCOC_6H_5}{C}C_6H_5$$

Acylation of Diethyl Malonate with *p*-Chlorobenzoyl Chloride.—Diethyl *p*-chlorobenzoylmalonate (V), ethyl di-*p*-chlorobenzoylacetate (VI), di-*p*-chlorobenzoylmethane (VII) and tri-*p*-chlorobenzoylmethane (VIII) were obtained by this reaction. Besides these, aluminum chelate of di-*p*-chlorobenzoylmethane (VIIa) of a high melting point was also obtained. These reaction products are given in Table I. From this table, it can be seen that V, VI, VII and VIIa are obtained when two molecular equivalents of *p*-chlorobenzoyl chloride are used, but ester V and VI disappear with the increase in the combined yield of VII and VIIa by the use of three molecular equivalents of *p*-chlorobenzoyl chloride. What differs from the experimental results in the previous paper[1] is the formation of VIII, an increase in the yield of VI accompanied with V, and an increase in the combined yield of VII and VIIa.

Acylation of Diethyl Malonate with *p*-Nitrobenzoyl Chloride.—*p*-Nitroacetophenone (IX), ethyl *p*-nitrobenzoylacetate (X), di-*p*-nitrobenzoylmethane (XI) and its aluminum chelate (XIa) were obtained by this reaction, but tri-*p*-nitrobenzoylmethane was not obtained. These reaction products are given in Table I. From this table, it can be seen that the yield of ester X is decreased, while the combined yield of XI and XIa is increased, when a large quantity of *p*-nitrobenzoyl chloride is used. A good yield of XI and XIa alone is obtained at a high reaction temperature. The species of reaction products are the same as in the case of the previous paper[1], in which equimolecular amounts of *p*-nitrobenzoyl chloride were used. The difference is the increase in the combined yield of XI and XIa.

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[1] H. Kaneyuki, This Bulletin, 35, 519 (1962).

TABLE I. ACYLATION OF DIETHYL MALONATE WITH BENZOYL CHLORIDE AND *p*-SUBSTITUTED BENZOYL CHLORIDES

Reaction condition: 65°C, *** 90°C; 8 hr. Solvent: Nitrobenzene 8 ml., ** 15 ml.

Substituent	Reactant			Product and yield								
X	X-C_6H_4COCl mol.×10^2	$CH_2(COOC_2H_5)_2$ mol.×10^2	$AlCl_3$ mol.×10^2	X-BME[a] %	X-DBA[b] %	X-DBM[c] %	X-DBM-Al[d] %	X-TBM[e] %	X-TBM-*O*-B[f] %	X-AP[g] %	X-BAE[h] %	X-C_6H_4COOH %
H	3.6	1.8	5.4**		1.9	47.0	4.8	12.8	2.6			16.1
	5.4	1.8	5.4**		2.8*	51.8*	11.9*	24.0	5.2			27.7
Cl	1.1	0.5	1.7	16.8*	10.0	40.7	10.5	3.7				15.1
	1.7	0.5	1.7			40.7*	23.3*	trace				50.0
NO_2	1.1	0.5	1.6			26.6*	6.6*			22.6*	9.0*	49.0
	1.6	0.5	1.6			16.4*	41.3*			16.7*	trace	50.0
	1.6	0.5	1.6***			70.0*	22.6*				traec	31.4

Yield: Calculated from X-C_6H_4COCl (X=H, Cl, NO_2).

* Calculated from $CH_2(COOC_2H_5)_2$.

a) X-BME(V); X-$C_6H_4COCH(COOC_2H_5)_2$

b) X-DBA(I, VI); (X-$C_6H_4CO)_2CHCOOC_2H_5$

c) X-DBM(II, VII, XI); (X-$C_6H_4CO)_2CH_2$

d) X-DBM-Al(IIa, VIIa, XIa); [(X-$C_6H_4CO)_2CH]_3Al$

e) X-TBM(III, VIII); (X-$C_6H_4CO)_3CH$

f) X-TBM-*O*-B(IV); (X-$C_6H_4CO)_2C:C(OCOC_6H_4$-X)C_6H_5

g) X-AP(IX); X-$C_6H_4COCH_3$

h) X-BAE(X); X-$C_6H_4COCH_2COOC_2H_5$

Experimental*

Materials and reaction method were the same as in the previous paper¹⁾. The reaction conditions are shown in the above table. The treatment of the reaction mixture was also the same; that is, the product was separated into the aqueous layer containing aluminum chloride, sodium bicarbonate extract, sodium hydroxide extract, water extract and residual solution.

Acylation of Diethyl Malonate with Benzoyl Chloride.—Precipitates were separated after the aqueous layer containing aluminum chloride was heated and left standing. These precipitates were recrystallized from methanol to yield II. Benzoic acid was obtained when the sodium bicarbonate extract was acidified. The sodium hydroxide extract was acidified to give I, which recrystallized from ethanol. By acidifying the water extract, solid A was obtained. By distilling off the ether and the nitrobenzene, together witht he water, under reduced pressure from the residual solution, a residue was obtained. This was separated into an ether soluble substance B and an ether insoluble substance C. Yields of the various products are shown in Table I.

Tribenzoylmethane (III).—The solid A was recrystallized from a large quantity of ethanol to afford colorless needles, m. p. 223~240°C. The melting point was not depressed when melted together with tribenzoylmethane which had been prepared by the method of the literature²⁾. The infrared spectrum of this compound was identical with that of an authentic specimen.

Found: C, 80.72; H, 5.19. Calcd. for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

Tribenzoylmethane-*O*-benzoate (IV).—The solid B was recrystallized from ethyl acetate-petroleum ether to give colorless granular crystals, m. p. 125~126°C. When recrystallized from ethanol, however, the same product gave colorless plates, m. p. 112~113.5°C. Tribenzoylmethane-*O*-benzoate prepared according to the method of the literature³⁾ (m. p. 121~123°C, ethyl acetate-ligroin) gave the same kinds of crystals.

Found: C, 80.26; H, 4.74. Calcd. for $C_{29}H_{20}O_4$: C, 80.54; H, 4.66%.

Tris-(1, 3-diphenyl-1, 3-propanediono) - aluminum (**IIa**).—A small quantity of concentrated hydrochloric acid was added to a tetrahydrofuran solution of the ether insoluble substance C (0.5 g., m. p. above 270°C). The solution was allowed to stand for an hour, and then water was added until preciptation was complete. The precipitate was filtered and recrystallized from methanol to give needle crystals, 0.44 g., m. p. 76.5~78°C. The melting point and mixed melting point with dibenzoylmethane proved the identity of this material. A colloidal precipitate of aluminum hydroxide was produced on the addition of aqueous ammonia to the acidic filtrate.

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* Confirmation of compounds which were confirmed in the previous paper¹⁾ is omitted here. Melting points are uncorrected values.

2) "Beilsteins Handbuch der organischen Chemie", H., 7, 877 (1925).

3) Ibid., H., 9, 158 (1926).

Found: C, 77.52; H, 4.90; Al, 3.90. Calcd. for $C_{45}H_{33}O_6Al$: C, 77.57; H, 4.77; Al, 3.87%.

Acylation of Diethyl Malonate with *p*-Chlorobenzoyl Chloride.—Precipitates obtained from the aqueous layer containing aluminum chloride were separated into ether insoluble D and ether soluble substances. This ether soluble substance was recrystallized from ethanol to yield VII. *p*-Chlorobenzoic acid was obtained by acidifying the sodium bicarbonate extract. A precipitate was not obtained by acidifying the sodium hydroxide extract. Crystals obtained by acidifying the water extract were treated with ether, and ether insoluble substance E was separated. After the removal of the ether, the residue was separated to V and VI by fractional crystallization with ethanol. The residue, which was obtained after removing nitrobenzene from the residual solution of extraction, was recrystallized from ethanol to afford VII. The products and yields are shown in Table I.

Tris-(1, 3-dichloro-diphenyl-1, 3-propanediono)-aluminum (VIIa).—The tetrahydrofuran solution of the solid D (0.18 g., m. p. above 270°C) was treated with hydrochloric acid as has been mentioned above. The resulting precipitate was recrystallized from ethanol as colorless plates, 0.17 g., m. p. 159~160°C. The melting point and mixed melting point with di-*p*-chlorobenzoylmethane proved the identity of this material.

Found: C, 60.20; H, 3.29. Calcd. for $C_{45}H_{27}O_6 \cdot Cl_6Al$: C, 59.83; H, 3.01%.

Tri-*p*-chlorobenzoylmethane (VIII).—The solid E was recrystallized from a large quantity of ethanol to yield colorless long needles, m. p. 225~239°C.

Found: C, 61.59; H, 3.13; Cl, 24.58. Calcd. for $C_{22}H_{13}O_3Cl_3$: C, 61.21; H, 3.03; Cl, 24.64%.

Acylation of Diethyl Malonate with *p*-Nitrobenzoyl Chloride.—Precipitates obtained from the aqueous layer containing aluminum chloride were washed with water, and extracted with hot ethanol and then with a mixed solution of ethanol-tetrahydrofuran (1:2). The solid obtained by the evaporation of the ethanol extract was recrystallized from ethanol to give IX. By evaporating the ethanol-tetrahydrofuran solution, solid I was obtained. The residue, insoluble in an ethanol-tetrahydrofuran solution, was recrystallized from ethyl acetate to give XI. *p*-Nitrobenzoic acid was obtained when sodium bicarbonate extract was acidified. The reddish orange precipitate produced during sodium hydroxide extraction was filtered, washed with ether and hydrochloric acid, and then recrystallized from ethyl acetate to give XI. The water extract was acidified, and the resulting precipitate was recrystallized from ethanol to afford X.

Tris-(1, 3-dinitro-diphenyl-1, 3-propanediono)-aluminum (XIa).—The tetrahydrofuran solution of the solid F (0.75 g., m. p. above 270°C) was treated with hydrochloric acid, as has been mentioned above. The resulting precipitate was recrystallized from ethyl acetate to afford yellow needles, 0.70 g., m. p. 238~243°C. The melting point and mixed melting point with di-*p*-nitrobenzoyl methane proved the identity of this material.

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