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The Reaction of the Ester with Acyl Chloride in the Presence of Aluminum Chloride. VIII.1) The Attempted Synthesis of the Carbethoxy Derivative of Polymalonylphenylene[*1]

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The treatment of ethyl acetoacetate with terephthaloyl chloride in the presence of two equivalents of aluminum chloride in nitrobenzene at 55°C affords a polymer which may be designated as an aluminum chelate of the polymalonylphenylene derivative with some carbethoxy groups.

Recently we have reported that aluminum chloride is an effective agent for the acylation of active methylene group in compounds, such as diethyl malonate2) or ethyl acetoacetate,1,3) with acid chloride. For example, the reaction of ethyl acetoacetate with two equivalents of benzoyl chloride in the presence of a small amount of aluminum chloride in nitrobenzene at 35°C gave ethyl benzoylacetate, a small amount of ethyl benzoylacetoacetate, and traces of ethyl dibenzoylacetate and dibenzoylmethane. When the reaction was carried out by bubbling dry nitrogen gas into the reacting mixture, the yields of the above β-diketo esters and of dibenzoylmethane were increased and that of ethyl benzoylacetate was decreased. Under similar conditions, however, the use of a larger amount of aluminum chloride at the temperature of 55°C afforded dibenzoylmethane and its aluminum chelate in higher yields, besides small amounts of ethyl benzoylacetate, ethyl dibenzoylacetate, and tribenzoylmethane. Thus, the pathway of this reaction may be expressed as follows:

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1) Part VII: T. Nojiri and K. Matsui, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 880 (1966).

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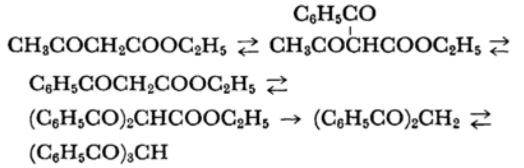
2) H. Kaneyuki, This Bulletin, **35**, 519, 523, 713 (1962).

3) K. Matsui and T. Nojiri, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 531 (1965).



$$CH_3COCH_2COOC_2H_5 \rightleftarrows CH_3CO\overset{C_6H_5CO}{\overset{|}{C}}HCOOC_2H_5 \rightleftarrows$$
$$C_6H_5COCH_2COOC_2H_5 \rightleftarrows$$
$$(C_6H_5CO)_2CHCOOC_2H_5 \rightarrow (C_6H_5CO)_2CH_2 \rightleftarrows$$
$$(C_6H_5CO)_3CH$$

In view of the above facts, the fact that the formation of di- and tri-benzoylated methane derivatives is accompanied by cleavages of carbon-carbon linkages suggests that ethyl acetoacetate may behave as a polyfunctional molecule toward acid chloride. It is the purpose of this paper to report the possibility of the formation of a polymer bearing the β-diketo structure, which will be formed by the above condensation reaction with terephthaloyl chloride.

Some reports on the synthesis of this kind of polymer have been published. Oda[4] and Furukawa *et al.*[5] prepared the polymer by treating ketene or diketene with aluminum chloride, but its purification was difficult owing to the contamination of aluminum. Nose *et al.*[6] also reported how polymers could be prepared from dimethyl terephthalate and the *p,p'*-diacetyl derivative of diphenyl ether or diphenylmethane by the use of metallic sodium.

When ethyl acetoacetate was treated with an equimolar amount of terephthaloyl chloride at 30°C by blowing nitrogen gas through the reaction mixture in the presence of a 0.5 equivalent of aluminum chloride in nitrobenzene, the resulting mixture was separated into ethyl *p*-carboxybenzoylacetate (I), diethyl terephthaloyldiacetate (II), an acidic (III) and a neutral polymer-like substance (IV), and a metal chelate polymer (V). Both III and IV are fusible, are soluble in ethanol or ether, and contain traces of aluminum, which combines to form a chelate more firmly than does aluminum chelating with dibenzoylmethane molecules.[1] In another run similar to the above, the viscous reaction mixture of the early stage was treated immediately with aqueous sodium hydroxide under the Schotten-Baumann conditions described in the Experimental section. The resulting mixture gave products similar to the above, but the acidic fraction, III, was of a relatively high molecular weight.

The infrared spectrum of III shows a broad absorption band, which corresponds to the β-diketo and carbethoxy absorption bands. Since this acylation reaction is often accompanied not only by a deacetylation reaction but also by a certain decarbethoxylation reaction, the structure of this substance is identified as that of a polymalonylphenylene derivative which does not contain as units, $-COCH_2COC_6H_4-$.
many carbethoxy groups as malonylphenylene

This substance was treated with aqueous sodium carbonate at room temperature in an attempt to hydrolyze its ester linkings. The infrared spectrum of the resulting product shows an absorption peak at 1362 cm^{-1} due to acetyl and the above-mentioned broad absorption, which is weakened in one region, as shown in Fig. 1. These features appear to be attributable to the ketonic hydrolysis of β-diketone linkings in the molecule. It should be noted that

TABLE 1. REACTION OF ETHYL ACETOACETATE WITH TEREPHTHALOYL CHLORIDE

Reactant : $CH_3COCH_2COOC_2H_5$ 1.9g (0.0146mol)
p-$C_6H_4(COCl)_2$ 3.0g (0.0148 mol)
Solvent : Nitrobenzene 15 m*l*, * 55 m*l*

$AlCl_3$ mol×10^2	Condition[a)]		Product and yield (g)				
	Temp., °C	Time, hr	I	II	III	IV	V
3.0	55	24	s	s			2.5
0.75*	30	24	1.1	0.2			0.9
0.75	30	45	0.9	0.3	0.6 (440)	s	0.8
0.75	30	48	1.5	s	0.2 (630)	s	0.9
0.45[b)]	30	48	0.3	s	0.6 (890) (450)[c)]	0.1	0.8

I : p-$HOOCC_6H_4COCH_2COOC_2H_5$, II : p-$C_6H_4(COCH_2COOC_2H_5)_2$, III : Acidic polymer-like substance, IV : Neutral polymer-like substance, V : metal chelate polymer.
"s" means a small amount of product. ( ) indicates molecular weight.
a) Nitrogen gas was passed during the reaction except for the run at 55°C.
b) Reaction under Schotten-Baumann condition.
c) Molecular weight of hydrolyzed polymer.

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[4] R. Oda, S. Munemiya and M. Okano, *Makromol. Chem.*, **43**, 149 (1961).

[5] J. Furukawa, T. Saegusa and N. Mise, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **65**, 254 (1962).

[6] Y. Nose, M. Hatano and S. Kambara, *ibid.*, **69**, 566 (1966).

the substance partly undergoes fission, although all of its ester linkings may not be hydrolyzed. The yields of products and some molecular weights are summarized in Table 1.

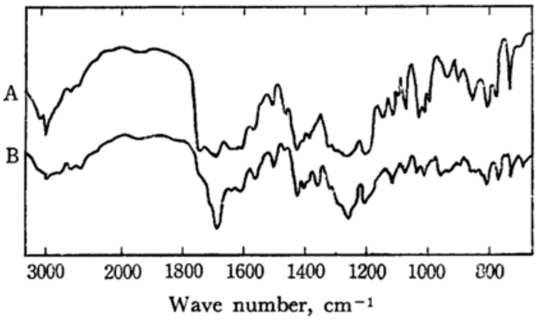

Fig. 1. Infrared spectra of carbethoxy derivative of polymalonylphenylene (KBr) (A) and its hyrdolyzed polymer (B).

When a similar treatment was carried out at 55°C in the presence of two equivalents of aluminum chloride but without passing nitrogen gas through, a vapor which seemed to be composed of carbon dioxide, hydrogen chloride, ethyl, and acetyl chloride bubbled out in a manner analogous to that in the reaction of ethyl acetoacetate with benzoyl chloride. The resulting product gave, in a very good yield, a polymer corresponding to V without any III and IV. It appears clear that this polymer was formed by the further condensation of the reaction intermediates corresponding to the substances, from I to V, though having its carbethoxy groups decreased markedly, as was expected from the above benzoylation reaction. The polymer is infusible, insoluble in ordinary organic solvents, swollen with ethanol on heating, and contains aluminum which can not be removed by any means. These findings suggest that aluminum is incorporated into stable intermolecular chelate linking to form the polymer. From the formation of tribenzoylmethane mentioned above, moreover, there is a possibility of a three-dimensional structure with some methine carbon atoms.

Experimental

Materials. The terephthaloyl chloride was prepared from phosphorus pentachloride and terephthalic acid which had been obtained by the hydrolysis of dimethyl terephthalate supplied by the Teijin Co., Ltd. Commercial ethyl acetoacetate was used after purification by distillation *in vacuo*.

Reaction of Ethyl Acetoacetate with Terephthaloyl Chloride. To a solution of aluminum chloride and terephthaloyl chloride in dry nitrobenzene, ethyl acetoacetate was added, and the mixture was kept in a thermostat at a given temperature. When it became gelatinous or viscous, the reaction mixture was poured into a mixture of hydrochloric acid and crushed ice. The aqueous solution containing aluminum chloride was removed from the organic layer by a centrifuge. The organic layer, after the removal of the nitrobenzene by steam distillation *in vacuo*, gave a solid which was then triturated with ether and filtered from an ether-insoluble chelate polymer. The filtrate was separated into an acidic and a neutral fraction by shaking with aqueous sodium bicarbonate. The former was extracted with hot water and purified by several reprecipitations from ethanol to water, thus giving an amorphous polymer-like substance. The hot-water extract obtained gave a crystal on cooling. Similarly, the latter, neutral fraction was separated into a crystal and a rather polymer-like substance by the use of ethanol and water. After the removal of the ether-insoluble substance which had formed during the above separations, the acidic, polymer-like substances generally melted at 120—130°C and the neutral, at 80—90°C. The molecular weights of the former were determined by the ebulioscopic method, using diethyl ether as a solvent.

Reaction under Schotten-Baumann Conditions. A viscous reaction mixture obtained as above was treated with ether (about 20 m*l*) and a 33% sodium hydroxide solution under conditions similar to those of the Schotten-Baumann reaction described in the literature.[7] The resulting mixture was separated into two layers by a centrifuge. Each layer was filtered to remove a rather insoluble substance. The organic layer gave a little viscous liquid on steam distillation *in vacuo*. The aqueous layer was then stirred into 6 N hydrochloric acid to give a solid of an acidic nature. The liquid and the solid were treated individually as above. A part of the acidic polymer-like substance was dissolved in aqueous sodium carbonate, left to stand for about 14 days at room temperature, and then acidified with hydrochloric acid to give a hydrolyzed polymer.

Ethyl p-Carboxybenzoylacetate (*I*). The crystal obtained from the acidic fraction was recrystallized from ethanol. Mp 151°C.

Found: C, 60.96; H, 4.96%. Calcd for $C_{12}H_{12}O_5$ C, 61.05; H, 5.12%. When refluxed with 20% sulfuric acid for 5 hr, this crystal gave colorless needles melting at 209—210°C (ethanol), (lit.,[8] mp 205°C of *p*-acetylbenzoic acid). Its methyl ester melts at 95—96°C (water) (lit.,[9] mp 92°C).

Diethyl Terephthaloyldiacetate (*II*). The neutral crystal was recrystallized from ethanol, mp 70°C (lit.,[10] mp 70°C). (Found: C, 63.01; H, 5.88%).

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7) J. M. Straley and A. C. Adams, " Organic Syntheses," Coll. Vol. IV, p. 415 (1963).

8) H. Rupe and A. Steinbach, *Ber.*, **43**, 3466 (1910).

9) R. Meyer, *Ann.*, **219**, 264 (1883).

10) L. Berend and P. Herms, *J. prakt. Chem.*, [2], **74**, 112 (1906).