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Friedel-Crafts Acylation with 2-Methyl- or 2-Benzylbutanedioic Anhydride

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Synopsis. The $AlCl_3$-catalyzed acylation of benzene with 2-methylbutanedioic anhydride afforded a mixture of 3-benzoyl-2-methylpropanoic acid and 3-benzoylbutanoic acid. The intramolecular acylation of 2-benzylbutanedioic anhydride in the presence of $AlCl_3$ gave a mixture of 4-oxo-1,2,3,4-tetrahydro-2-naphthoic acid and 3-oxo-2-indanacetic acid. The results were discussed in terms of the solvent effect on the acylations.

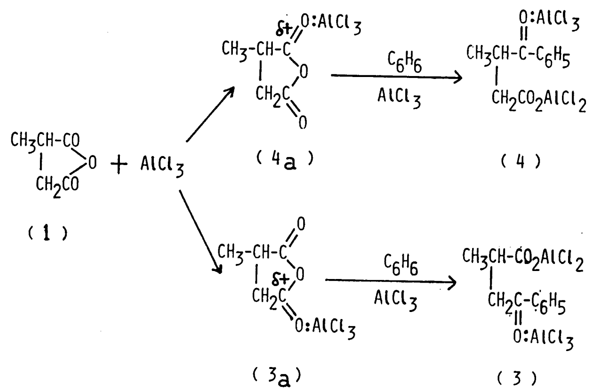
We have previously reported[1,2] that the $AlCl_3$-catalyzed acylations of benzene with 2-phenyl-butanedioic or -pentanedioic anhydride proceeded by means of competitive inter- and intramolecular acylations, where an electron-attracting phenyl group in the anhydrides had a strong influence on the direction of each acylation. A more detailed mechanism of the acylation with unsymmetrical dibasic acid anhydrides may be get by introducing an electron-donating methyl group into the dibasic acid anhydride and by treating individually the inter- and intramolecular acylations. The present paper deals with the acylation of benzene with 2-methybutanedioic anhydride (**1**) in the presence of $AlCl_3$ as an example of the intermolecular acylation, and with the $AlCl_3$-catalyzed condensation of 2-benzylbutanedioic anhydride (**2**) as an intramolecular example.

Table 1. $AlCl_3$-catalyzed acylation with 2-methyl- or 2-benzylbutanedioic anhydride at 30 °C for 5 h

Anhydride	Solvent (20 cm)	$[AlCl_3]$ / mmol	$[C_6H_6]$ / mmol	Product yields[a)] / %	
1				**3**	**4**
	—	20	250[b)]	62	39
	—	10	250[b)]	28	14
	$(ClCH_2)_2$	20	10	61	34
	$(ClCH_2)_2$	10	10	14	6
	$C_6H_5NO_2$	30	10[c)]	21	2
	$C_6H_5NO_2$	20	10[c)]	12	1
2				**5**	**6**
	—	20	250[d)]	37	63
	—	10	250[d)]	28	37
	—	—[e)]	250[d)]	65	1
	—	—[f)]	250[d)]	34	66
	$(ClCH_2)_2$	20	10	34	59
	$(ClCH_2)_2$	10	10	26	35
	$(ClCH_2)_2$	20	0	32	60
	$C_6H_5NO_2$	30	10	81	5

a) Calculated on the basis of the amount of anhydride used. b) At 40 °C for 2 h. c) For 24 h. d) At 40 °C. e) Two hundred mmole of concd H_2SO_4 were used as the catalyst. f) Twenty mmol of $AlBr_3$ were used as the catalyst.

Several investigators[3,4] have isolated only 2-aroyl-2-methylpropanoic acid in the condensations of some aromatic compounds with **1** in the presence of $AlCl_3$. However, when 10 mmol of **1** was condensed in the presence of 20 mmol of $AlCl_3$ with benzene, which was used in a large excess as a reactant and as a solvent, a mixture of 3-benzoyl-2-methylpropanoic acid (**3**) and the isomeric 3-benzoylbutanoic acid (**4**) was obtained; the yield of **3** was about twice that of **4**. The predominant formation of **3** was also observed in the cases using a limited amount (10 mmol) of benzene in 1,2-dichloroethane or in nitrobenzene. The lower yield of the keto acids in nitrobenzene may be a complex formation between $AlCl_3$ and nitrobenzene. The small solvent effect on the acylation of benzene with **1** suggests that the actual acylating agent in this acylation is a type of oxonium compound (**3a** and **4a**); since they are less polarized than the acylium ions, the solvent effect on them appears smaller.

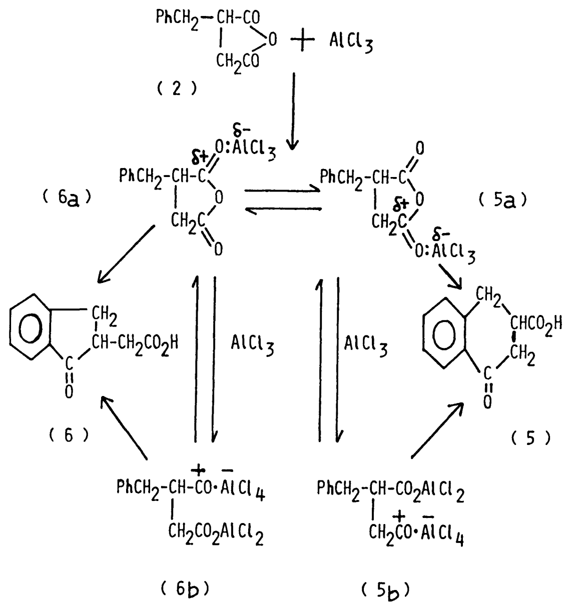


Scheme 1.

The electron-donating effect of a methyl group reduces the electrophilic reactivity of the $\rangle\overset{\delta+}{C}{=}O$ located closely to the methyl group; hence, the production of **3** is more favored than that of **4**.

The acylation with **2** in the presence of two equivalents of $AlCl_3$ in a large excess of benzene proceeded only intramolecularly to yield two isomeric keto acids, 4-oxo-1,2,3,4-tetrahydro-2-naphthoic acid (**5**) and 3-oxo-2-indanacetic acid (**6**), in a predominant yield, although early workers[5-8] in an analogous case succeeded in isolating only **5**. Similar results were also observed in 1,2-dichloroethane, whereas an overwhelming yield of **5** was obtained in nitrobenzene. Since the polarity of the solvent appears to affect markedly the relative yields between **5** and **6**, a reaction path including either the oxonium compounds (**5a** and **6a**) or the acylium ions (**5b** and **6b**) as the actual acylating agents may be formulated for the intramolecular acylation of **2** in the presence of $AlCl_3$.

The formation of **6a** is probably more favored than that of **5a** due to the electron-donating effect of a benzyl group,[9] although the electrophilic reactivity of $\rangle\overset{+}{C}{-}O$ of **5b** to a benzene nucleus may be greater than that of **6b**; a higher concentration of **6a** results in a predominant yield of **6**. On the other hand, in a polar



Scheme 2.

solvent such as nitrobenzene or in the presence of a large amount of concd H_2SO_4, the acylium ions bearing a more positive charge than the oxonium compounds may be greatly stabilized by solvation; therefore, a more reactive **5b** should give **5** in an overwhelming yield.

The product ratio obtained above dose not result from the thermodynamic equilibrium, since no isomerization between **5** and **6** was observed in the presence of two equivalents of $AlCl_3$ in 1,2-dichloroethane.

Experimental

Materials. 2-Methylbutanedioic anhydride: bp 238—240 °C. 2-Benzylbutanedioic anhydride was prepared by the method of Haworth *et al.*: mp 98.5 °C (lit,[7] mp 95—97 °C).

Acylation Procedures. The general procedure was as previously described.[1] A mixed solution of diethyl ether and methyl acetate was used to extract the keto acids.

Analyses of the Products. The acylation products of benzene with 2-methylbutanedioic anhydride, after being esterfied with an ethereal solution of diazomethane, were analyzed by GLC employing a Yanagimoto G-180 F model on a 1.5 m×3 mm column packed with Ucon Oil 50 LB 550 X (3 wt %) on Uniport KS of 60—80 mesh at 180 °C. GC analyses of the intramolecular acylation products of 2-benzylbutanedioic anhydride in the presence of $AlCl_3$ were made by using a column packed with Apiezon Grease L (3 wt %) at 170 °C or Ucon Oil 50 LB 550 X (3 wt %) at 171 °C. The compounds, **3**, **4** and **5**, were synthesized according to the method described in the literature: 3-benzoyl-2-methylpropanoic acid (**3**): mp 142 °C (lit,[10] mp 140.5 °C); 3-benzoylbutanoic acid (**4**): mp 55 °C (lit,[11] mp 59 °C); 4-oxo-1,2,3,4-tetrahydro-2-naphthoic acid (**5**): mp 149 °C (lit,[5] mp 149 °C).

*3-Oxo-2-indanacetic Acid (**6**).* A solution of 2-benzylbutanedioic anhydride (1.90 g) in benzene (12.1 cm^3) was treated with $AlBr_3$ (5.34 g) in benzene (10 cm^3) at 30 °C for 5 h. The reaction mixture was then work up in a usual manner. The crude keto acid was repeatedly recrystallyzed from acetic acid and then methyl acetate–petroleum ether: mp 150.5—151 °C; IR (KBr disk), 1750 (C=O), 1669, 1600 cm^{-1}; MS (methyl ester) *m/e* (%) 204 (M^+, 30), 173, 172 (M^+-OCH_3, 25), 145 ($M^+-COOCH_3$, 75), 131 ($M^+-CH_2COOCH_3$, 49), 116 (100); ^1H-NMR [$(CD_3)_2CO$] δ 7.4—7.7 (m, 4H, arom.), 3.5 (q, 1H, J=8), 3.0 (m, 2H), 2.7 (q, 2H, J=8); ^{13}C-NMR [$(CD_3)_2CO$] δ 209.0 (s, C=O), 175.5 (s, -COOH), 156.0 (s, C-9), 139.0 (s, C-4), 137.0, 129.5, 129.0 and 125.5 (d, C-arom.), 45.0 (d, C-2), 35.5 (t, $\underline{C}H_2$–COOH), 34.0 (t, C-3); Found: C, 69.43; H, 5.31%. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30%.

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