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Acylation of Aluminum Trisacetylacetonate with *n*-Butyryl Chloride in the Presence of Aluminum Chloride[1]

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It was reported[2] that acetylacetone reacts with *n*-butyryl chloride to give *n*-butyrylacetone (I) and di-*n*-butyrylmethane (II) in the presence of more than 2 equivalents of aluminum chloride in nitrobenzene at 45°C. These products can be rationalized by assuming initial formation of dichloroaluminum enolate of the β-diketones, acetylacetone and I, followed by butyrylation leading to the respective deacetylated products, I and II. Murdoch *et al.* and Barry reported that the metal chelates (excluding aluminum chelate) of β-diketones react with acyl chlorides in refluxing toluene or cyclohexane,[3,4] or in chloroform at room temperature[5] to afford initially triacylated methanes. Doolan and Gore[6] pointed out that aluminum trisacetylacetonate (III) or acetylacetone (regarded as converting into III during the reaction) reacts as in aromatic acylation with acetyl chloride to give diacetylated III in the presence of the excess of aluminum chloride in boiling carbon disulfide. This paper deals with the problem of deciding how the reaction of III with *n*-butyryl chloride proceeds under conditions similar to those of the above butyrylation of acetylacetone.[2]

The conditions of the present reactions and the product yields based on acetylacetone to be formed from III are given in Table 1. All the experimental procedures are similar to those for acetylacetone.[2]

The non-catalyzed reaction of III with 3 equivalents of *n*-butyryl chloride afforded I as a single product in a low yield only when the temperature was raised to 65°C. This shows that there is some difficulty at 45°C in acylating through coordination of *n*-butyryl chloride with the central metal atom of the chelate as with the mechanism proposed by Murdoch *et al.*[3,4] Even at low temperature, however, the addition of 1.5 equivalent of aluminum chloride gave II as well as I. The formation of II suggests that III can be acylated through its ring-opening during the reaction.

In the presence of 3 equivalents of aluminum chloride (1 equivalent for each acetylacetone component in III) the yields of both I and II obtained using 6 equivalents of *n*-butyryl chloride (2 equivalents for each acetylacetone component in III) increased to

TABLE 1. REACTION OF ALUMINUM TRISACETYLACETONATE WITH *n*-BUTYRYL CHLORIDE

$AlCl_3$ mole ratio	Reaction time (hr)	Product[a] and yield (%)			
		$PrCOCH_2COCH_3$	$PrCOCH_2COPr$	Total	Recovery as $(CH_3CO)_2CH_2$
0*	1	0	0	0	39
0*	1**	8	0	8	28
1.5*	1	27	6	33	17
1.5	1	34	16	50	13
3	1	37	17	54	15
3	0.5	36	18	54	14
3	24	30	21	51	11

Substrate: $Al[(CH_3CO)_2CH]_3$ 1.62 g (0.005 mol), Reactant: C_3H_7COCl 3.2 g (0.03 mol), * 1.6 g (0.015 mol)
Reaction temp.: 45°C, ** 65°C, Solvent: $C_6H_5NO_2$ 10 ml

a) Very small amounts of methyl ethyl ketone and neutral oily substance were obtained.

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2) T. Nojiri, I. Hashimoto, M. Motoi, and K. Matsui, This Bulletin, **42**, 3359 (1969).

3) H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc.*, **1962**, 2153; *ibid.*, *C*, **1968**, 2298.

4) D. C. Nonhebel and J. Smith, *ibid.*, *C*, **1967**, 1919; D. C. Nonhebel, *ibid.*, **1962**, 4628.

5) W. J. Barry, *ibid.*, **1960**, 670.

6) P. C. Doolan and P. H. Gore, *ibid.*, *C*, **1967**, 211.

near maximum and were almost unaffected even when the reaction time was extended from 0.5 to 1 hr, but the extension of time to 24 hr allowed II to increase at the expense of I. Although the total yields increased somewhat, these findings are similar to those observed in the butyrylation reactions of acetylacetone under analogous conditions.

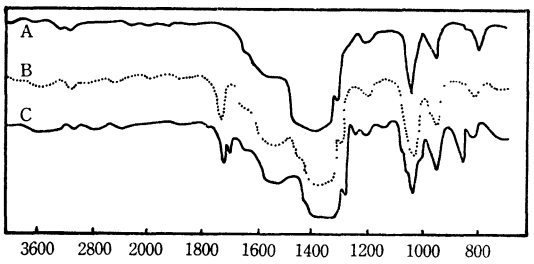
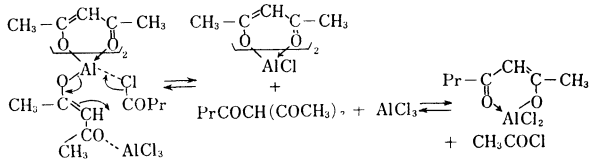


Fig. 1. Infrared spectrum of aluminum trisacetylacetonate in nitrobenzene (A); with 0.5 (B); and with 1.5 equivalent of $AlCl_3$ (C).

The infrared spectra of III in nitrobenzene solutions containing 0.5 and 1.5 equivalent of aluminum chloride show medium absorption peaks at 1688, and 1715 and 1688 cm^{-1} due to carbonyl group, respectively, which cannot be observed with the spectrum of III in nitrobenzene, as shown in Fig. 1. It can be seen that, concurrent with the ring-opening of III, a carbonyl group appears and leaves a site capable of coordinating with *n*-butyryl chloride on the central aluminum so that the butyrylation reaction proceeds easily as follows:



The chloroaluminum bisacetylacetonate and dichloroaluminum *n*-butyrylacetonate which were formed must be further butyrylated and then deacetylated in the same way as illustrated in the above equation. Although not produced from acetylacetone by using 0.5 equivalent of aluminum chloride,[2] II was provided from III in a nearly maximum yield of 16% even under the corresponding conditions. This high yield seems to be ascribable to the easier enolate formation of III by its ring-opening as compared with that of acetylacetone.

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