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THE ACYLATION OF ENOLATE ANION BY ACID HALIDES AND DIMETHYLKETENE

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For the anionic polymerization of dimethylketene the growing end was shown to be an enolate anion and to have ambident nature (1). Hence, it is interesting to study.the acylating reaction of enolate anion with dimethylketene.

We studied the acylation of enolate anions derived from isobutyrophenone and diisopropylketone by acid halides (including acetylchloride and isobutyrylchloride) besides dimethylketene. The enolate anions were formed by triphenylmethylpotassium in 1,2-dimethoxyethane at room temperature (2), and by lithium hydride or sodium hydride in 1,2-dimethoxyethane, tetrahydrofuran, and dimethylformamide at refluxing temperatures.

Into the solution of enolate anion equimolar quantity of the acylating reagent was added at 0°C~ room temperature. In the case of dimethylketene the solution of dimethylketene in 1,2-dimethoxyethane was added rapidly at -30°~ -20°C. The reaction conditions are summarized in table 1.

Table 1 Reaction conditions (0.04 mole scale)

Expt. No.	Proton abstructing reagent	Solvent(a) 50 ml	Acylating reagent 0.05 mole
	(A) Isobutyrophenone		
1	NaH	DME	Acetylchloride
2	NaH	THF	Acetylchloride
6(b)	Ph_3CK	DME	Acetylchloride
19	NaH	DMF	Acetylchloride
8(b)	Ph_3CK	DME	Isobutyrylchloride
12	NaH	THF	Isobutyrylchloride
18	NaH	DMF	Isobutyrylchloride
21	LiH	DMF	Isobutyrylchloride
10(b,c)	Ph_3CK	DME	Dimethylketene
	(B) Diisopropylketone		
25	NaH	THF	Isobutyrylchloride
26	NaH	DME	Isobutyrylchloride
27(b)	Ph_3CK	DME	Isobutyrylchloride
30(b,c)	Ph_3CK	DME	Dimethylketene

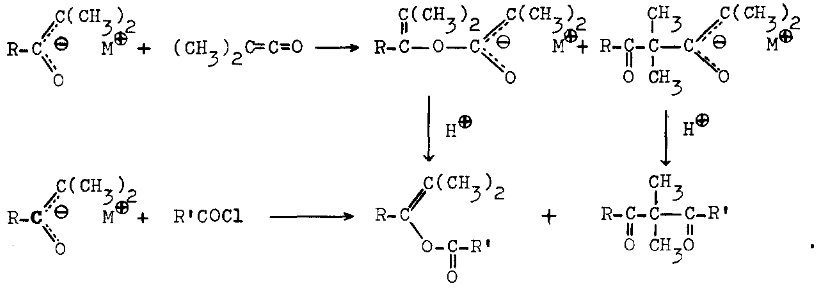
(a) DME; 1,2-Dimethoxyethane: THF; tetrahydrofuran: DMF; dimethylformamide.

(b) At least three components of decomposition products of triphenylmethane were formed, containing diphenylmethane.

(c) Solid polymer of dimethylketene was not produced.

The products were analyzed and isolated by gas chromatography, and identified by IR and NMR spectrum of these almost pure samples. The data of these spectra are listed in table 2. For the first two compounds in table 2 (Ia and Ib), the observed saponification equivalents are 183.4 (calcd. 189.1) and 221.9 (calcd. 220.2), respectively.

O- and C-acylated products are expected as a result of reaction according to the following shema:



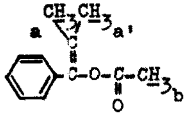
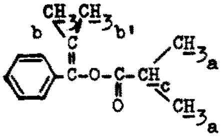
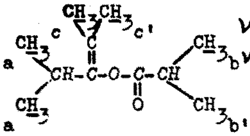
(I) (II)

a; R = Ph, R' = Me
b; R = Ph, R' = i-Pr
c; R = i-Pr, R' = i-Pr

But in all cases of table 1, even with dimethylketene, the enolate anions are exclusively O-acylated, and the C-acylated products were not detected. In the case of acetylchloride as acylating reagent, a small quantity of another product was formed, area ratio of this to O-acylated product being <0.05 by gas chromatography, but this compound could not be identified.

Though several authors (3,4) reported the syntheses of 1,3-dicarbonyl compounds by reaction of enolates with acid chlorides or acid anhydrides, in our system acylation occurred on the O-atom of the enolate anion. The reaction was not influenced by counter ion or by bulkiness of substituents, and more electronegative O-atom was shown to be more reactive. The C-acylated products must then result from the reaction of the initially formed enol-esters with excess of the employed enolate (4), as suggested by the observation by House and Kramar (5) in the reaction of enolate anions of unsymmetrical ketones with acetic anhydride in 1,2-dimethoxethane.

Table 2 IR and NMR data of O-acylated products

Compound	IR cm^{-1}(a)	NMR τ ppm (b)
(Ia) 	$\nu_{C=C}$; 1680 $\nu_{C=O}$; 1755	a,a'; 8.29, 8.23 b; 7.92 arom.H.; 2.62
(Ib) 	$\nu_{C=C}$; 1685 $\nu_{C=O}$; 1753	a;8.81 doublet (J=7cps) b,b'; 8.30, 8.21 c; 7.41 multiplet arom.H.; 2.63
(Ic) 	$\nu_{C=C}$; 1690 $\nu_{C=O}$; 1755	a; 9.03 doublet (J=7cps) b; 8.73 doublet (J=7cps) c,c'; 8.54, 8.24

(a) neat, (b) CCl_4 soln., tetramethylsilane as internal standard

REFERENCES

(1) Y.Yamashita, S.Miura, and M.Nakamura, Makromol. Chem., 68, 31 (1963)

(2) H.O.House, and V.Kramar, J. Org. Chem., 27, 4146 (1962)

(3) C.R.Hauser, F.W.Swamer, and J.L.Adams, Org. Reactions, 8, 59 (1954)

(4) B.O.Linn, and C.R.Hauser, J.Amer. Chem. Soc., 78, 6066 (1956)

(5) H.O.House, and V.Kramar, J. Org. Chem., 28, 3362 (1963)