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Preliminary communication

Catalytic alkylations of allylic carbonates under argon in the presence of nitrosylcarbonyliron complexes

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Abstract

Under argon and at reflux of THF, crotyl and α-methallyl ethylcarbonates are alkylated by sodium dimethylmalonate in the presence of nitrosylcarbonyliron complexes. In every case, the carbon atom bound to the leaving group is alkylated preferentially. The rate of alkylation increases in the sequence $NBu_4{}^+Fe(CO)_3(NO)^-$ (> 8 h), $Na^+Fe(CO)_3(NO)^-$ (≤ 2.5 h), $Fe(CO)_2(NO)_2$ ($\frac{1}{2}$ h).

Several years ago, we reported [1] the catalytic alkylation of a few allylic acetates in the presence of $Na^+Fe(CO)_3(NO)^-$ (Na^+-**1**), in refluxing tetrahydrofuran (6–24 h) under argon or nitrogen. Under these conditions, alkylation occurred preferentially at the carbon atom originally bearing the leaving group, and contrary to a mechanistic interpretation erroneously attributed [2a] to us, we never assumed the involvement of η^3-allyl intermediates.

An interesting extension of these iron-mediated alkylations to allylic carbonates, which expectedly are more reactive [3], has been reported [2]. In that study, the tetrabutylammonium salt of the aforementioned nitrosyliron anion **1**, Bu_4N^+-**1**, which is less air-sensitive than Na^+-**1**, was employed. It was stated that an atmosphere of carbon monoxide is required for alkylation to proceed, as under argon the starting allylic carbonates apparently were recovered.

This communication reports the alkylation of an isomeric pair of monoethyl carbonates, namely, the crotyl and α-methallyl esters, with sodium diethylmalonate ($DEMH^-Na^+$) in the presence of either $Fe(CO)_3(NO)^-$ anion **1** or $Fe(CO)_2(NO)_2$ (**2**). The latter reagent has recently been shown to be catalytically active for alkylation of crotyl and α-methallyl acetates [4].

The most interesting result of practical importance is that, in the presence of Na^+-**1**, the reactions proceed effectively under argon, affording the monoalkylated products in 80–90% isolated yields (see entries 1 and 2 of Table 1). The observed regioselectivities parallel those found [1] in the acetates, but the reaction time was sharply reduced from ~ 14 h to no more than 2.5 h. The latter value is probably a

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Table 1

Alkylation of crotyl ($R_L = CH_3CH{=}CHCH_2$) and α-methylallyl ($R_R = CH_2{=}CHCH(CH_3)$) ethylcarbonates with sodium diethylmalonate (Na^+ $DEMH^-$)

Typical conditions: Substrate/Na^+ $DEMH^-/DEMH_2$/catalyst = 5/5.5/5/1, with 2 to 5 mmol of substrate and [catalyst] 0.02–0.03 *M* in argon-saturated THF (distilled over benzophenone/sodium). Reactions at reflux temperature of the solvent under a positive pressure of argon regulated by a mercury valve. At the end of the indicated time, solvent evaporated to dryness under diminished pressure, residue exposed to air, ether added followed by hydrolysis with aqueous NH_4^+ Cl^-. Extraction of the aqueous phase with ether, drying of the organic phase over $MgSO_4$, followed by filtration and removal of the solvent. Residue chromatographed on a SiO_2 column and mixture of monoalkylated products eluted with 8/2 hexane/ethyl acetate.

Entry	Substrate	Catalyst [a]	Reaction time (h)	Regioselectivity [b] R_L-DEMH/R_R-DEMH	Yield (%) [c]
1	R_L–OCO_2Et	Na^+-**1**	2.5	84/16	90
2	R_R–OCO_2Et	Na^+-**1**	2.5	20/80	85
3	R_R–OCO_2Et	NBu_4^+-**1**	8	29/71	35
4	R_L–OCO_2Et	**2**	0.5	95/5	72
5	R_R–OCO_2Et	**2**	0.5	5/95	72

[a] **1** = $Fe(CO)_3(NO)^-$. **2** = $Fe(CO)_2(NO)_2$ [10]. The samples of Na^+-**1** used contained one 1,4-dioxane per iron in the solid state [11]. NBu_4^+-**1** was prepared under phase transfer conditions (NBu_4H^+ $HSO_4^-/NaNO_2/NaOH/Fe(CO)_5$ as in ref. 12 but with CH_2Cl_2 instead of benzene. The complex was recrystallized from ethanol/water as yellow crystals, and stored under N_2. [b] Determined by ^1H NMR of the mixture of alkylation products after separation by column chromatography. [c] Isolated yields.

conservative estimate of the time actually required, for monitoring of the reactions by infrared spectroscopy revealed that the intensity of the carbonyl bands for Na^+DEMH^-, centered at 1680 and 1560 cm^{-1}, decreased further only negligibly after a period of 1.5 h. The catalytic activity of Bu_4N^+-**1** was compared to that of Na^+-**1** with ethyl α-methallyl carbonate as a test substrate. In our hands, alkylation did occur under argon, but much more slowly, and after a reaction time of 8 h there was obtained a 35% yield of alkylated products (Table 1, entry 3).

A possible rationalization of the difference in reactivity between Na^+-**1** and Bu_4N^+-**1** is suggested by the infrared spectra of the catalytically active tetrahydrofuran solutions. The sodium salt is present as a mixture of tight (ν(CO) 1989 and 1887, ν(NO) 1613 cm^{-1}) and solvent-separated (ν(CO) 1977 and 1877, ν(NO) 1643 cm^{-1}) ion pairs (as observed already for THF solutions containing solely Na^+-**1** [5]), whereas only solvent-separated ion pairs (ν(CO) 1980 and 1865, ν(NO) 1645 cm^{-1}) are seen in Bu_4N^+-**1**. The bis(triphenylphosphine)imminium salt of **1** (PPN^+-**1**) likewise exists as separated ion pairs in tetrahedrofuran [5], and when it was used instead of Na^+-**1** in alkylations of crotyl and α-methallyl acetates with $DEMH^-Na^+$, a sixfold decrease in rate was observed [6]. It therefore appears that these catalytic systems provide a further example for the influence of ion pairing upon reactivity; for earlier examples, see refs. 7 and 8, and references cited therein. The observations suggest that a more-reactive system is obtained when tight ion pairs involving **1** are present, but, interestingly, this is the opposite of what was observed [5] in reactions of PPN^+-**1** and K^+-**1** with methyl iodide.

It is interesting to note that the neutral dinitrosyl species $Fe(CO)_2(NO)_2$ (**2**) also constitutes a highly active promotor of alkylation. As shown by entries 4 and 5 (Table 1), the reactions were even faster than those using Na^+-**1**. However, whereas the intensities of the CO absorption bands of the latter are not affected significantly over a period of 2.5 h, compound **2** appears to be consumed in the process, as indicated by absence of its CO-bands from the IR spectrum after 0.5 h, even though iron is still present in a soluble, but as yet unidentified, form (evidences for the involvement of Fe/malonate complex in the $Fe_2(CO)_9$ mediated alkylation of crotylic substrates have been obtained recently [9]).

The stereochemistry of alkylations using **1** and **2** is under investigation.

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References

1 J.L. Roustan, J.Y. Merour, F. Houlihan, Tetrahedron Lett. 39 (1979) 3721.
2 (a) Y. Xu, B. Zhou, J. Org. Chem., 52 (1987) 974; (b) B. Zhou, Y. Xu, ibid., 53 (1988) 4419.
3 J. Tsuji, I. Minami, Acc. Chem. Res. 20 (1987) 140.
4 J.L. Roustan, M. Bisnaire, G. Park, P. Guillaume, J. Organomet. Chem., 356 (1988) 195.
5 K.H. Pannell, Y. Chen, K. Belknap, C.C. Wu, I. Bernal, M.W. Crewick, N.H. Hsu, Inorg. Chem., 22 (1983) 418.
6 J.L. Roustan, F. Houlihan, unpublished observations.
7 (a) J.P. Collman, R.G. Finke, J.N. Cawse, J.I. Brauman, J. Am. Chem. Soc., 99 (1977) 2515; (b) 100 (1978) 4767.
8 M.Y. Darensbourg, D. Burns, J. Am. Chem. Soc., 94 (1976) 3127.
9 G.S. Silverman, S. Strickland, K.M. Nicholas, Organometallics, 5 (1986) 2117.
10 R.B. King, Organometallic Synthesis, Vol. 1, p. 167. Academic Press, New York, 1965.
11 W. Hieber, H. Beutner, Z. Anorg. Allgem. Chem., 320 (1963) 101.
12 Y. Otsuji, T. Ueda, New Front. Organomet. Inorg. Chem. Sci. Proc. China-Japan-USA. Trilateral Semin. 2nd 1982 (Pub. 1984) 179–187. Boon-Keng Teo. Sci. Press: Beijing, P.R. China.