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Reaction of 1,3-Dicarbonyl Compounds with Nitryl Chloride

Short Communication

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Reaction of 1,3-dicarbonyl compounds with nitryl chloride through substitution on the activated methylene group, resulted in the formation of chloro, dichloro and oximino derivatives.

(Keywords: 3-Oxobutanoic acid ethyl ester, 2,4-Pentanedione, reaction with nitryl chloride)

Die Reaktion der 1,3-Dicarbonylverbindungen mit Nitrylchlorid

Umsetzung von 1,3-Dicarbonylverbindungen mit Nitrylchlorid ergab die entsprechende Chloro-, Dichloro- und Oximinoderivate in einer Substitutionsreaktion an der aktivierten Methylengruppe.

Nitryl chloride reacts with aliphatic[1], alicyclic[2] and heterocyclic olefins[3] to give mixtures of addition products, such as vicinal dichloro and chloro-nitro compounds, whereas aromatic[4] and heteroaromatic[5] hydrocarbons are substituted and chloro or nitro compounds or their mixtures are formed. Substitution reactions with nitryl chloride in the aliphatic series have not been known so far.

We now wish to report that reaction of 1,3-dicarbonyl compounds with nitryl chloride gives rise to substitution on the activated methylene group. Various examples with reaction conditions and yields of the products are shown in Table 1. The variation in yields depends on the solvent as well as on the molar ratio of nitryl chloride/1,3-dicarbonyl compound, while they are almost temperature independent.

The reaction is carried out by passing nitryl chloride through the solution of the dicarbonyl compound in inert solvents. The products were isolated by fractional distillation, and their structure confirmed by spectral data and compared with authentic samples prepared by known procedures.

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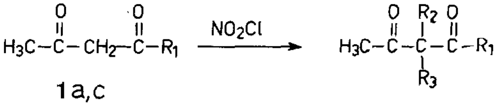
Table 1. *Reaction of 1,3-dicarbonyl compounds* **1 a** *and* **c** *with nitryl chloride*

	NO_2Cl/**1 a, c** molar ratio	Solvent	Reaction temp. (°C)	Products[a] chloro (%)	dichloro (%)	oxime (%)
1 a	1	CH_2Cl_2	40		30[b]	57[c]
1 a	2	CH_2Cl_2	40		59	15
1 c	1	CH_2Cl_2	20	30[d]	11[e]	57[f]
1 c	2	CH_2Cl_2	20	36	58	
1 c	1	C_6H_6	20	24	12	63
1 c	2	CH_2Cl_2	40	60	40	
1 c	2	acetic acid	40		80	19

[a] Yields determined by G.c.; [b] b.p.$_{18}$ 85-87 °C (lit.[9] b.p.$_{18-20}$ 87 °C); [c] m.p. 72 °C (lit.[10] 75 °C); [d] b.p.$_{30}$ 93-98 °C (lit.[11] b.p.$_{30}$ 94-96 °C); [e] b.p.$_{30}$ 108-109 °C (lit.[11] b.p.$_{30}$ 106-108 °C); [f] m.p. 56-58 °C (lit.[12] m.p. 58-58.5 °C).

Special attention was paid to the detection of products having a nitro group but the results were unsatisfactory: High yields of the oxime **2 e** (obtained at a 1:1 molar ratio of nitryl chloride and ethyl acetoacetate, **1 c**) indicate the presence of an ONO^- species. In some experiments, anhydrous calcium chloride or sodium sulphate was added, thus slightly increasing the yield of the oxime **2 e** from 63% to 69% (in benzene). At higher molar ratios of NO_2Cl/diketone, chlorination predominated.

The results confirmed earlier observations that chlorination with nitryl chloride through substitution releases nitrite ions[5, 6]. The ionic structures of nitryl chloride (cf. *Paul* et. al.)[7] do not prefer those with positive chlorine and nitrite ion, but the results presented as well as those reported earlier[5, 6, 8] indicate that such a structure may exist.



$$H_3C-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-R_1 \xrightarrow{NO_2Cl} H_3C-\overset{\overset{O}{\|}}{C}-\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-R_1$$

1 a,c

2 a-e

	R_1	R_2	R_3
a	CH_3	Cl	Cl
b	CH_3	=NOH	
c	OC_2H_5	Cl	H
d	OC_2H_5	Cl	Cl
e	OC_2H_5	=NOH	

Experimental

Gas-liquid chromatographic analyses were performed on a Perkin Elmer F-11 Model using column 2 × 0.004 m, 2% diethyleneglycol succinate on 80-100 mesh Chromosorb G (AW-DMCS), isothermal at 80 °C (23 min) and programed (10°/min) to 180 °C. Ir spectra were taken on a Perkin Elmer 257 instrument. 3,3-Dichloro-2,4-pentanedione[9], 3-oximino-2,4-pentanedione[10], ethyl 2-chloroacetoacetate[11], ethyl 2,2-dichloroacetoacetate[11], and ethyl 2-oximinoacetoacetate[12] used as test substances were prepared according to known procedures.

General Reaction of 1,3-diketones with Nitryl Chloride

Nitryl chloride (prepared according to *Schechter* et al.[13]), liquified in an acetone-dry ice bath, was allowed to evaporate into a stirred solution of 0.25 mol of 1,3-diketone **1 a** or **1 c** in 100 ml of solvent during one hour and stirring was then continued for an additional hour. Samples for gas chromatography were taken at this stage. The solvent was evaporated in vacuo on a Büchi Rotavapor. On fractionation the liquid chloro derivatives **1 a, c, d** were obtained, whereas the crystalline oximes **2 b** and **e** were isolated from the residue.

The infrared spectra of the products isolated were identical with those of the authentic samples.

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