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Essential Steps in the Catalytic Condensation of Aldehydes. IV. Nitroparaffin Condensations

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In previous communications[3] from this Laboratory it was shown that there is a fundamental qualitative difference in the catalytic activity of aluminum ethoxide and magnesium aluminum ethoxide in aldehyde condensations. In view of this fact, it was decided to extend these observations to several nitroparaffin aldehyde condensations utilizing these aluminum ethoxides as catalytic agents.

When aldehydes react with nitroparaffins, nitroalcohols are formed as follows

$$R{-}CHO + H{-}\underset{R'}{\overset{H}{C}}{-}NO_2 \longrightarrow R{-}\underset{OH}{\overset{H}{C}}{-}\overset{H}{\underset{R'}{C}}{-}NO_2$$

In earlier studies of this type of condensation emphasis has been placed on the strongly basic nature of the condensing agent.[4] We were able to effect this reaction in the presence of a slightly acidic aluminum ethylate or a weakly basic magnesium aluminum ethylate. The condensation of aldehydes with nitroparaffins proceeds smoothly in the presence of the aluminum ethoxides.

The nitroparaffins used in this study were nitromethane, nitroethane and 1-nitropropane. These compounds were condensed with the following aldehydes, acetaldehyde, propionaldehyde, butyraldehyde, hexaldehyde, crotonaldehyde, chloral, benzaldehyde, *i*-butyraldehyde, α-ethyl butyraldehyde and α-ethyl hexaldehyde. The yields of the isolated nitroalcohols ranged from 10–70% depending on the catalyst used and the structure of the aldehyde.

Experimental

Equimolecular (0.5 mole) quantities of the aldehyde and the nitroparaffin were placed in an Erlenmeyer flask submerged in an ice-water-bath.[5] Ten per cent. of catalyst was added and the flask was quickly stoppered. After two to three hours the flask was removed from the water-bath and left for several days at room temperature. A large excess of 10% hydrochloric acid was then added and the mixture was warmed on the steam-bath for twenty to thirty minutes. Preliminary experiments showed that the catalyst must be destroyed prior to the distillation. After ether extraction and drying over anhydrous sodium sulfate, the ethereal solution was fractionated.

The nitroalcohol fractions were purified by washing with 5% sodium carbonate, extraction with ether, drying and final rectification in a Claisen flask.

The physical constants and the yields of the new compounds are summarized in Table I.

Discussion

It was shown that aluminum ethoxides are efficient catalysts in aldehyde nitroparaffin condensations. Qualitatively, in this type of reaction no difference in the action of these two catalysts was observed as each catalyzed the formation of identical end-products. Quantitatively however, aluminum ethylate produced a slightly higher yield of the nitroalcohol from the alpha CH_2 aldehydes. In the case of the alpha substituted aldehydes, a higher yield of the nitroalcohol is obtained in the presence of the more basic magnesium aluminum ethylate.

The use of aluminum ethoxides in these condensations eliminates two undesirable side reactions always encountered when using the strongly basic inorganic media, namely, self-aldolization of the aldehyde and polymerization. Polymerization was encountered in only two cases using the aluminum ethoxides, *viz.*, chloral and crotonaldehyde. One side reaction which could not be fully avoided was the formation of simple esters.

TABLE I

Aldehyde	Nitro paraffin	Isolated product	B. p., °C.	Mm.	D	(*t*, °C.)	*n*	(*t*, °C.)	Analyses, % N Calcd.	Found	% Yield Al-$(OC_2H_5)_3$	Mg-$[Al(OC_2H_5)_3]_2$
	CH_3NO_2	1 Nitro-3-pentene-2-ol	79–80	1	1.0946	(25)	1.4655	(25)	10.63	10.80	33.2	30.0
Crotonaldehyde	$C_2H_5NO_2$	2 Nitro-4-hexene-2-ol	87–88	1	1.0657	(25)	1.4578	(25)	9.65	9.48	30.7	28.9
	$C_3H_7NO_2$	5 Nitro-2-heptene-4-ol	107–108	4	1.0450	(25)	1.4571	(25)	8.80	8.64	15.6	8.7

These nitroparaffin aldehyde condensations illustrate another application of the versatile aluminum alkoxides as catalytic agents.

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Summary

Aluminum ethoxide and magnesium aluminum ethoxide are effective catalysts in the condensation of nitroparaffins with aldehydes. In this type of reaction there is no qualitative difference in the action of these two alkoxides.

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(2) Presented in part before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., April, 1946.

(3) Kulpinski and Nord, *J. Org. Chem.*, **8**, 256 (1943); Villani and Nord, THIS JOURNAL, **69**, 2605 (1947).

(4) The catalysts previously used in this reaction include NaOH, $NaHCO_3$, KOH, K_2CO_3 and Na in absolute ether.

(5) With the lower aldehydes the initial reaction was quite exothermic and the heat of reaction was removed by external cooling.