

A New Approach of Ethoxylation Catalyzed by Bridge-Head Nitrogen Containing Compounds

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Bridge-head nitrogen-containing compounds, (1,4-diazabicyclo-[2.2.2]-octane, 1-azabicyclo-[2.2.2]-octane, 1,5-diazabicyclo-[5.4.0]-undec-5-ene and 1-azabicyclo-[2.2.2]-octane-3-one), successfully catalyze the ethoxylation of dodecyl alcohol. The catalytic activity of any of the first two compounds was four to five times higher than that of an open-chain, symmetrical trialkylamine of similar basicity. The molar mass distribution of the ethoxylated dodecyl alcohol derivatives was of the Weibull-Nycander-Gold type. No Weibull-Törnquist effect could be detected, however, unlike the case realized in ethoxylated systems gained in the presence of trialkylamines. No change in the distribution constant (calculated according to Natta and Mantica) could be observed in the course of these ethoxylation reactions.

The amine catalyzed ethoxylation of dodecyl alcohol has been reported recently (1). In accordance with earlier published observations, amines catalyze the reaction at 80 C well. Particularly good catalytic effect could be achieved with asymmetric amines containing two methyl groups (e.g. N,N-dimethyl octyl amine). In this case the free pair of electrons needed for the catalytic action is not sterically screened. Very good catalytic activity could be expected from amines of favorable steric structure. Consequently, bridge-head nitrogen containing quinuclidines and other molecules of similar structure has been selected as a catalyst in the ethoxylation of dodecyl alcohol.

EXPERIMENTAL

Ethoxylation on a semi-micro scale, gas chromatographic analysis of the reaction products, and calculation of molar mass distribution and of the distribution constants were carried out as described earlier (2). Cyclic amines used were the following: 1,4-diazabicyclo-[2.2.2]-octane (DABCO), 1-azabicyclo-[2.2.2]-octane (ABCO), 1-azabicyclo-[2.2.2]-octane-3-one (ABCON) and 1,5-diazabicyclo-[5.4.0]-undec-5-ene (DABCU), each of them Fluka pss. products. ABCO and ABCON were set free from their hydrochlorides by means of sodium hydroxide (Fig. 1).

RESULTS AND DISCUSSION

Ethylene oxide consumption was plotted against the duration of the reaction time. As in the case of tertiary amines investigated earlier (1), ethylene oxide consumption (v) was a linear function of time (t). Correlation coefficients (r) are better than 0.99. The slope of the straight line is equal to the rate of reaction ($w = v/t$). Rates of reaction in the presence of different catalysts are summarized in Table 1.

Each catalyst investigated accelerated the reaction as expected. Rate of reaction catalyzed by DABCU was nearly equal to that catalyzed by tributylamine or tri-

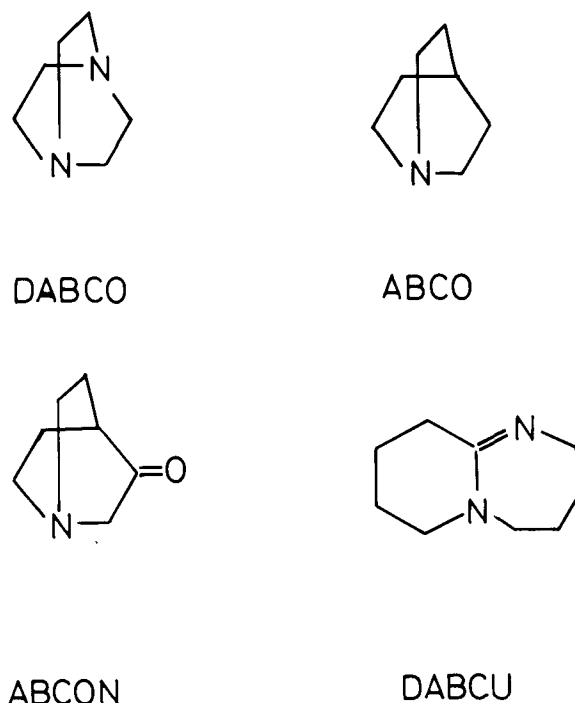


FIG. 1. The structure of the cyclic amines.

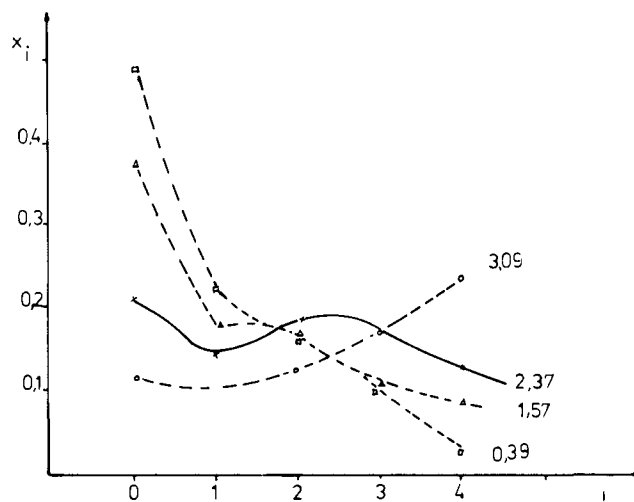


FIG. 2. Molar mass distribution of ethoxylated dodecyl alcohol derivatives gained in a reaction catalyzed by DABCO at 80 C.

octylamine ($w = 0.0258$ and 0.0201 , respectively). The effect of ABCON was similar to that of dimethyloctylamine or dimethylbutylamine ($w = 0.058$ and 0.0573 , respectively). DABCO and ABCO were particularly efficient. Rates of reaction, due to their catalytic activity, were nearly fivefold greater than that obtained with tributyl-

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TABLE 1

The Rate of Ethoxylation Reaction with Different Catalysts at 80 C and with a Catalyst Concentration of 20%

Catalyst	$10^2 \cdot w$ mol/mol min	r
DABCO	12.42	0.996
ABCO	11.88	0.999
DABCU	2.33	0.991
ABCON	4.98	0.990

w, rate of reaction; r, correlation coefficient.

TABLE 3

Distribution Coefficients Calculated According to Natta and Mantica

Catalyst	v	c_1	c_2	c_3	c_4
DABCO	0.99	2.40	2.19	0.75	>15
	1.57	2.65	2.85	3.67	3.09
	2.37	2.26	2.07	2.14	2.18
	3.06	1.96	2.25	1.97	1.15
ABCO	0.93	1.93	1.69	>15	>15
	1.59	2.86	2.23	2.84	0.79
	2.46	2.13	2.14	2.59	2.19
	3.41	2.31	2.28	1.67	1.78
ABCON	2.99	2.28	2.46	2.08	2.43
ABCU	2.10	2.40	1.74	2.75	1.51

v, average degree of ethoxylation mol/mol.

$c_i = k_i/k_0$, distribution constant of the i^{th} homologue, i.e., the rate constant related to that of the dodecyl alcohol.

amine catalyst though the basicity of the three catalysts is almost the same (3).

The effect achieved strongly depends on the concentration of the catalyst (Table 2). Unlike linear tertiary amines the rate of reaction in the presence of DABCO or ABCO is proportional to the concentration of the catalyst in the whole range investigated (0–25%).

Consequently, if the bridge-head nitrogen is of a rigid,

TABLE 2

Dependence of the Rate of Reaction on the Catalyst Concentration at 80 C

Catalyst concentration (mol %)	$10^2 \cdot w$ (mol/mol min)	
	DABCO	ABCO
5	2.22	3.59
10	5.47	7.88
15	8.03	10.08
20	12.12	11.08
25	16.26	—

symmetric structure (e.g., DABCO and ABCO), very good catalytic effect is likely. An electron attracting group (e.g., carbonyl group) diminishes the nucleophilicity of the amino group (ABCON). Asymmetric ring systems or longer alkyl chains unfavorably influence the rate of reaction (DABCU), so that the usual catalytic effect of tertiary amines cannot be exceeded.

The molar mass distributions of ethoxylated dodecyl alcohol derivatives under the catalytic action of DABCO are shown on Figure 2. Distribution constants calculated according to Natta and Mantica (4) are contained in Table 3.

For all the bridge-head nitrogen containing catalysts the distribution is of the Weibull-Nycander-Gold type. The distribution constants do not change according to a definite tendency with the average degree of ethoxylation. Thus, in ethoxylations catalyzed by this type of compounds, no Weibull-Törnquist effect (1,5) is manifested.

REFERENCES

- Sallay, P., J. Morgós, L. Farkas, I. Rusznák, B. Bartha and G. Veress, *J. Amer. Oil Chem. Soc.* 62:824 (1985).
- Farkas, L., J. Morgós, P. Sallay, I. Rusznák, B. Bartha and G. Veress, *J. Amer. Oil Chem. Soc.* 58:650 (1981).
- Brown, H.C., and N.R. Eldred, *J. Am. Chem. Soc.* 71:445 (1949).
- Natta, G., and E. Mantica, *Ibid.* 74:3152 (1952).
- Sallay, P., J. Morgós, L. Farkas, I. Rusznák, G. Veress and B. Bartha, *Tenside Deterg.* 17:298 (1980).

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