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Base-Catalyzed Reaction of 2-Alkylaminoethanols with Acrylic and Methacrylic Esters[1]

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Received February 7, 1957

The reaction of 2-alkylaminoethanols with acrylic and methacrylic esters depends on the nature of the alkyl substituent. The 2-*t*-alkylaminoethanols give the corresponding *t*-alkylaminoethyl esters, but with less highly branched 2-alkylaminoethanols there is a predominance of amide-forming side-reactions which lead to high-boiling mixtures.

The base-catalyzed reaction of 2-dialkylaminoethanols with acrylic and methacrylic esters yields the corresponding 2-dialkylaminoethyl esters, by simple transesterification.[3] The secondary amino groups which are present in monoalkylaminoethanols should bring about a much more complicated reaction. The formation of the *N*-methyl-*N*-2-hydroxyethyl amide is reported in one case from the reaction of a carboxylic ester with 2-methylaminoethanol in the presence of sodium methoxide.[4] Amide formation can therefore be expected to be a major factor. Addition to the acrylic unsaturation may also occur. Addition of secondary amines to acrylic esters is particularly easy. This reaction is usually much slower with methacrylic esters. The base-catalyzed addition of hydroxyl groups to acrylic unsaturation can also occur.[5]

The reaction of several 2-alkylaminoethanols with methyl methacrylate in the presence of aluminum isopropoxide catalyst was studied using the customary transesterification procedures. The extent to which the possible reactions took place was controlled very largely by the nature of the *N*-alkyl substituent. This can best be seen by examining the reactions of three 2-alkylaminoethanols of increasing complexity (methyl, isopropyl and *t*-butyl) with methyl methacrylate. These are therefore given in detail in the experimental section.

The products obtained from 2-methyl- and 2-isopropylaminoethanol were high-boiling mixtures which had high neutralization equivalents, indicating a predominance of the amide-forming reaction. They were low in nitrogen content, indicating further transesterification of the hydroxy amide with another mole of the acrylic ester. All of the distilled fractions had low hydrogenation equivalents, showing little addition to the double bond. Large residues were always present. These may in part have resulted from vinyl polymerization, but condensation polymerization was probably involved. This would occur by addition of secondary amine or alcohol groups to the double bond, with accompanying transesterification and amide-forming reaction. A small fraction (b) was obtained from 2-isopropylaminoethanol which had the expected boiling point for the aminoethyl ester, but this could not be purified.

In contrast, a single distilled product, 2-*t*-butylaminoethyl methacrylate was obtained from 2-*t*-butylaminoethanol in good yield and purity. This structure was established by elementary analysis, neutralization equivalent, and determination of unsaturation by hydrogenation. The distillation residues obtained were relatively small. The small amount of high-boiling by-products and residue indicates that the addition of amine and the amide-forming reaction occurred to a negligible extent. By inference, since the hydroxyl group of the amino alcohol should behave independently of the nature of the *N*-substituent, the addition through the hydroxyl group can be accounted minor in all three reactions. The absence of large residues also shows that vinyl polymerization was probably well-controlled in all three reactions.

A consideration of the kinetic behavior of *t*-butylamine in the two interfering reactions (no data are available for 2-*t*-butylaminoethanol) explains the isolation of this ester in good yield. *t*-Butylamine reacts very poorly with esters;[6] its addition to methyl methacrylate is slow when compared with the addition of other primary amines.[7]

Base-catalyzed reactions of *t*-butylaminoethanol with acrylic esters and other methacrylic esters were equally successful. Examples of other effective catalysts were metallic sodium, sodium methoxide, and tetra-*n*-butyl titanate. The reaction was equally good with other 2-*t*-alkylaminoethanols of which 2-(1,1,3,3-tetramethylbutyl)aminoethanol is representative (Table I).

The hydrochlorides of a number of 2-alkylam-

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TABLE I

PREPARATION OF 2-*t*-ALKYLAMINOETHYL ESTERS, $CH_2{=}C(R^1)COOCH_2CH_2NHR^2$

R^1	R^2	Empirical Formula	Yield, %	B.P., °C.[a]	Mm.	n_D^{25}	d_4^{25}	Anal., % N Calcd.	Anal., % N Found	Equivalent Weight NE[b]	Equivalent Weight HE[b]
CH_3	$(CH_3)_3C$	$C_{10}H_{19}O_2N$	80[c]	100–105	12	1.4401	0.9165	7.6	7.6	185	192
CH_3	C_8H_{17}[d]	$C_{14}H_{27}O_2N$	63	135–138	12	1.4535	0.9130	5.8	5.8	241	254
H	$(CH_3)_3C$	$C_9H_{17}O_2N$	66	84–87	12	1.4396	0.9305	8.2	8.5	166	176
H	C_8H_{17}[d]	$C_{13}H_{25}O_2N$	43	129–131	12	1.4520	0.9175	6.2	6.3	224	228

[a] On redistilled samples. Yields are on basis of slightly less pure fractions, as determined by neutralization and hydrogenation equivalents. [b] NE is equivalent weight by titration with aqeuous HCl, HE is equivalent weight as determined by quantitative hydrogenation. Bromine number is also a satisfactory way to determine unsaturation. [c] Yield with sodium metal, 45%; with sodium methoxide, 61%; with tetra-*n*-butyl titanate, 79%. All yields in the table are given as obtained with aluminum isopropoxide catalyst. [d] 1,1,3,3-Tetramethylbutyl.

inoethyl esters have been prepared by the reaction of acid chlorides with 2-alkylaminoethanol hydrochlorides.[8] By neutralization and careful isolation, some of these have been obtained as the free amino esters, which have been distilled.[8b] However, they rearranged on standing, at a rate dependent on their structure, to the corresponding hydroxyethylamides.[8b, c]

A sample of 2-*t*-butylaminoethyl methacrylate which had been stored for six months in a refrigerator was redistilled and almost all of the compound was recovered. The residue appeared to be vinyl polymer. This ester appears to be considerably more stable than other reported 2-alkylaminoethyl esters.

These new monomers could be polymerized in solution or in bulk by heating with a small amount of azoisobutyronitrile initiator; 2-*t*-butylaminoethyl methacrylate, for example, yielded a hard, colorless, transparent polymer.

EXPERIMENTAL

Raw materials. The 2-alkylaminoethanols were prepared by the addition of ethylene oxide to the corresponding primary amines.[9] Other chemicals used were commercial materials.

Reaction of 2-alkylaminoethanols with methyl methacrylate. General procedure. A mixture of methyl methacrylate (100 g., 1 mole), 2-alkylaminoethanol (0.5 mole), di-β-naphthol inhibitor (6.7 g.), and aluminum isopropoxide (1 g.) was brought to reflux and carefully distilled through a 6-inch Vigreux column equipped with a total reflux-partial take-off stillhead. When the temperature at the stillhead reached 65°, the methanol–methyl methacrylate azeotrope was collected, using a reflux ratio such as to maintain the temperature of distillation below 70°. The elapsed time of distillation was approximately 24 hr. At the end, the temperature rose to the boiling point of methyl methacrylate. Determination of the saponification number of the distillates gave the per cent of methyl methacrylate. The rest of the material was assumed to be methanol. About 80% of the theoretical amount of methanol was recovered. The product was then distilled through a 12-inch packed column and fractions taken as noted. Data are given on the basis of grams per 100 grams of starting alkylaminoethanol. Analytical data obtained were NE (equivalent weight by acid titration), HE (equivalent weight by quantitative hydrogen absorption) and % N. *With methylaminoethanol*[9a] calcd. for $C_7H_{13}O_2N$,[10] mol. wt. 143, % N 9.8. Fraction (a) 10 g., b.p. 44–58° (1 mm.), NE, 257; HE, 359; % N 8.1. (b) 22 g., b.p. 58–123° (0.8 mm.), NE, 495; HE, 141; % N 7.7. (c) 15.9 g., b.p. 123° (0.8 mm.), NE, 1829; HE, 167; % N 7.3. (d) 20.7 g., b.p. 123–126° (1 mm.), NE, 1735; HE, 150; % N 7.1. (e) 16.0 g., b.p. 126–145° (1.5 mm.), NE, 831; HE, 135; % N 7.4. (f) residue 83 g. *With isopropylaminoethanol*[9b] calcd. for $C_9H_{17}O_2N$,[10] mol. wt. 171, % N, 8.2. Fraction (a) 13.8 g., b.p. 99–113° (28 mm.), % N, 11.2. (b) 19 g., b.p. 115° (28 mm.), NE, 221; HE, 285; % N, 9.0. (c) 3.5 g., b.p. 115–155° (28 mm.). (d) 30.2 g., b.p. 155–185° (28 mm.), NE, 821; HE, 257; % N, 6.6. (e) 10.0 g., b.p. 185° (28 mm.), % N, 6.4. (f) residue 70.5 g. *With t-butylaminoethanol*[9c] calcd. for $C_{10}H_{19}O_2N$,[10] mol. wt. 185; % N, 7.6. Fraction (a) 19.5 g., b.p. 105–116° (30 mm.), NE, 165; % N, 8.5. (b) 20.4 g., b.p. 117° (30 mm.), NE, 183; %N, 7.8. (c) 56 g., b.p. 120° (30 mm.), NE, 185; HE, 198; % N 7.5. (d) 6.0 g., b.p. 122° (30 mm.), NE, 190; HE, 181; % N, 7.5. (e) 11.0 g., b.p. 122–127° (30 mm.), NE, 242; HE, 155; % N, 5.6. (f) residue 19.0 g. The product fractions b, c, and d therefore distilled at 117–122° (30 mm.), and amounted to 82.4 g. from 100 g. *t*-butylaminoethanol (52%). Yields as high as 80% were obtained in later runs.

Reactions were carried out using sodium methoxide or tetra-*n*-butyl titanate in essentially the same manner. It was later found advantageous to dry the starting materials by refluxing the reaction mixture before adding the catalyst, and removing a small forerun. When metallic sodium was used as a catalyst, it was dissolved in the *t*-butylaminoethanol before the addition of the methyl methacrylate.

t-Butylaminoethyl acrylate. A mixture of *t*-butylaminoethanol[9c] (58.5 g., 0.5 mole), methyl acrylate (86 g., 1 mole), di-β-naphthol (7.2 g., 0.025 mole) and aluminum isopropoxide (1 g.) was distilled as described previously. After about 10 hr. distillation, there was obtained a fraction amounting to 29 g., b.p. 65–78°. The temperature of the distillate then was constant at 78°, the boiling point of methyl acrylate. Distillation was continued under reduced pressure. After removal of a small forerun, the product (56 g., 66%) was collected at 90–100° (13 mm.). On careful redistillation, the pure product, b.p. 84–87°/12 mm., was obtained.

2-(1,1,3,3-Tetramethylbutyl)aminoethyl acrylate. A mixture

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(9) (a) L. Knorr and H. Matthes, *Ber.*, **31**, 1069 (1898); (b) H. Matthes, *Ann.*, **316**, 312 (1901); (c) N. Bortnick, L. S. Luskin, M. D. Hurwitz, W E Craig, L. J. Exner, and J. Mirza, *J. Am. Chem. Soc.*, **78**, 4040 (1956).

(10) The empirical formula corresponds to the sum of the atoms in the starting materials less a mole of methanol.

of 2-(1,1,3,3-tetramethylbutyl)aminoethanol[9c] (173 g., 1 mole), ethyl acrylate (200 g., 2 moles), di-β-naphthol (14 g.) and aluminum isopropoxide (2 g.) was distilled as before. There was collected 53 g., b.p. 74–80°, over a period of 21 hr. and then the temperature was allowed to rise and 74 g. of excess ethyl acrylate was collected, b.p. 80–95° over the next 6 hr. The product was then distilled and 135 g. (59%), b.p. 140–147° (25 mm.) was collected. A residue of 69 g. remained in the flask.

2-(1,1,3,3-Tetramethylbutyl)aminoethyl methacrylate. The procedure given above for the corresponding *t*-butylaminoethyl methacrylate was followed. On distillation of the product there was obtained a small forerun boiling 115–125° (9 mm.) which was apparently a mixture of the aminoethanol and the methacrylate. The product (63%) was collected at 125–132° (9 mm.).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE UNION OIL COMPANY OF CALIFORNIA]

Synthesis of Unsymmetrical Trialkyl Phosphorotetrathioates

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Received February 8, 1957

Mercaptans react with phosphorus pentasulfide to give, among other products, alkyl phosphenotrithioates, dialkyl hydrogen phosphorotetrathioates, and trialkyl phosphorotetrathioates. This paper is concerned with the use of these reactions, as well as the addition of olefins to dialkyl hydrogen phosphorotetrathioates, to produce unsymmetrical trialkyl phosphorotetrathioates.

Infrared spectra of these compounds were helpful in their identification.

Trialkyl phosphorotetrathioates are organophosphorus compounds of the general structure $(RS)_3PS$. They are classified as symmetrical if all the R groups are identical; unsymmetrical if at least one R group is dissimilar.

A few compounds of this type are described in the literature. Schulze, Short, and Crouch prepared several tri-*t*-alkyl phosphorotetrathioates from phosphorus pentasulfide and *t*-alkyl mercaptans.[1] Triethyl phosphorotetrathioate, tri-*t*-amyl phosphorotetrathioate, tribenzyl phosphorotetrathioate, tri-*p*-tolyl phosphorotetrathioate, and triphenyl phosphorotetrathioate are described by Kosolapoff,[2] and tridodecyl phosphorotetrathioate is discussed by Salzberg and Werntz in a patent.[3] Methods of preparing these compounds include the reactions of mercaptans or sodium mercaptides with thiophosphoryl chloride, of mercaptans with alkyl phosphenotrithioates ($RSPS_2$), as well as of mercaptans with phosphorus pentasulfide.[4] Reference 2 is a general reference for all these reactions.

From the known reactivity of the alkyl phosphenates,[5] it appeared that if the corresponding alkyl phosphenotrithioates could be prepared easily they could become key intermediates in the synthesis of a wide variety of organophosphorus compounds. This paper, part of such a program, is concerned with unsymmetrical trialkyl phosphorotetrathioates prepared from methyl phosphenotrithioate as the intermediate.

The pertinent reactions in the preparation of unsymmetrical trialkyl phosphorotetrathioates are

$$2CH_3SH + P_2S_5 \longrightarrow 2CH_3SPS_2 + H_2S \qquad (1)$$

$$CH_3SPS_2 + RSH \longrightarrow \begin{matrix} CH_3S \\ | \\ P(S)SH \\ | \\ RS \end{matrix} \qquad (2)$$

$$\begin{matrix} CH_3S \\ RS \end{matrix}\!\!>\!P(S)SH + \text{olefin} \longrightarrow \begin{matrix} CH_3S \\ RS \end{matrix}\!\!>\!P(S)SR' \qquad (3)$$

Methyl mercaptan can react with phosphorus pentasulfide to yield a number of products. The simplest route to methyl phosphenotrithioate is shown in reaction (1), in which two moles of the mercaptan react with one mole of phosphorus pentasulfide. As the ratio of mercaptan to phosphorus pentasulfide increases, reactions (4) and (5) assume importance and eventually predominate.

$$4CH_3SH + P_2S_5 \longrightarrow 2(CH_3S)_2P(S)SH + H_2S \qquad (4)$$

$$6CH_3SH + P_2S_5 \longrightarrow 2(CH_3S)_3PS + 3H_2S \qquad (5)$$

The use of excess phosphorus pentasulfide results in a higher yield of methyl phosphenotrithioate

$$(CH_3S)_3PS + P_2S_5 \longrightarrow 3CH_3SPS_2 \qquad (6)$$

By using the proper amounts of reactants, and by carefully controlling the release of hydrogen sulfide, reaction (1) can provide at least 60 mole percent yields of methyl phosphenotrithioate. Control of hydrogen sulfide enhances the yield because of the possibility of reaction (7).

$$CH_3SPS_2 + H_2S \longrightarrow CH_3SP(S)(SH)_2 \qquad (7)$$

A simple way to achieve this control is to run reac-

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