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The Synthesis and Cyclopolymerization of the N, N-Diallyl- and N, N-Dimethallyl-Derivatives of Methanesulfonamide and Ethanesulfonamide

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The Synthesis and Cyclopolymerization of the N,N-Diallyl- and N,N-Dimethallyl-Derivatives of Methanesulfonamide and Ethanesulfonamide

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SUMMARY

A series of new N,N-diallyl- and N,N-dimethallylalkanesulfonamides are prepared by the reaction of diallyl- or dimethallylamine with the requisite alkylsulfonyl chloride. Radical polymerization gives soluble polymers which do not contain any residual double bonds. Evidence for a cyclopolymer structure containing six-membered rings is obtained from spectroscopic comparisons with model piperidine derivatives.

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INTRODUCTION

Matsoyan [1] and Ostroverkov [2] and their respective co-workers have studied the polymerization of N-substituted diallylamines. In all cases in which an electron-attracting group is attached to the nitrogen atom the compounds polymerized by the cyclopolymerization mechanism to form substituted piperidine rings in the main polymer chain. We have prepared and studied the polymerization of a series of new N,N-diallyl- and N,N-dimethallyl-derivatives of methane- and ethanesulfonamide [3].

RESULTS AND DISCUSSION

The monomers were obtained in good yields by the general reaction:

$$R.SO_2Cl + NH(CH_2.C(R')=CH_2)_2 \xrightarrow{\text{base}} R.SO_2N(CH_2.C(R')=CH_2)_2$$

where R = Me or Et and R' = H or Me. The pure monomers were colorless, high-boiling liquids showing strong absorption bands in the IR spectrum at 1150 and 1325 cm^{-1} (S=O), and at 910 and 995 cm^{-1} ($-CH=CH_2$) or 915 and 1005 cm^{-1} ($-CMe=CH_2$). Sodium hydroxide solution was used as the base in the preparation of the diallyl derivatives but better yields of the dimethallyl derivatives were obtained by using either trimethallylamine or excess dimethallylamine as the base.

The monomers polymerized readily in bulk with radical initiators to a maximum conversion of about 30%, giving polymers with softening points in the range 40-150° and molecular weights from 930 to 2300 (Table 1). The polymers, after purification, were obtained as white powders giving correct analytical data, and soluble in a variety of solvents from which they could be recovered unchanged. The IR spectra of the polymers showed that the absorption bands associated with the carbon-carbon double bonds in the monomers were absent. On obtaining linear polymers with no residual carbon-carbon double bonds it was assumed that cyclopolymerization had occurred exclusively and that the linear polymer chains contained six-, or possibly five-, membered heterocyclic structures (Fig. 1).

TABLE 1. Polymerization of $R.SO_2N(CH_2.C(R')=CH_2)_2$

R	R'	Initiator[a] (mole-%) A	B	Time (hr)	Conversion (%)	Softening point (°C)	Molecular weight ($\bar{M}_n$)
CH_3	H	1		5	24	115-120	935
		3		5	31	103-115	1625
			1.4	5	19	116-121	2280
C_2H_5	H	1		20	22	46-82	1570
		3		5	28		
			2	20	23	43-105	1840
CH_3	CH_3	1		20	13	134-150	1920
		3		20	17	130-140	
			2	20	13		
C_2H_5	CH_3	1		20	12	138-150	1256
		3		20	16	130-140	
			2	20	19		

[a] A = azodiisobutyronitrile; B = benzoyl peroxide.

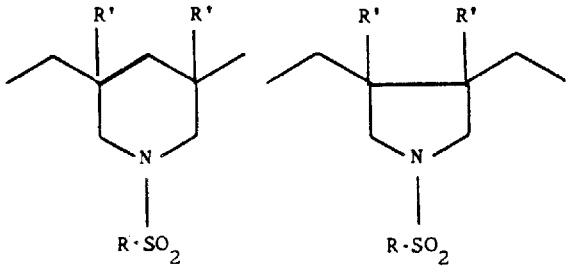
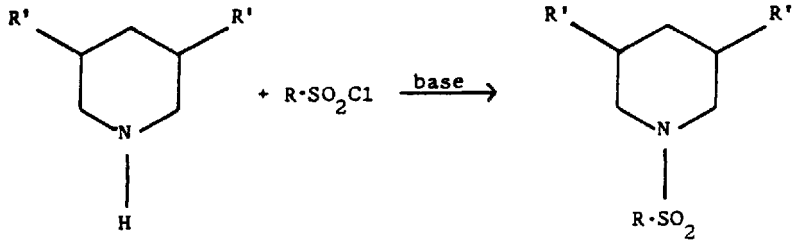


FIG. 1. Possible cyclopolymer unit structures.

For spectroscopic comparisons, four model piperidine derivatives were prepared as shown (Fig. 2). Although a number of dimethylpiperidines can be obtained by reducing the corresponding dimethylpyridine, the preparation of 3,5-lupetidine (R' = Me) is reported only from cyclization reactions [4, 5]. However, by using sodium in absolute alcohol, 3,5-dimethylpyridine was reduced to 3,5-lupetidine in 33% yield.



R = Me or Et. R' = H or Me

FIG. 2. Preparation of model compounds.

A comparison of the IR spectra of the model compounds with the corresponding cyclopolymers showed close similarities, particularly in the key absorption bands associated with the C–H bonds of the piperidine ring. For example, the C–H valency vibrations of the CH_2 groups in the piperidine ring, at approximately 2875 and 2930 cm^{-1}, as well as the asymmetric stretch for a CH_2 group from 1453-1458 cm^{-1} characteristic of a strainless ring, were present in the spectra of both model compounds and the corresponding polymers.

The low molecular weights of this series of polymers are presumably the consequence of the degradative chain transfer commonly observed with allyl and methallyl monomers. Further work is directed towards the preparation of the diacrylyl- and dimethacrylyl-derivatives of the two alkanesulfonamides. Such monomers should afford cyclopolymers of high molecular weight.

EXPERIMENTAL

Infrared spectra were recorded as liquid films or as potassium bromide disks using a Perkin-Elmer "Infracord 137," and calibrated against a polystyrene film absorption peak at 1603 cm^{-1}. Melting points were recorded on a Gallenkamp melting apparatus and are uncorrected.

N,N-Diallylalkanesulfonamides

Diallylamine (3.1 g, 0.032 mole) and a solution of sodium hydroxide (1.35 g) in water (3.1 ml) were mixed and the mixture cooled in ice during the dropwise addition of the alkanesulfonyl chloride (0.032 mole). The mixture was heated at 50° for 3 hr with vigorous stirring and then treated with an aqueous solution of potassium carbonate, extracted with ether, and the ether extract dried over magnesium sulphate. Removal of the ether gave the N,N-diallylalkanesulfonamides as colorless liquids; N,N-diallylmethanesulfonamide (4.85 g, 87% yield), bp 98-99°/2 mm, n_D^{20} 1.4741 (found: C, 48.18; H, 7.46; N, 7.82; $C_7H_{13}NO_2S$ requires C, 47.99; H, 7.48; N, 8.00) and N,N-diallylethanesulfonamide (5.5 g, 91% yield), bp 148°/18 mm, n_D^{20} 1.4728 (found: C, 50.98; H, 8.12; N, 7.20; $C_8H_{15}NO_2S$ requires C, 50.76; H, 7.99; N, 7.40).

N,N-Dimethallylmethanesulfonamide

To a vigorously stirring mixture of trimethallylamine (15.7 g, 0.088 mole) and methanesulfonyl chloride (10.1 g, 0.088 mole) in dry benzene (28 ml), dimethallylamine (10.96 g, 0.088 mole) was added dropwise over 20 min. After the exothermic reaction was complete, the mixture was cooled to room temperature when a white crystalline precipitate of dimethallylamine hydrochloride (5.1 g), mp 142-143° was formed. The filtrate was made alkaline and extracted with ether. The ether was removed and the residue distilled under reduced pressure, giving dimethallylamine and trimethallylamine and N,N-dimethallylmethanesulfonamide (9 g, 51% yield), bp 145-146°/11 mm, n_D^{20} 1.4761 (found: C, 53.50; H, 8.42; N, 6.61; $C_9H_{17}NO_2S$ requires C, 53.20; H, 8.44; N, 6.90).

N,N-Dimethallylethanesulfonamide

Ethanesulfonyl chloride (13.7 g, 0.107 mole) was added dropwise over 20 min to a solution of dimethallylamine (26.8 g, 0.214 mole) in dry benzene (100 ml) and the mixture heated at 50° for 3 hr. Dimethallylamine hydrochloride precipitated from the solution on cooling, the solvent was then removed in vacuo, and excess dilute hydrochloric acid added to the residue. Ether extraction of the aqueous mixture and distillation of the dried extract gave N,N-dimethallylethanesulfonamide as a colorless liquid in 57% yield, bp 159-160°/19 mm, n_D^{20} 1.4747 (found: C, 55.01; H, 8.66; N, 6.29; $C_{10}H_{19}NO_2S$ requires C, 55.26; H, 8.81; N, 6.45).

3,5-Lupetidine

To a stirred solution of 3,5-dimethylpyridine (42.8 g, 0.4 mole) in dry ethanol (1000 ml) was added sodium (110.4 g, 4.8 g atom) in small portions at a rate sufficient to maintain vigorous boiling. The solution was refluxed for 1 hr, cooled, excess water added, and the mixture distilled under reduced pressure to obtain, as distillate, an alcoholic solution of the product. Most of the alcohol was removed from this solution by careful distillation, and on adding water to the residue an oily upper layer separated which was extracted with ether. Removal of the ether and distillation of the residue at atmospheric pressure gave 3,5-lupetidine (15 g, 33% yield) as a colorless liquid, bp 144° (found: C, 74.22; H, 12.89; N, 12.15; calculated for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37).

N-(Alkylsulfonyl)piperidines

A mixture of piperidine (2.72 g, 0.032 mole) and sodium hydroxide solution (1.35 g in 3.1 ml) was cooled before the dropwise addition of the alkanesulfonyl chloride (0.032 mole). The mixture was heated at 70° for 3 hr with vigorous stirring and was then treated with potassium carbonate solution before extracting the product with ether. This method was used to prepare N-(methylsulfonyl)piperidine (4.4 g, 85% yield), mp 49-50°, as silvery white flakes from petroleum

ether (60-80) (found: C, 44.45; H, 7.91; N, 8.82; calculated for $C_6H_{13}NO_2S$: C, 44.15; H, 8.03; N, 8.58) and N-(ethylsulfonyl)-piperidine (4.6 g, 81% yield), bp 148°/11 mm (found: C, 47.15; H, 8.67; N, 7.78; $C_7H_{15}NO_2S$ requires C, 47.42; H, 8.53; N, 7.90).

N-(Alkylsulfonyl)-3,5-dimethylpiperidines

The same molar amounts of the corresponding reactants and the same reaction conditions as above gave white precipitates, crystallizing from petroleum ether (80-100) as N-(methylsulfonyl)-3,5-dimethylpiperidine (4.2 g, 69% yield), mp 109-110° (found: C, 50.30; H, 8.69; N, 7.24; $C_8H_{17}NO_2S$ requires C, 50.23; H, 8.96; N, 7.32), and N-(ethylsulfonyl)-3,5-dimethylpiperidine (4 g, 58% yield), mp 78-79° (found: C, 52.49; H, 9.60; N, 6.63; $C_9H_{19}NO_2S$ requires C, 52.65; H, 9.33; N, 6.82).

Polymerization of N,N-diallyl- and N,N-dimethallylalkanesulfonamides

The general polymerization procedure was as follows: The monomer (1.0-3.0 g) and initiator (1-3 mole-% of monomer) were sealed in vacuo in a Pyrex tube and heated at 80° for the requisite period of time. The mixture was then added to an excess of ether to precipitate the polymer, which was then purified either by continuous ether extraction or by solution in chloroform followed by reprecipitation with ether, and finally vacuum dried. The variety of polymerization experiments is summarized in Table 1. Confirmatory microanalytical data were obtained for all the polymers described.

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