Fig. 1. Percentage of bromo ketones plotted versus time (in hours) for the rearrangement of 1,1-dibromobutanone-2. 1, $\text{CH}_3\text{CH}_2\text{COCHBr}_2$; 2, $\text{CH}_3\text{CHBrCOCH}_2\text{Br}$; 3, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{Br}$; 4, $\text{CH}_3\text{CHBrCOCHBr}_2$; 5, $\text{CH}_3\text{CHBrCOCH}_3$; 6, $\text{CH}_3\text{CBr}_2\text{COCH}_2\text{Br}$; 7, $\text{CH}_3\text{CBr}_2\text{COCH}_3$.

case it was also found that the addition of hydrogen bromide catalyzed the rearrangement. 16.6 mg of 66% hydrobromic acid were added to 1.18 g of 1,1-dibromobutanone-2. Already after 5 h 1,3-dibromobutanone-2 was the main component in this sample.

The variety of products indicates that the rearrangement is complex. A discussion of the different reactions taking part will be published elsewhere together with a discussion of the rearrangement of 1,1-dibromoacetone.

Experimental. The NMR-spectra were recorded on a Varian Associates Model A 60 spectrometer.

1,1-Dibromobutanone-2. To 10.0 g of diazomethane in 680 ml of ether, 7.4 g of propionyl chloride dissolved in 100 ml of ether were added dropwise under stirring. After standing for 24 h one third of the ether was distilled off together with the excess of diazomethane. 13.0 g of bromine dissolved in 20 ml of carbon tetrachloride were added, the organic layer was washed with water, the solvents were distilled off at reduced pressure and the crude product was distilled at once. A fraction, 10.3 g, b.p. 60–64°C at 8 mm, was collected. On redistillation the b.p. 63–65°C at 9 mm and $n_D^{25} = 1.5112$ were obtained.

1,1-Dibromopentanone-2. The synthesis was performed as above; 9.8 g of diazomethane in 750 ml of ether, 8.3 g of butyryl chloride and 12.5 g of bromine gave 9.6 g of 1,1-dibromopentanone-2, b.p. 73–76°C at 10 mm, $n_D^{25} = 1.5030$, purity 90% (NMR).

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Monoalkylsulfamyl Chlorides

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In the search for new compounds with possible drug action intermediates with the constitution RNHSO_2Cl (R being lower alkyl) were desirable. Although the corresponding dialkylsulfamyl chlorides $\text{R}_2\text{NSO}_2\text{Cl}$ have been known for nearly a century,^{1,2} and the unsubstituted sulfamyl chloride for some years³ monoalkylsulfamyl chlorides do not seem to be described. As dialkylsulfamyl chlorides can be made by the reaction between sulfur chloride and the hydrochlorides of lower secondary amines^{2,4} a similar reaction might be expected to take place when the hydrochloride of a primary amine is used. In fact this was found to be the case with the normal C_2 – C_8 alkyl amines. When the hydrochlorides of methyl-, hexyl-, cyclohexyl-, and octylamine were used the yields were too low to permit the isolation of monoalkylsulfamyl chlorides. That at least methylsulfamyl chloride was formed can be concluded from the fact that N-methyl-N'-propylsulfamide could be ob-

Table 1. Monoalkylsulfamyl chlorides: RNHSO_2Cl

R	Quantities			Yield ^a %	B.p. ^b °C/mm	Formula	Analyses ^{b,c}			
	RNH ₂ , HCl		SO ₂ Cl ₂ ml					C	H	N
	used g	recd. g								
C ₂ H ₅	52	23	105 ^d	42	52/0.05	C ₂ H ₆ ClNO ₂ S	Found Calc.	16.55 16.73	4.24 4.21	9.93 9.76
n-C ₃ H ₇	52	26	350	13	78/0.2	C ₃ H ₈ ClNO ₂ S	Found Calc.	22.75 22.87	5.13 5.12	8.70 8.89
n-C ₄ H ₉	77	27	450	39	80/0.11	C ₄ H ₁₀ ClNO ₂ S	Found Calc.	28.16 27.99	5.92 5.87	7.91 8.16
n-C ₅ H ₁₁	19	12	150	8	95/0.15	C ₅ H ₁₂ ClNO ₂ S	Found Calc.	32.12 32.33	6.37 6.52	7.31 7.54

^a Based on RNH₂, HCl used. ^b Redistilled samples.^c Microanalyses conducted by G. Cornali and W. Egger.^d A further 100 ml portion of sulfuryl chloride was added after 4 h of reflux.

tained when the impure product was treated with propylamine.

The four monoalkylsulfamyl chlorides which were prepared in the pure state are tabulated in Table 1. They are all clear liquids with a characteristic smell similar to that of the dialkylsulfamyl chlorides, and they react very rapidly with water, ammonia, etc. Ethylsulfamyl chloride was reacted with butylamine, and the resulting N-ethyl-N'-butylsulfamide was characterized by its melting point and elementary analysis.

Experimental. Monoalkylsulfamyl chlorides. General procedure. The amine hydrochloride was heated for about 18 hours on a water thermostat at approximately 75°C with excess sulfuryl chloride (for quantities, see Table 1). At the end of this period most of the sulfuryl chloride had generally disappeared even if a 1 m long Allihn-type condenser was employed. In some cases, therefore, more sulfuryl chloride was added during the reaction. The resulting oily substance was treated with dry

ether, and a precipitate of unreacted amine hydrochloride was filtered off. The filtrate was evaporated, and the residual oil was distilled under reduced pressure (0.2–2 mm).

N-Methyl-N'-propylsulfamide was obtained by the reaction between propylamine and impure methylsulfamyl chloride in ethereal solution. M.p. 57–58°C (ether-light petroleum). (Found: C 31.20; H 8.02; N 18.36. Calc. for C₄H₁₂N₂O₂S: C 31.56; H 7.95; N 18.41).

N-Ethyl-N'-butylsulfamide was obtained in a similar way from ethylsulfamyl chloride. M.p. 73–75°C (hexane). (Found: C 39.90; H 8.87; N 15.39. Calc. for C₆H₁₆N₂O₂S: C 39.99; H 8.95; N 15.55).

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