[7] Experimental procedure: 2: 30% H_2O_2 (11.3 g, 100 mmol) was added with stirring to ethyl pyruvate (17.3 g, 150 mmol) at -10 to $0°C$ [3]. This solution was then added with stirring and cooling (-5 to $0°C$) to a mixture of 1 (10 mmol), conc. H_2SO_4 (3 g), H_2O (8 g), $FeSO_4 \cdot 7H_2O$ (28 g, 100 mmol), and CH_2Cl_2 (150 mL). After 15 min of further stirring, the resulting mixture was poured into ice water, the phases were separated, and the aqueous phase was exhaustively extracted with CH_2Cl_2. After drying over anhydrous Na_2SO_4, the solvent and excess ethyl pyruvate were removed in vacuo. The spontaneously crystallizing, colorless needles were recrystallized from diethyl ether: Yield: 1.4 g (81%) 2; mp $= 89-93°$; correct C,H,N analyses. IR (KBr): 1715 ($v_{C=O}$), 2250 cm^{-1} ($v_{C=N}$): MS: m/z 176 (2%, M^+), 104 (100%); ^{1}H-NMR (CDCl$_3$, 90 MHz): $\delta = 9.00$ (d, 1H, $J = 5$ Hz, H-6), 8.39 (d, 1H, $J = 2$ Hz, H-3), 7.75 (dd, 1H, $J = 5$ Hz, 2 Hz, H-5), 4.53 (q, 2H, $J = 7$ Hz, CH$_2$), 1.48 (t, 3H, $J = 7$ Hz, CH$_3$).

[8] 8-10, 12: 30% H_2O_2 (3.4 g, 30 mmol) was added with stirring to ethyl pyruvate (5.2 g, 45 mmol) at -10 to $0°C$ [3]. This solution was then added with stirring and cooling (-5 to $0°C$) to a mixture of 7 or 11 (10 mmol), conc. H_2SO_4 (3 g), H_2O (8 g), $FeSO_4 \cdot 7H_2O$ (8.3 g, 30 mmol), and CH_2Cl_2 (30 mL).—8-10: After a work-up similar to that for 2, the residue is separated by medium pressure chromatography (Lobar® size B, LiChroprep® Si60, Merck; dichloromethane/ethyl acetate 5:1). Fraction I: 394 mg 10 [11] (22%); fraction II: 580 mg 9 [10] (33%); fraction III: 366 mg 8 [9] (21%).—12: After washing the spontaneously crystallizing, pale yellow needles with diisopropyl ether, 1.2 g (80%) of the product is obtained, whose spectroscopic data are identical with those of authentic material [12].

[9] 8: Structure determination on the basis of the ^{1}H-NMR spectrum [CDCl$_3$, 90 MHz: $\delta = 9.10-8.90$ (m, 1H, H-6), 8.38-8.18 (m, 1H, H-4), 7.83-7.60 (m, 1H, H-5), 4.58 (q, 2H, $J = 7$ Hz, CH$_2$), 1.49 (t, 3H, $J = 7$ Hz, CH$_3$)] as well as the hydrolysis in 2 N Na$_2$CO$_3$ solution to 3-cyano-2-pyridinecarboxylic acid [13].

[10] L. Novacek, K. Palat, M. Celadnik, E. Matuskova, Cesk. Farm. 11 (1962) 76; Chem. Abstr. 57 (1962) 15067i.

[11] H. Watanabe, Y. Kikugawa, S. Yamada, Chem. Pharm. Bull. 21 (1973) 465.

[12] H. Shindo, Chem. Pharm. Bull 8 (1960) 33.

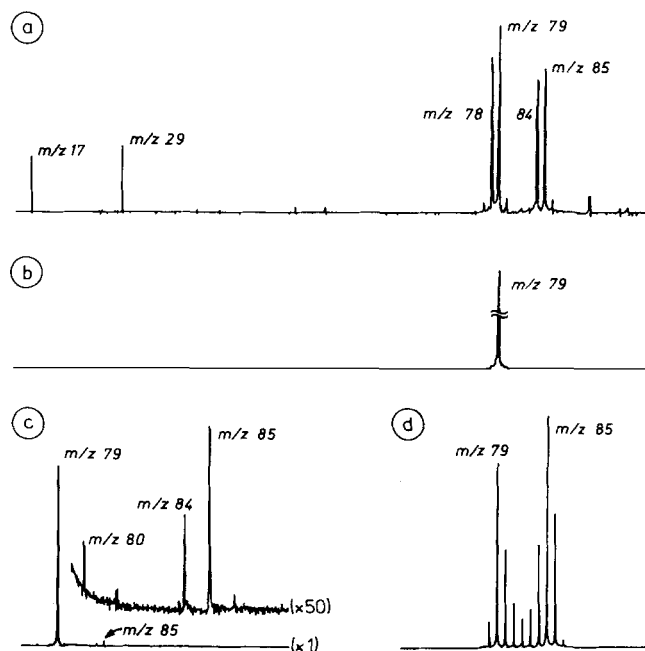[13] S. Fallab, H. Erlenmeyer, Helv. Chim. Acta 34 (1951) 488.

Proton Exchange between Arenium Ions and Arenes in the Gas Phase**

By Dietmar Kuck,* Steen Ingemann, Leo J. de Koning, Hans-Friedrich Grützmacher, and Nico M. M. Nibbering

Proton transfer reactions are known to be extremely fast in general.[1] In the gas phase, they can be studied by modern, time-resolved mass spectrometry. Thus, MIKE spectrometry of metastable ions[2] (time scale 10^{-5} to 10^{-4} s) is used for the investigation of intramolecular hydrogen migration reactions, e.g., the proton exchange in protonated α,ω-diphenylalkanes [Eq. (1a)],[3] while, for intermolecular exchange reactions,[4] Fourier transform ion cyclotron resonance (FT-ICR) spectrometry[5] is becoming increasingly important (time scale 10^{-3} to 10^{+1} s). We report here on the intermolecular proton exchange [Eq. (1b)] between simple arenium ions and arenes[4c] in the cell of a FT-ICR mass spectrometer[6] (Ar, Ar' = aryl).

$$ArH^\oplus-(CH_2)_n-Ar' \rightleftharpoons Ar-(CH_2)_n-Ar'H^\oplus \qquad (1a)$$
$$2 \leq n \leq 20$$

$$ArH_2^\oplus + Ar'H \rightleftharpoons ArH + Ar'H_2^\oplus \qquad (1b)$$

[*] Dr. D. Kuck, Prof. Dr. H.-F. Grützmacher
Fakultät für Chemie der Universität
Postfach 8640, D-4800 Bielefeld 1 (FRG)

Prof. Dr. N. M. M. Nibbering, Dr. S. Ingemann, L. J. de Koning
Laboratorium voor Organische Scheikunde, Universiteit van Amsterdam
Nieuwe Achtergracht 129, NL-1018 WS Amsterdam (The Netherlands)

[**] D. K. thanks the Deutscher Akademischer Austauschdienst, Bonn, and the Ministerie voor Onderwijs en Wetenschappen, The Hague, for a grant.

Fig. 1. a) FT-ICR mass spectrum of a mixture of CH$_4$, C$_6$H$_6$, and C$_6$D$_6$ [7a]; b) after ejection of all ions except C$_6$H$_7^\oplus$ (m/z 79) at the time $t_r = 0$; c) after $t_r = 190$ ms, and d) after $t_r = 6290$ ms.

We generated the benzenium ions $C_6H_7^\oplus$ and $C_6HD_6^\oplus$ by electron-impact ionization of a mixture of benzene, [D$_6$]benzene, and methane at 10^{-4} Pa (Fig. 1a).[7a] All ions except $C_6H_7^\oplus$ (m/z 79) were then removed from the ICR cell by "notch ejection"[8] (Fig. 1b); subsequently, the ion-molecule reactions of the benzenium ions isolated in this way with the C_6H_6/C_6D_6 mixture were followed as a function of time (t_r). Figures 1c and 1d show all ions present in the cell at $t_r = 190$ and 6290 ms, respectively; Figure 2 displays the dependence of the relative abundance of the product ions $C_6(H,D)_7^\oplus$ on t_r.
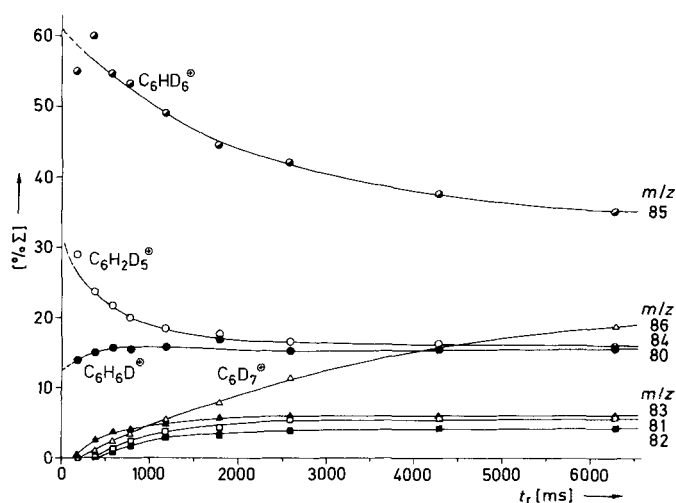

Fig. 2. Relative abundances of the product ions in the system $C_6H_7^\oplus/C_6H_6/C_6D_6$ as a function of the reaction time t_r given relative to the sum of all product ions and corrected for naturally occurring ^{13}C.
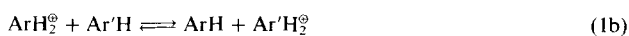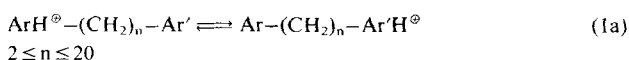
The measurements allow two conclusions to be drawn:
1. The proton exchange between benzenium ions and benzene is a surprisingly slow process (cf., for example, the system $D_3O^\oplus/C_6H_6$[4a]). For short reaction times t_r (under

"single collision conditions"), no isotopomers other than $C_6HD_6^{\oplus}$ (simple $H^{\oplus}$ transfer), $C_6H_6D^{\oplus}$ (simple $H^{\oplus}/D^{\oplus}$ exchange), and $C_6H_2D_5^{\oplus[9]}$ are formed. The light and the heavy benzenium ions also predominate under "multiple collision" conditions ($t_r \gtrsim 300$ ms).

2. The proton exchange occurs not only by consecutive ion-molecule reactions, but also within the collision complexes (e.g., $[C_6H_7^{\oplus} \cdot C_6D_6]^*$). This follows from extrapolation of the relative abundances of the product ions to $t_r = 0$: The exchange products $C_6H_6D^{\oplus}$ (m/z 80) and $C_6H_2D_5^{\oplus}$ (m/z 84) are already present there (Fig. 2).

Similar results are obtained from the corresponding investigation of the reaction of isolated $C_6HD_6^{\oplus}$ ions with the C_6H_6/C_6D_6 mixture.

A further experiment allows a clear distinction to be made between these two exchange processes (Scheme 1). If the ions $C_6HD_6^{\oplus}$ (m/z 85) are continuously removed from the cell for the entire reaction time,[7b] the formation of all further $C_6(H,D)_7^{\oplus}$ ions is suppressed to the extent that they are formed via $C_6HD_6^{\oplus}$ (Scheme 1a). In contrast, $C_6(H,D)_7^{\oplus}$ ions that arise via $H^{\oplus}/D^{\oplus}$ exchange *within* the collision complexes $[C_6H_7^{\oplus} \cdot C_6D_6]^*$ are *not* suppressed (Scheme 1b). In Table 1 the relative abundances of the ions present in the cell after $t_r = 790$ ms—with and without continuous removal of the ions m/z 85—are compared.

albeit in lower absolute abundances. Thus, for example, the abundance of the ions $C_6H_6D^{\oplus}$ (m/z 80) decreases by only a relative 19%; in contrast, the formation of the ions $C_6D_7^{\oplus}$ (m/z 86), which are formed *exclusively* by consecutive ion-molecule reactions (Scheme 1a), is completely suppressed.[10]

The proton exchange between toluenium ions and toluene ($C_7H_8/C_7D_8/CD_4$)[7a] is even slower than that between the lower homologues. Here, too, the exchange takes place partly within the collision complexes (e.g., $[C_7D_9^{\oplus} \cdot C_7H_8]^*$). Thus, a fraction of the $C_7(H,D)_9^{\oplus}$ isotopomers are still formed despite continuous removal of the ions $C_7H_8D^{\oplus}$. A possible reason is that the proton exchange in the collision complex $[C_7H_9^{\oplus} \cdot C_7H_8]^*$ only occurs between positions having the same proton affinity (primarily *para* ⇌ *para'*), which must lead to a considerable slowing of the reaction compared with the exchange in the collision complex $[C_6H_7^{\oplus} \cdot C_6H_6]^*$.

In fact, no proton exchange is observed for non-degenerate proton-transfer reactions, such as in the system benzene/toluene/methane.[7a] Accordingly, solely proton *transfer* is observed at all t_r in the exothermic direction of the reaction [Eq. (2a)], and no other toluene isotopomers are formed in the endothermic direction of the reaction [Eq. (2b)].[11]

$$C_6D_7^{\oplus} + C_7H_8 \longrightarrow C_6D_6 + C_7H_8D^{\oplus} \qquad (2a)$$

$$\nrightarrow C_6(H,D)_7^{\oplus} \text{ and } C_7H_7D_2^{\oplus} \text{ etc.}$$

$$C_7H_9^{\oplus} + C_6D_6 \nrightarrow C_7(H,D)_9^{\oplus} + C_6(H,D)_6 \qquad (2b)$$

Scheme 1.

Fig. 3. Energy profiles for the H transfer between arenium ions and arenes (enthalpy values [11, 13] in kJ/mol^{-1}). (—): thermoneutral $H^{\oplus}$ transfer, $Ar = Ar' = C_6H_5$ or $C_6H_4CH_3$; (---): non-thermoneutral $H^{\oplus}$ transfer, $Ar = C_6H_5$, $Ar' = C_6H_4CH_3$.

Table 1. Ion abundances in the system $C_6H_7^{\oplus}/C_6H_6/C_6D_6$ after $t_r = 790$ ms without ($-$) and with ($+$) continuous removal of the ions $C_6HD_6^{\oplus}$ (m/z 85) [a].

m/z	78	79	80	81	82	83	84	85	86
($-$)	30	1000	49	8.6	7.9	14.3	70	168	15.8
($+$)	30	1000	40	6.4	4.2	10.4	62	0	1.0

[a] ^{13}C-corrected values. The absolute abundance of the ions $C_6H_7^{\oplus}$ ($\equiv$ 1000) was constant in both experiments. In order to continuously remove the ions $C_6HD_6^{\oplus}$, a radiofrequency pulse with an amplitude of 2.5 V peak-to-peak was used.

The data confirm that the proton exchange takes place within the collision complex: even upon ejection of the ions m/z 85, all $C_6(H,D)_7^{\oplus}$ isotopomers are formed,

These observations can be explained qualitatively by a symmetrical ($Ar = Ar'$) or an asymmetrical ($Ar \neq Ar'$) double-minimum energy profile[12] (Fig. 3).[13] According to our results, the activation barrier between the minima $[ArH_2^{\oplus} \cdot Ar'H]$ and $[ArH \cdot Ar'H_2^{\oplus}]$ must be relatively high. This is especially noteworthy in comparison with the extremely fast *intra*molecular proton exchange in protonated α,ω-diphenylalkanes and related arenium ions.[3]

[1] a) R. P. Bell: *The Proton in Chemistry*, 2nd ed., Cornell University Press, New York 1973; b) M. Eigen, *Angew. Chem.* 75 (1963) 489; *Angew. Chem. Int. Ed. Engl.* 3 (1964) 1; c) J. E. Crooks in E. Caldin, V. Gold (Eds.): *Proton Transfer Reactions*, Wiley, New York 1975, chap. 6.

[2] a) R. G. Cooks, J. H. Beynon, R. M. Caprioli, G. Lester: *Metastable Ions*, Elsevier, Amsterdam 1973; b) K. Levsen: *Fundamental Aspects of Mass Spectrometry*, Verlag Chemie, Weinheim 1978.

[3] a) D. Kuck, *Int. J. Mass Spectrom. Ion Phys.* 47 (1983) 499; b) D. Kuck, W. Bäther, H. F. Grützmacher, *J. Am. Chem. Soc.* 101 (1979) 7154; c) D. Kuck, W. Bäther, H. F. Grützmacher, *Int. J. Spectrom. Ion Proc.*, in press.

[4] a) B. S. Freiser, R. L. Woodin, J. L. Beauchamp, *J. Am. Chem. Soc.* 97 (1975) 6893; b) S. Ghaderi, P. S. Kulkarni, E. B. Ledford, Jr., C. L. Wilkins, M. L. Gross, *Anal. Chem.* 53 (1981) 428; c) Y. Yamamoto, S. Takamuku, H. Sakurai, *Chem. Lett. 1974*, 849; *1975*, 683.

[5] a) C. L. Johlman, R. L. White, C. L. Wilkins, *Mass Spectrom. Rev.* 2 (1983) 389; b) M. L. Gross, D. L. Rempel, *Science* 226 (1984) 261; c) N. M. M. Nibbering, *Nachr. Chem. Tech. Lab.* 32 (1984) 1044; d) K. P. Wanczek, *Int. J. Mass Spectrom. Ion Proc.* 60 (1984) 11.

[6] The FT-ICR mass spectrometer was built at the University of Amsterdam. a) Electronics: J. H. J. Dawson in H. Hartmann, K. P. Wanczek: *Lecture Notes in Chemistry, Vol. 31*, Springer, Berlin 1982, p. 331; b) software: A. J. Noest, C. W. F. Kort, *Comput. Chem.* 6 (1982) 111, 115; c) general methods of measurement: J. C. Kleingeld, N. M. M. Nibbering, *Org. Mass Spectrom.* 17 (1982) 136; S. Ingemann, N. M. M. Nibbering, S. A. Sullivan, C. H. DePuy, *J. Am. Chem. Soc.* 104 (1982) 6520.

[7] a) Experimental conditions: The magnetic field strength was 1.4 T in all experiments. The cell of the FT-ICR mass spectrometer [6] was filled with $\approx 1 \cdot 10^{-5}$ Pa of each of the two arenes and with $\approx 8 \cdot 10^{-5}$ Pa of methane. $CH_5^\oplus$ and $C_2H_5^\oplus$ ions, among others, were generated by an electron pulse (20 eV, 5 ms); they protonated the arenes in the following 200 ms to give $ArH_2^\oplus$ and $Ar'H_2^\oplus$. Subsequently, all ions except $ArH_2^\oplus$ (or $Ar'H_2^\oplus$) were removed from the cell by "notch ejection" [8] (radiofrequency pulse with a scan length of 10 ms); then, in the following reaction time ($t_r = 0$ to $t_r = 6290$ ms), the ions formed from $ArH_2^\oplus$ (or $Ar'H_2^\oplus$), ArH and Ar'H were measured. b) By applying a radiofrequency pulse for m/z 85 (amplitude 3.5 V peak-to-peak) during the entire reaction time t_r, all $^{12}C_6HD_6^\oplus$ ions were removed from the cell within ≤ 300 μs after their formation. During this time, no collisions with molecules of the gas mixture took place (average rate of collision $\approx 10\,s^{-1}$).

[8] a) A. J. Noest, C. W. F. Kort, *Comput. Chem.* 7 (1983) 81; b) J. C. Kleingeld, N. M. M. Nibbering, *Tetrahedron* 39 (1983) 4193; c) A. G. Marshall, T. C. Lin Wang, T. Lebatnan Ricca, *Chem. Phys. Lett.* 105 (1984) 233.

[9] A fraction of the ions m/z 84 are $C_6D_6^{\oplus\circleddash}$ molecular ions formed by charge exchange (cf. m/z 78, $C_6H_6^\oplus$: Table 1).

[10] The ions $^{13}C^{12}C_5HD_6^\oplus$ (m/z 86, rel. abundance 0.066 [$^{12}C_6HD_6^\oplus$] were *not* ejected and therefore generated ca. 1/16th of the $C_6D_7^\oplus$ ions formed without ejection of m/z 85.

[11] $PA(C_6H_6) = 777$ kJ mol^{-1}, $PA(C_7H_8) = 808$ kJ mol^{-1} (PA = proton affinity); D. H. Aue, M. T. Bowers in M. T. Bowers (Ed.): *Gas Phase Ion Chemistry, Vol. 2*, Academic Press, New York 1979, p. 33.

[12] a) M. Jasinski, J. I. Brauman, *J. Am. Chem. Soc.* 102 (1980) 2906; b) H. Zimmermann, *Angew. Chem.* 76 (1964) 1; *Angew. Chem. Int. Ed. Engl.* 3 (1964) 157.

[13] The proton-bound dimer $[C_6H_7^\oplus \cdot C_6H_6]$ is more stable by $\Delta H = 46$ kJ mol^{-1} than $C_6H_7^\oplus$ and C_6H_6; M. Mautner, P. Hamlet, E. P. Hunter, F. H. Field, *J. Am. Chem. Soc.* 100 (1978) 5466.

Reaction of Ethylene Oxide with Sulfur Dioxide in the Presence of Cesium Ions: Synthesis of 1,3,6,9,2λ⁴-Tetraoxathia-2-cycloundecanone

By *Herbert W. Roesky** and *Hans Georg Schmidt*

Cyclic homologues of ethylene oxide have attracted great interest because of their unusual complexation properties in the presence of alkali metal ions and other cations.[1] Their properties can be changed by incorporation

[*] Prof. Dr. H. W. Roesky, H. G. Schmidt
Institut für Anorganische Chemie der Universität
Tammannstrasse 4, D-3400 Göttingen (FRG)

of further heteroatoms. Reactions of ethylene oxide and sulfur dioxide in the presence of catalysts have been well documented.[2] Ethylene sulfite is formed. We have now found that the reaction of ethylene oxide, sulfur dioxide,
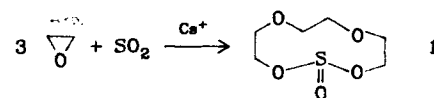
and cesium salts[3] at room temperature leads to higher membered ring compounds, of which the title compound 1 has been isolated in 20% yield as a white solid.[4]

In the field ion mass spectrum, M^+ of 1 (m/z 196) is observed as sole peak. 1 polymerizes on storage at room temperature for several weeks in a sealed flask. Poor quality single crystals were obtained from ethylene oxide and examined X-ray crystallographically.[5]
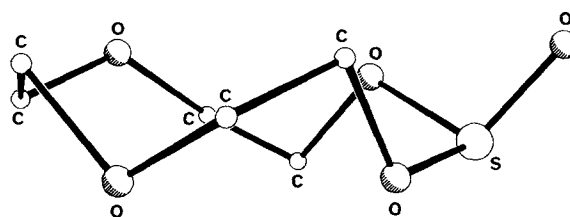
Fig. 1. Crystal structure of 1.

The structure contains two independent conformationally isomeric molecules of 1 (Fig. 1). A final refinement was not possible owing to disorder and/or thermal motions.[6]

[1] C. J. Pedersen, *J. Am. Chem. Soc.* 89 (1967) 7017; J. Dale, G. Borgen, K. Daasvatn, *Acta Chem. Scand. B28* (1974) 378.

[2] Review: G. Dittus in *Houben-Weyl, Methoden der Organischen Chemie, Bd. 6/3*, 4th ed., Thieme, Stuttgart 1965, p. 482; Farbwerke Hoechst AG, Brit. Pat. 753872 (August 1, 1956); *Chem. Abstr. 51* (1957) 5821; Chemische Werke Hüls AG, Brit. Pat. 783561 (September 25, 1957); *Chem. Abstr. 52* (1958) 5455; G. M. Gibson, C. R. Heald, D. J. Hartley, Brotherton and Co. Ltd., Brit. Pat. 844104 (August 10, 1960); *Chem. Abstr. 55* (1961) 11308; W. A. Rogers, Jr., J. E. Woekst, R. M. Smith, Dow Chemical Co., U. S. Pat. 3022315 (February 20, 1962); *Chem. Abstr. 57* (1962) 5802; A. J. Shipman, ICI Ltd., Brit. Pat. 898630 (June 14, 1962); *Chem. Abstr. 57* (1962) 13697; H. Distler, G. Dittus, BASF AG, DBP 1217970 (June 2, 1966); *Chem. Abstr. 65* (1966) 7189; H. Distler, BASF AG, DBP 1223397 (August 1966); *Chem. Abstr. 65* (1966) 20008.

[3] F. Vögtle, F. Ley, *Chem. Ber. 116* (1983) 3000.

[4] C_2H_4O (25 g, 570 mmol) and SO_2 (10 mL) were condensed into two 1.5 g (4.65 mmol) batches of $CsAsF_6$ in a Schlenk apparatus under vacuum. The mixtures were allowed to warm to room temperature and stirred for 48 h. The volatile products SO_2, C_2H_4O and dioxane were removed at 20 mbar. Both batches were then combined and distilled in a vacuum. Three fractions were obtained: 1) B.p. 38°C/0.05 mbar, $C_2H_4SO_3$, yield 1.9 g (1.5%); 2) B.p. 38-65°C/0.05 mbar, mixture of $C_2H_4SO_3$ and SO_2 with two and three ethylene oxide molecules, 0.8 g; 3) B.p. 95°C/0.01 mbar, **1**, yield 15 g (20.2%), m.p. 41°C.—IR (Nujol): $\nu = 1300$, 1248, 1204, 1150, 1130, 1105, 1080, 1015, 905, 870 cm^{-1}, and further bands.

[5] $P2_1/c$, $a = 11.873(4)$, $b = 18.219(6)$, $c = 8.981(3)$ Å; $\beta = 112.11(1)°$; $\rho_{calc} = 1.448$ g/cm^3 with $M = 196.22$ and $Z = 8$; $T = -40°C$, $2\theta < 40°$, direct methods.

[6] G. M. Sheldrick, M. Noltemeyer, private communication.