Table III. Energy Increments (kcal/mol) for Various Gauche Interactions

ϵ	Me/Me	Me/OH	OH/OH
1.5	0.69	0.61	-0.88
80	0.68	0.25	-0.50

lecularly hydrogen-bonded species is present.[17,31] According to Levy et al.[34] the change from apolar to polar nonprotic solvents has a shielding effect upon the ^{13}C chemical shifts of the methyl groups, which was interpreted as a change in the equilibrium from g^- to a. For an aqueous solution the shielding effect is larger, and we explain this with a conformational change from g^- to g^+. These two equilibrium shifts both agree with the different intermolecular hydrogen bonding in both nonprotic and protic polar solvents.

Steric Interactions in the Series of Vicinal Diols. $\Delta\bar{E}$ values in the present series of diols can be seen as the sum of gauche interactions between the substituents on the ethane backbone (Table III). For example, $\Delta\bar{E}$ for 1,2-ethanediol is explained by a gauche OH/OH interaction. As can be expected the Me/Me interaction is independent of ϵ and is close to the experimental Me/Me interaction in *n*-butane.[36] The Me/OH interaction decreases upon increase of ϵ because the C-C-O-H torsion angles in the conformations of lowest energy change from +60° or -60° to 180°. Finally the OH/OH interaction becomes less favorable when ϵ is increased due to breaking of the intramolecular hydrogen bonds; this interaction remains stabilizing due to the gauche effect. The data in Table III can be used to predict $\Delta\bar{E}$ values for other alcohols in the gas phase and in apolar solvents (ϵ = 1.5) or polar noninteractive solvents (ϵ = 80).

Conclusions

Summarizing the experimental data for the vicinal diols we can distinguish several types of environments, each with characteristic influences upon the conformational preferences. Diols in the gas phase or dissolved in apolar solvents are able to form intramolecular hydrogen bonds. These hydrogen bonds stabilize the gauche forms relative to the anti form. Intermolecular hydrogen bonds exist in polar solvents. In polar nonprotic solvents this results in stabilization of the anti form, in polar protic environments in stabilization of the gauche forms.

Our calculations at ϵ = 1.5 for 1,2-ethanediol and the 2,3-butanediols show stabilization of gauche forms due to large dipole-dipole interactions and a negative V_2 torsional term. The results are generally in good agreement with the experimental data. Increasing ϵ diminishes the dipole-dipole interactions. Going from apolar to polar solvents not only does ϵ increase but intermolecular hydrogen bonds can be formed. These are not incorporated in the MM2 force field. Therefore, our calculations at ϵ = 80 cannot result in a good description of compounds dissolved in polar interactive solvents. The difference between the calculated results and the available experimental data points to a specific solvation of gauche forms in polar protic environments.

Energy increments for gauche Me/Me, Me/OH, and OH/OH interactions rationalize the $\Delta\bar{E}$ values in the series of the vicinal diols and may be used to predict $\Delta\bar{E}$ for other alcohols.

Acknowledgment. This investigation was carried out under the auspices of the Netherlands Foundation for Chemical Research (SON) with support from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. 1,2-Ethanediol, 107-21-1; (*S*)-1,2-propanediol, 4254-15-3; (*R,S*)-2,3-butanediol, 5341-95-7; (*S,S*)-2,3-butanediol, 19132-06-0; 1,3-propanediol, 504-63-2; 1,2-dimethoxyethane, 110-71-4.

Supplementary Material Available: Characteristic torsion angles and conformational energies of all conformers of the diols as calculated with the MM2 force field (8 pages). Ordering information is given on any current masthead page.

(36) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982; ACS Monogr. No. 177, p 47.

Halogenated Epoxides. 9.[1] Reaction of *trans*-2,3-Dichlorooxirane with Dimethyl Sulfide

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Reaction of *trans*-2,3-dichlorooxirane (**1**) with dimethyl sulfide afforded in high yield dimethyl(1-chloro-2-hydroxyethenyl)sulfonium chloride (**2a**). The latter was converted into 1-chloro-2-methoxy-1-(methylthio)ethene (**3b**) and into 2-acetoxy-1-chloro-1-(methylthio)ethene (**3c**) by reaction with diazomethane and with ketene, respectively. Pyrolysis of **2a** gave chloro(methylthio)acetaldehyde (**4a**) and dichloroacetaldehyde (**6**), along with a series of minor byproducts.

Introduction

In previous work we have examined oxidation reactions of unsubstituted and of alkyl-substituted 1,2-dichloroethylenes with oxygen in the liquid phase.[2] As one of several means to detect products containing hydroperoxide groups, we have treated the crude reaction mixtures with dimethyl sulfide (Me_2S) and determined the amount of dimethyl sulfoxide formed. When this method was applied to the crude reaction product obtained from the oxidation

(1) Previous paper in this series: Spraul, M.; Keul, H.; Pfeffer, B.; Hähnle, J.; Griesbaum, K. *Magn. Reson. Chem.* **1985**, *23*, 324.

(2) Hayes, M. P. Dissertation, University of Karlsruhe, 1979.

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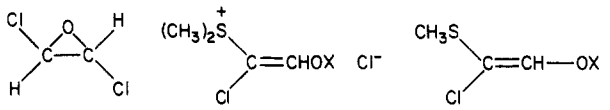
of *trans*-1,2-dichloroethylene, a colorless, crystalline solid precipitated slowly from the liquid reaction mixture.[3] GLC analysis revealed, that concurrent with the formation of this solid, there was a decrease in the amount of the major oxidation product *trans*-2,3-dichlorooxirane (**1**) in the reaction mixture. This observation was indicative of a reaction between **1** and Me_2S. Since to our knowledge reactions between ring chlorinated epoxides and Me_2S had not been reported at that time,[4] we have followed this observation by examining the reaction of Me_2S with pure **1**.

Results and Discussion

Mixtures of *trans*-2,3-dichlorooxirane (**1**) and equimolar or excess amounts of Me_2S gave a colorless solid when kept at room temperature for ca. 24 h. The solid was insoluble in most common organic solvents with the exception of highly polar media such as dimethyl sulfoxide or dimethylformamide. Its ^1H NMR spectrum showed three singlet signals with relative intensities of 6:1:1 and the IR spectrum showed bands in the OH- and in the C=C stretching region. Based on these properties and on the results of the elemental analysis, we assigned it the structure of the sulfonium salt **2a**, i.e., a product composed of equimolar amounts of Me_2S and of *trans*-2,3-dichlorooxirane (**1**).

The structure of **2a**, and in particular its enol moiety could be further substantiated by the results of the following reactions: Treatment of a solution of **2a** in Me_2SO with diazomethane and subsequent separation of the reaction mixture by preparative gas chromatography afforded the enolic ether **3b**, and reaction of **2a** with ketene by the same procedure gave the enolic ester **3c**. These reactions probably proceed via the sulfonium salts **2b** and **2c**, respectively, which are subsequently demethylated by solvolysis during the aqueous workup procedure and/or by thermolysis during GLC separation. Indeed, the crude product mixture from the reaction of **2a** with diazomethane exhibited singlet signals with relative intensities of 6:3:1, which are consistent with structure **2b**.

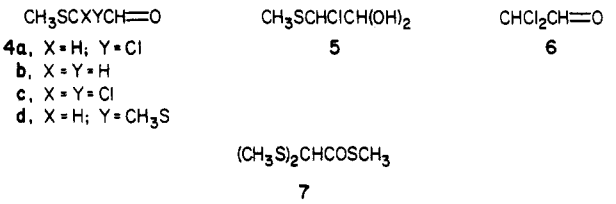


1 **2** **3**

a, X = H;
b, X = CH_3;
c, X = CH_3CO

The sulfonium salt **2a** is hygroscopic and is readily dissolved in water, albeit followed by decomposition. By monitoring the reaction of a 1:1 mixture of **2a** and water in Me_2SO-d_6 by ^1H NMR spectroscopy, chloromethane and aldehyde **4a** could be identified as initial decomposition products. After prolonged exposure to water, aldehyde **4a** disappeared to give rise to new products among which dimethyl disulfide and **5** have been tentatively recognized on the basis of ^1H NMR data.

The sulfonium salt **2a** is thermally labile. It decomposes slowly when stored at room temperature and rapidly upon melting at approximately 123 °C. Deliberate thermal decomposition of **2a** at 170 °C in vacuum occurred with less than 5% residue to give **4a** (70%),[5] **4b** (1%), **4c** (2%), **4d** (10%), **6** (16%) and **7** (1%), along with chloromethane, Me_2S, and dimethyl disulfide. Compounds **4a**, **4b**, **4d**, **6**, Me_2S, and dimethyl disulfide have been isolated by preparative GLC and identified by comparison of pertinent analytical data with those of authentic samples. Compounds **4c** and **7** have been identified by comparison of their GLC retention times and GC/MS data with those of authentic samples. Authentic **4b**[6] and **6**[7] have been obtained by known procedures, authentic **4a** and **4c** by chlorination of **4b** with sulfuryl chloride, authentic **4d** by reaction of **1** with sodium methyl thiolate, and authentic **7** by reaction of **1** with dimethyl disulfide.



$CH_3SCXYCH{=}O$ (**4a**, X = H; Y = Cl; **b**, X = Y = H; **c**, X = Y = Cl; **d**, X = H; Y = CH_3S) $CH_3SCHClCH(OH)_2$ (**5**) $CHCl_2CH{=}O$ (**6**)

$(CH_3S)_2CHCOSCH_3$ (**7**)

Compounds **4b-d**, **7**, and dimethyl disulfide have been also obtained when the major thermolysis product of **2a**, viz., **4a** has been heated to 170 °C for 1 min at vacuum. We assume, therefore, that they are secondary products in the degradation of **2a**, whereas aldehydes **4a** and **6** represent the primary products. Since the latter have been obtained in a ratio of ca. 4:1, it can be concluded that the thermolysis of **2a** occured predominantly by initial cleavage of one of the CH_3–S bonds and to a lesser degree by initial cleavage of the S–CCl bond.

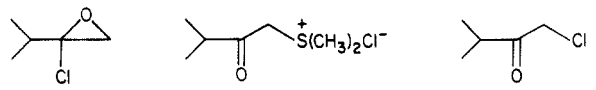
The formation of the secondary thermolysis products **4b** and **4c** can be rationalized by appropriate radical-type substitutions at the CHCl group of **4a**, i.e., by initial scission of the C–H and of the C–Cl bonds, respectively. The formation of **4d** and of dimethyl disulfide, on the other hand, requires a scission of the CH_3S–C bond of **4a** as the initial step and the concurrent generation of methylthiyl radicals. The formation of **7** could be imagined by substitution of the aldehydic hydrogen in **4d** by a methylthiyl group, though other modes of formation are also conceiveable.

In recent years, reactions of a variety of chlorooxiranes with nucleophiles have been reported.[8] Some authors[9] have postulated that the first step in such reactions is the isomerization of the chlorooxirane to give the corresponding α-chloro carbonyl compound, followed by reaction of the latter with the nucleophile to yield the final product. Contrary to this view, it has been demonstrated by other groups that reactions of nucleophiles with mono-[4] and with dichlorinated epoxides[8] can proceed via their own routes, rather than via prior isomerization of the chlorooxiranes to α-chloro carbonyl compounds. The evidence presented was either based on the formation of different products or on enhanced rates in the reactions of nucleophiles with chlorooxiranes.

To our knowledge, there is only one previous report about a 1:1 reaction of a chlorooxirane with Me_2S, viz., the formation of ca. 30% of **9** from **8**, along with 60% of the isomerization product **10**.[4] Since in this reaction Me_2S has

(3) Döhling, T. Diplomarbeit, University of Karlsruhe, 1979.
(4) In the meantime, one example for a reaction between dimethyl sulfide and a monochlorooxirane has been reported: Gasteiger, J.; Herzig, Ch. *Angew. Chem.* **1981**, *93*, 933.
(5) The GLC percent figures are based on peak areas and represent relative proportions of those compounds which are derived from the C_2 moiety of **2a**. The proportion of products related to unidentified peaks is generally below 10% and mostly below 5%.
(6) Gassman, P. G.; van Bergen, T. J.; Gilbert, D. P.; Cue, B. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 5495.
(7) Wohl, A.; Roth, H. *Chem. Ber.* **1907**, *40*, 212.
(8) For a summary of leading references see: Griesbaum, K.; Lie, G. O.; Keul, H. *J. Org. Chem.* **1984**, *49*, 679.
(9) Voronina, T. A.; Fomina, N. V.; Suminov, S. I. *Zh. Org. Khim.* **1983**, *19*, 1188.

been applied in excess over 8, it was inferred that 9 was formed by direct reaction of Me_2S with 8, though it was not reported whether partial formation of 9 by alkylation of Me_2S with the chloro ketone 10 has been experimentally exculded.[4]



8 9 10

The formation of the sulfonium salt **2a** in the present investigation has been shown to proceed exclusively by direct reaction of 1 with Me_2S, since a mixture of Me_2S and 6 did not undergo any reaction under the conditions which were employed for the preparation of **2a**. This allows, furthermore, the conclusion that in contrast to the results with the chlorooxirane 8,[4] isomerization of the chlorooxirane 1 does not compete with the nucleophilic attack during the reaction of Me_2S with 1, since 6 was not detected as a reaction product. It appears, thus, that the formation of the sulfonium salt **2a** is favored by the resistance of 1 toward isomerization and by the pronounced reactivity of 1 toward Me_2S. This reactivity is somewhat surprising, since 1 had been previously found to be rather unreactive, e.g., towards $AgBF_4$[10] which normally undergoes spontaneous reactions with chlorooxiranes even at low temperatures.

Finally, it should be pointed out, that the formation of the enolic sulfonium salt **2a** is unique and differs from the type of product obtained in the reaction of the monochlorooxirane 8, viz., the carbonylic sulfonium salt 9.[4] This may be attributed to joint steric and electron-withdrawing effects of the sulfonium and of the chloro substituent in **2a**.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Bruker WP 60, IR spectra on a Beckman IR 4260, and GC/MS spectra on a Hewlett-Packard 5985 B instrument. GLC analyses were carried out on a Varian model 3700 instrument (glass column, 0.3 × 340 cm; 2.5% Nitrilesilicon oil on Chromosorb G; 60–180 °C at 4 °C/min). The PGC separations were performed on a Perkin-Elmer F 21 instrument.

Reaction of *trans*-2,3-Dichlorooxirane (1) with Dimethyl Sulfide. A mixture of 1.12 g (9.9 mmol) of 1[11] and 1.00 g (16.1 mmol) of dimethyl sulfide was kept in a 20-mL round-bottom flask for 24 h at room temperature and under a dry atmosphere of nitrogen. From the solid precipitate unreacted starting materials were removed by suction at room temperature and ca. 0.1 torr to give 1.36 g (78.3%) of colorless, crystalline **2a**, which was stored at −20 °C by exclusion of moisture.

Dimethyl(1-chloro-2-hydroxyethenyl)sulfonium chloride (2a): mp 123 °C dec; ^1H NMR (Me_2SO-d_6, Me_4Si) δ 2.98 (s, 6 H), 7.89 (s, 1 H), 12.07 (broad s, 1 H); IR (KBr) 3200 (OH), 1635 (C=C) cm^{-1}.

Anal. Calcd for $C_4H_8Cl_2OS$: C, 27.44; H, 4.61; Cl, 40.50; S, 18.31. Found: C, 27.45; H, 4.49; Cl, 40.50; S, 18.12.

Reaction of 2a with Diazomethane. To a suspension of 1.75 g (10.0 mmol) of **2a** in 3 mL of dry dimethyl sulfoxide which was kept at 15 °C in a 25-mL round-bottom flask under an atmosphere of dry nitrogen and at vigorous stirring, a solution of diazomethane in diethyl ether[12] was dropwise added until the originally colorless mixture turned yellow. The stirring was continued for 3 h at 15 °C, diethyl ether was removed through a 20-cm Vigreux column at 15 torr, the liquid residue was poured on ice, extracted with 10 mL of trichloromethane, dried over sodium sulfate, and filtered, and the solvent was removed by distillation through a 20-cm Vigreux column at atmospheric pressure. The remaining brown liquid residue (0.850 g) contained as the single major product **2b**. ^1H NMR (Me_2SO-d_6, Me_4Si): δ 2.72 (s, 6 H), 3.33 (s, 3 H), 8.15 (s, 1 H). GLC analysis showed the peaks of chloromethane (t_R = 1.1 min) and of **3b** (t_R = 17.1 min; 9%). Separation of the above liquid residue by PGC (glass column, 0.8 × 400 cm; 5% Nitrilesilicon oil on Chromosorb G; 60–180 °C at 5 °C/min) afforded 70 mg (ca. 5%) of pure **3b**.

1-Chloro-2-methoxy-1-(methylthio)ethene (3b): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.27 (s, 3 H), 3.78 (s, 3 H), 6.70 (s, 1 H); IR (film) 2940, 2922, 2840, 1630, 1297, 1230, 1135, 905 cm^{-1}; MS, *m/e* (relative intensity) 140, 138 (38, 100, M^+), 125, 123 [21, 51, $(M - CH_3)^+$], 103 [14, $(M - Cl)^+$]; GLC t_R = 17.1 min.

Anal. Calcd for C_4H_7ClOS: C, 34.66; H, 5.09; Cl, 25.58; S, 23.13. Found: C, 34.58; H, 5.02; Cl, 25.77; S, 23.24.

Reaction of 2a with Ketene. Through a suspension of 1.75 g (10.0 mmol) of **2a** in 1.5 mL of dry dimethyl sulfoxide which was kept at ca. 10 °C was passed a stream of gaseous ketene[13] until the mixture became a dark solution. The latter was poured on ice, extracted with dichloromethane, and dried over sodium sulfate, and the solvent was removed by distillation through a 20-cm Vigreux column at atmospheric pressure to leave 1.40 g of a liquid brown residue. Analysis by GLC and by GC/MS showed the presence of chloromethane (t_R = 1.1 min; *m/e* = 52, 50) and of **3c** (t_R = 19.4 min; 23%). Separation of the liquid residue by PGC (glass column, 0.8 × 400 cm, 5% Carbowax 20 M on Chromosorb G; 60–180 °C at 5 °C/min) afforded 300 mg (18%) of pure **3c**.

2-Acetoxy-1-chloro-1-(methylthio)ethene (3c): colorless liquid; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.22 (s, 3 H), 2.34 (s, 3 H), 7.73 (s, 1 H); IR (film) 3080, 2920, 1770, 1625, 1370, 1195, 1115, 848 cm^{-1}; MS, *m/e* (relative intensity) 168, 166 (6, 17, M^+), 126, 124 [34, 100, $(CH_3SCHClCHO)^+$], 43 [70, $(CH_3CO)^+$].

Anal. Calcd for $C_5H_7ClO_2S$: C, 36.04; H, 4.23; Cl, 21.28; S, 19.24. Found: C, 36.23; H, 4.38; Cl, 21.06; S, 19.05.

Decomposition of 2a by Water in Me_2SO-d_6 Solution. A solution of 21.1 mg (0.12 mmol) of **2a** and 2.2 μL (ca. 0.12 mmol) of water in 0.3 mL of Me_2SO-d_6 was monitored by ^1H NMR analysis in the presence of Me_4Si. After 4 h the signals of chloromethane (δ 3.06, s) and of **4a** (δ 2.05, s; 5.24, d; 9.28, d) appeared in addition to those of **2a**. After 24 h the signals of **2a** had almost completely disappeared. The major signal was that of chloromethane, along with those of **4a** and with a new set of signals which have been tentatively assigned to **5** (δ 2.22, s; AB system with δ_A 5.35, δ_B 5.98, J_{AB} = 3.9 Hz; δ 6.0, broad s). After 3 d the major peak was a singlet signal at δ 2.42 which was assigned to dimethyl disulfide.

Thermal Decomposition of 2a. In a 25-mL round-bottom flask 1.0 g (5.7 mmol) of **2a** was heated to 170 °C for 20 min at 2 torr. The volatile reaction products were collected in a series of four consecutive traps which were cooled to 0 °C (fraction 1), −20 °C (fraction 2), −78 °C (fraction 3) and −196 °C (fraction 4).

Fraction 1 contained 467 mg of a slightly brown liquid. GLC analysis showed the presence of dimethyl sulfide (t_R = 1.6 min; 5%), dimethyl disulfide (t_R = 4.8 min; 1%), **4a** (t_R = 14.4 min; 78%), **4b** (t_R = 8.3 min; 1%), **4c** (t_R = 12.8 min; 2%), **4d** (t_R = 20.9 min; 8%), **6** (t_R = 4.4 min; 4%), **7** (t_R = 30.6 min; 1%), and chloromethane (t_R = 1.1 min; ca. 1%), as confirmed by coinjection of the corresponding authentic compounds. By PGC separation (glass column, 0.8 × 400 cm, 5% Nitrilesilicone oil on Chromosorb G; 60–180 °C at 5 °C/min) of fraction 1 in admixture with ca. 2 mL of dichloromethane the components dimethyl sulfide, dimethyl disulfide, **4a**, **4b**, **4d**, and **6** have been isolated.

Fraction 2 comprised 84 mg of a colorless liquid, containing dimethyl sulfide (28%), **4a** (2%), **4b** (1%), **4d** (18%), **6** (45%), and two unidentified components (together 6%).

Fraction 3 comprised 60 mg of a colorless liquid, containing dimethyl sulfide (53%), dimethyl disulfide (ca. 1%), **4a** (2%), **6** (43%), and an unidentified component (2%).

Fraction 4 contained ca. 1 mL of a colorless, volatile liquid which consisted mainly of chloromethane. The residue in the pyrolysis

(10) Griesbaum, K.; Keul, H.; Kibar, R.; Pfeffer, B.; Spraul, M. *Chem. Ber.* **1981**, *114*, 1858.
(11) Griesbaum, K.; Kibar, R.; Pfeffer, B. *Liebigs Ann. Chem.* **1975**, 214.
(12) De Boer, Th. J.; Backer, H. J. "Organic Syntheses"; Wiley, New York, 1963; Collect. Vol. IV, p 250.
(13) Vogel, A. I. "Practical Organic Chemistry", 4th ed.; Longman: New York, 1978, p 79.

flask consisted of 30 mg of a dark, tarry product.

Based on the above reported material balances and GLC analyses, the following overall distribution has been calculated for the products derived from the C_2 moiety of **2a**: 70% of **4a**, 1% of **4b**, 2% of **4c**, 10% of **4d**, 16% of **6** and 1% of **7**.

The identification of the above described reaction products is based on the identity of the analytical data presented below for each compound with those of the corresponding authentic product:

Chloro(methylthio)acetaldehyde (4a): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.15 (s, 3 H), 5.32 (d, J = 1.83 Hz, 1 H), 9.28 (d, J = 1.83 Hz, 1 H); IR (film) 1728 cm^{-1} (C=O); MS, m/e (relative intensity) 126, 124 (17, 45, M^+), 97, 95 [38, 100 (M – CHO)$^+$], 89 [27, (M – Cl)$^+$]; t_R = 14.4 min.

Synthesis of 4a. To a solution of 0.90 g (10 mmol) of **4b**[6] in 50 mL of dichloromethane a solution of 1.35 g (10 mmol) of sulfuryl chloride in 20 mL of dichloromethane was added dropwise with stirring at −15 °C to −20 °C during a period of ca. 2 h. Then the solvent was removed in a rotary evaporator at room temperature and 20 torr, and the residue was distilled at vacuum through a 5-cm unpacked column to give 1.15 g (93%) of **4a**: bp 53 °C/10 torr.

(Methylthio)acetaldehyde (4b): MS, m/e (relative intensity) 90 (60, M^+), 61 [100, (M – CHO)$^+$]; t_R = 8.3 min. Authentic sample prepared according to ref 6.

Dichloro(methylthio)acetaldehyde (4c): GC/MS, m/e (relative intensity) 162, 160, 158 (5, 24, 33, M^+), 133, 131, 129 [14, 73, 100, (M – CHO)$^+$], 125, 123 [21, 58, (M – Cl)$^+$]; t_R = 12.8 min.

Synthesis of 4c. To a solution of 1.35 g (15 mmol) of **4b** in 40 mL of dichloromethane a solution of 4.05 g (30 mmol) of sulfuryl chloride in 10 mL of dichloromethane was added with stirring at 0 °C during a period of 15 min. Stirring was continued for 30 min at 0 °C and for 1 h at room temperature, the solvent was removed in a rotary evaporator at room temperature and 15 torr, and the residue was distilled at vacuum through a 5-cm unpacked column to give 1.60 g (68%) of **4c**: bp 58 °C/16 torr; ^{1}H NMR ($CDCl_3$, Me_4Si): 2.27 (s, 3 H), 8.94 (s, 1 H); IR (film) 1740 cm^{-1} (C=O).

Anal. Calcd for $C_3H_4Cl_2OS$: C, 22.66; H, 2.54; Cl, 44.59; S, 20.16. Found: C, 22.79; H, 2.59; Cl, 44.43; S, 20.07.

Bis(methylthio)acetaldehyde (4d): colorless liquid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.10 (s, 6 H), 4.25 (d, J = 2.93 Hz, 1 H), 9.28 (d, J = 2.93 Hz, 1 H); IR (film) 1710 cm^{-1} (C=O); MS, m/e (relative intensity) 138, 136 (1, 9, M^+), 107 [100, (M – CHO)$^+$]; t_R = 20.9 min.

Synthesis of 4d. To a solution of 4.65 g (65 mmol) of sodium methanethiolate in 55 mL of methanol a solution of 3.36 g (10 mmol) of **1**[11] in 5 mL of methanol was added with stirring at 0 °C during a period of 15 min. Stirring was continued for 24 h at room temperature, sodium chloride was filtered off, and the filtrate was concentrated by distillation through a rotary evaporator at room temperature and 20 torr. The liquid residue was dissolved in 25 mL of dichloromethane, sequentially washed with 100 mL of 1% hydrochloric acid, aqueous sodium bicarbonate, and water, dried over sodium sulfate, and concentrated by removal of dichloromethane in a rotary evaporator. The residue (3.40 g) was purified by chromatography (column 2 × 60 cm; 75 g of silica gel; 1200 mL of n-pentane and diethyl ether in a volumetric ratio of 95:7) to give 2.1 g (51%) of **4d**.

Anal. Calcd for $C_4H_8OS_2$: C, 35.27; H, 5.92; S, 47.07. Found: C, 35.12; H, 5.90; S, 46.95.

Dichloroacetaldehyde (6): MS, m/e (relative intensity) 116, 114, 112 (1, 12, 18, M^+) 88, 86, 84 [4, 27, 42, (M – CO)$^+$], 51, 49 [30, 100, (M – COCl)$^+$], 29 (63, CHO$^+$); t_R = 4.7 min. Authentic sample prepared according to ref.[7]

Methyl bis(methylthio)thioacetate (7): GC/MS, m/e (relative intensity) 182, (5, M^+), 107 [100, $(CH_3S)_2CH^+$]; t_R = 30.6 min.

Synthesis of 7. A mixture of 5.6 g (50 mmol) of **1** and 8.0 g (85 mmol) of dimethyl disulfide was heated to 170 °C in an autoclave for 45 min. The reaction mixture was concentrated in a rotary evaporator at room temperature and 20 torr. The liquid residue was separated by column chromatography (column 2 × 60 cm; 75 g of silica gel; 500 mL of n-pentane and diethyl ether in a volumetric ratio of 95:5) to give 1.5 g of **7** with a purity of 65%. By PGC separation (glass column, 0.8 × 400 cm, 5% Nitrilesilicone oil on Chromosorb G; 60–180 °C at 5 °C/min) of this impure product, a sample of **7** has been isolated: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.19 (s, 6 H), 2.37 (s, 3 H), 4.45 (s, 1 H); IR (film) 1670 cm^{-1} (C=O); MS, m/e (relative intensity) 184, 182 (2, 14, M^+), 156, 154 [1, 7, (M – CO)$^+$], 109, 107 [10, 100, $(CH_3S)_2CH^+$]; t_R = 30.6 min.

Thermal Decomposition of 4a. A small glass tube containing 20 mg of **4a** has been cooled in liquid air, evacuated at 2 torr, sealed, and subsequently transferred to a heating bath at 170 °C for ca. 1 min. The tube was again cooled in liquid air and opened, and the product was admixed with dichloromethane. GLC analysis showed the presence of **4a** (68%), **4b** (5%), **4c** (2%), **4d** (8%), **7** (7%), dimethyl disulfide (2%), and two unidentified components (together 8%).

Attempted Reaction of Dichloroacetaldehyde (6) with Dimethyl Sulfide. A mixture of 0.56 g (4.9 mmol) of **6** and 1.0 g (16.1 mmol) of dimethyl sulfide was kept stirring at room temperature for 48 h. There was no precipitate formed and GLC and ^{1}H NMR analyses showed the presence of the unreacted starting materials.

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Registry No. **1**, 16650-12-7; **2a**, 101010-52-0; **2b**, 101010-53-1; **3b**, 101010-54-2; **3c**, 101010-55-3; **4a**, 101010-56-4; **4b**, 23328-62-3; **4c**, 101010-58-6; **4d**, 101010-59-7; **5**, 101010-57-5; **6**, 79-02-7; **7**, 101010-60-0; dimethyl sulfide, 75-18-3; ketene, 463-51-4; chloromethane, 74-87-3; sodium methanethiolate, 5188-07-8.

Unusual Temperature-Dependent Isotope Effects in the Reactions of Phenylcarbene with Cyclohexene and Cyclohexane

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The photochemistry of phenyldiazomethane in cyclohexene (cyclohexene-d_{10}) and cyclohexane (cyclohexane-d_{12}) was studied. The chemistry observed was found to be entirely consistent with singlet rather than triplet phenylcarbene reactions. Small (1.9–2.1) isotope effects to CH insertion were observed at 25 °C that increased on cooling. Cooling to very low temperature (−196 °C) reduced the isotope effect. The results are discussed in terms of the hardness of the polycrystalline solid matrix.

Phenylcarbene is the prototypical aromatic carbene and as such has received considerable examination. The triplet has been shown to be the ground state of the carbene by low-temperature EPR.[2] The EPR assignment is quite

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