The Formation of *cis*- and *trans*-1,2-Dimethoxyethylene in the Potassium *tert*-Butoxide Initiated Elimination on Substrate 1,1,2-Trimethoxyethane

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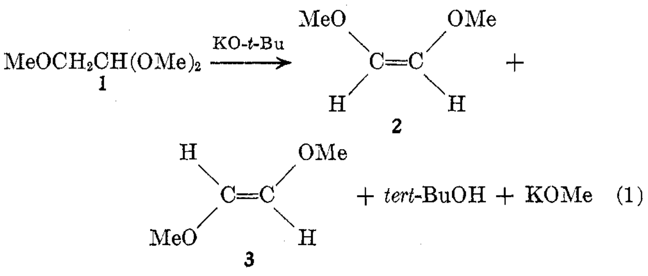
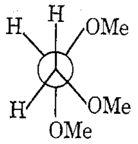
There is very little information in the literature on alkoxide initiated eliminations on substrates bearing poor leaving groups, such as RO^- where R = Me, Et, etc.[1] We report here on the potassium *tert*-butoxide initiated elimination on 1,1,2-trimethoxyethane (**1**) as substrate to produce *cis*- and *trans*-1,2-dimethoxyethylene (**2** and **3**, respectively), *tert*-butyl alcohol, and potassium methoxide (eq 1). Compounds **2** and **3** have been previously obtained by the dechlorination of 1,2-dimethoxy-1,2-dichloroethane.[2,3] Earlier attempts to prepare **2** and **3** *via* the dehydrochlorination of 1-chloro-1,2-dimethoxyethane have been reported by Scheibler[4] and Baganz, but in the present authors opinion these compounds were not unambiguously identified. Similarly McElvain and Stammer[5] failed to duplicate the olefin preparation as described by Scheibler.



$$\underset{\mathbf{1}}{MeOCH_2CH(OMe)_2} \xrightarrow{KO\text{-}t\text{-}Bu} \underset{\mathbf{2}}{cis\text{-}MeOCH{=}CHOMe} + \underset{\mathbf{3}}{trans\text{-}MeOCH{=}CHOMe} + tert\text{-}BuOH + KOMe \quad (1)$$

Results and Discussion

The results from two elimination runs performed in a bomb reactor at 165 ± 5° are shown in Table I. These data were obtained after a number of runs were made to determine the optimum conditions for carrying out the eliminations. The reaction was much too slow at 126° (the boiling point of **1**) and at 200° extensive amounts of dark-colored products were formed. Since the cis:trans ratio was ~2:1, the cis formation probably proceeds by a lower energy mechanism with one conformation of the substrate (**1**) reacting preferentially over the other. The eliminations could also proceed by a cis-syn departure of the leaving group and the β hydrogen, but our results cannot distinguish this possibility. Evidence in the literature for many E2 eliminations favors the anti elimination for the present case.[6-9] More recent investigations[10-12] on the "syn-anti dichotomy" reveal an intriguing pattern of results in which cis olefins are formed by anti elimination, but trans olefins by syn elimination. In support of the high cis:trans ratio found for reaction 1, anti elimination on conformer **1a** seems reasonable. In addition, the dealcoholation of **1** by a continuous pyrolysis over alumina yields the cis olefin (**2**) almost exclusively with no evidence for extensive side reactions.[13]



1a

The formation of methyl *tert*-butyl ether (**4**) as a reaction product (Table I) indicates that nucleophilic substitution was also taking place. In the reaction of diglyme with potassium *tert*-butoxide, no evidence for substitution was found.[1] Compound **4** can be produced by attack of the *tert*-butoxide on the starting substrate **1** and on the dimethoxyethylenes **2** and **3**. However, the most likely route to **4** was *via* the reaction of **2** and **3** with potassium *tert*-butoxide since the electron-delocalized enolate ion (**5**) of methoxyacetaldehyde would be the leaving group in this case (eq 2). Since the total number of moles of **2**, **3**,

$$\underset{\mathbf{2\ and\ 3}}{MeOCH{=}CHOMe} + KO\text{-}t\text{-}Bu \longrightarrow \underset{\mathbf{4}}{MeO\text{-}t\text{-}Bu} + \underset{\mathbf{5}}{MeOCH{=}CH{-}OK} \quad (2)$$

and **4** produced almost equals the amount of *tert*-butyl alcohol formed (Table I), substitution *via* the olefins **2** and **3** appears reasonable.

An independent experiment was carried out similar to reaction 2. The major product from the reaction of the olefins with potassium *tert*-butoxide was methyl *tert*-butyl ether (**4**). Compound **4** was observed in a 41% yield. If the total amount of both cis and trans olefins **2** and **3** that formed in reaction 1 equalled the amount of *tert*-butyl alcohol produced exclusively, a conversion of 44% (S_N2 substitution of potassium *tert*-butoxide on products **2** and **3**) would give the amount of **4** that formed (Table I). This appears to be confirming evidence for assigning the substrate undergoing substitution to the cis and trans olefins **2** and **3** and not methoxy acetal **1**. The product **5** was not isolated. The above reaction was carried out at 120° and not 165° to control the extent of reaction 2. Higher temperature would have led to too rapid reaction with the alcohol-free *tert*-butoxide that we employed.[14]

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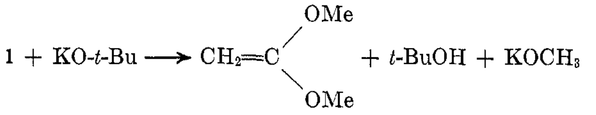
TABLE I

POTASSIUM *tert*-BUTOXIDE INITIATED ELIMINATION ON 1,1,2-TRIMETHOXYETHANE (1)

Run[a]	Time, hr	Reactants, mmol KO-*t*-Bu	1	Products, mmol *t*-BuOH	2	3	4	1[b]	X_A,%[c]
1	30	63.5	196	14.8	4.39	2.09	5.90	179	19.6
2	33	64.3	209	15.6	4.83	2.34	6.39	189	21.1

[a] The reaction was carried out in a Parr bomb reactor at 165 ± 5°. The products were separated on a 10-ft, 0.25-in. column containing 20% Carbowax 20M on Chromosorb W. The recovery of solid and liquid products was 96% in both runs. [b] Unreacted. [c] The conversion of limiting reactant, potassium *tert*-butoxide, to form products 2, 3, and 4.

Although the presence of ketene dimethyl acetal (6) was never observed in reaction 1, it could be argued that 6 was formed as in shown reaction 3 and under-



$$1 + \text{KO-}t\text{-Bu} \longrightarrow \mathrm{CH_2{=}C(OMe)_2} + t\text{-BuOH} + \mathrm{KOCH_3} \qquad (3)$$

went substitution with potassium *tert*-butoxide yielding methyl *tert*-butyl ether (4). If that were the case, 6 (a reaction intermediate) would not be observed. The fact that we observe $1 \rightarrow 2 + 3$ and not 6 is probably due to the decrease in acidity of the proton bound to the carbon atom bearing the two methoxy groups[15-17] in compound 1.

To support this argument 6 was prepared *in situ* in a bomb reactor (reaction 4) and allowed to be in

$$\underset{7}{\mathrm{BrCH_2CH(OMe)_2}} + \text{KO-}t\text{-Bu} \longrightarrow 6 + t\text{-BuOH} + \mathrm{KBr} \qquad (4)$$

the presence of excess potassium *tert*-butoxide at 120° for 8 hr. No methyl *tert*-butyl ether (4) was observed. This was confirmed by gas chromatography using an authentic sample of 4. McElvain, *et al.*, has used this procedure to produce a series of ketene acetals.[16,18,19] He also observed that ketene dimethyl acetal remains unaffected if heated alone for 6 hr at 200°.[20] The above results are reasonable in light of the work[19] that was done recycling 6 through a strong base, $\mathrm{NaOC(CH_3)_2Ph}$, at 175–185°. No substitution or elimination products were observed.

Elementary analysis, ir absorption (see Experimental Section) and nmr spectroscopy are in accord with the assigned structures 2 and 3. The τ values ($\mathrm{CCl_4}$) relative to TMS for 2 and 3 (3 values in parenthesis) are 4.28 (3.85) for the vinyl protons and 6.48 (6.60) for the methoxy protons. The absorptions appeared as sharp singlets and the peak areas were in the expected ratio of 1:3.

Details on the thermodynamics of cis–trans isomerization of the 1,2-dimethoxyethylenes are being reported elsewhere.[21]

Experimental Section

Methoxyacetaldehyde Dimethyl Acetal (1).—Methoxy acetal 1 was prepared from bromoacetaldehyde dimethyl acetal (7) and sodium methoxide *via* a Williamson ether synthesis employing a modification of that used by McElvain[5] for the ethoxy derivative. Compound 7 was either prepared by the addition of bromine to vinyl acetate in methanol[22,23] or purchased from Columbia Organic Inc.

Potassium *tert*-Butoxide.—This base was prepared by cleavage of di-*tert*-butyl peroxide with potassium metal in 1,2-dimethoxyethane solvent.[24] The solvent was removed under vacuum in a rotary evaporating apparatus. All transfers were made under purified nitrogen. The purity of KO-*t*-Bu was established as better than 98% by titration with standard HCl.

Elimination Reactions on Methoxy Acetal 1.—A number of exploratory runs were made with solid potassium *tert*-butoxide both at atmospheric and elevated pressures to determine the optimum conditions necessary for reaction to occur. The reactions under atmospheric pressure were much too slow and no appreciable amounts of products were formed at the boiling point of the acetal (126°) for periods of up to 48 hr. A number of runs were then made in a closed bomb reactor at 150–200°. It was found that reasonable reaction rates could be obtained at 165°. A typical quantitative run at 165 ± 5° was carried out as follows. Solid KO-*tert*-Bu (7.10 g, 0.0635 mol) and 23.5 g (0.196 mol) of 1 was weighed into the monel bomb reactor under a dry N_2 atmosphere. The bomb was sealed and immersed in an oil bath at 165 ± 5° for 30 hr. Final pressure at this temperature was 200 psig. The bomb was removed from the bath and cooled to room temperature. After cooling to 0°, the contents were transferred quantitatively to a small standard taper flask under N_2. The liquid (23.4 g) was removed under vacuum in a rotary evaporating apparatus and collected in a cooled receiver (−40°). A 0.6991-g sample of the solid residue (6.00 g) was titrated with 1.007 *N* $\mathrm{H_2SO_4}$ (5.65 ml) to pH 7 (Beckman Zeromatic pH meter). Thus, the solid residue contained 48.4 mequiv of base.

The liquid products were subjected to analytical and preparative gas chromatography (vpc) on Carbowax 20M on Chromosorb W. Five peaks were found which were in order of increasing retention time: *tert*-butyl methyl ether (4), *tert*-butyl alcohol, *trans*-1,2-dimethoxyethylene (3), *cis*-1,2-dimethoxyethylene (2), and methoxy acetal 1. The peaks were collected, identified by their ir absorption, and compared with authentic samples, except for 2 and 3. The reaction mixture was analyzed by quantitative gas chromatography using a synthetic mixture of reaction products prepared gravimetrically. The results for two runs are shown in Table I. The ratio of cis:trans isomer (2:3) for both runs was 2.1:1.0. After removal of most of the methyl *tert*-butyl ether and some of the *tert*-butyl alcohol on a Todd distillation column, preparative vpc on the pot residue gave sufficient quantities of 2 and 3 for running elementary analyses and for determining the nmr spectra.

Anal. for 2. Calcd for $\mathrm{C_4H_8O_2}$: C, 54.00; H, 9.10. Found: C, 53.97; H, 9.10.

Anal. for 3. Calcd for $\mathrm{C_4H_8O_2}$: Same as above. Found: C, 54.08; H, 9.46.

The average ir vibrational frequencies found (5% in $\mathrm{CCl_4}$) for 2 and 3 (3 values in parenthesis) were vinyl C–H stretching at 3031 (3084), double-bond stretching at 1693 (1661), C–O stretching at 1116 (1084), and C–H out of-plane bending at 718 (960) $\mathrm{cm^{-1}}$. Nmr absorption relative to tetramethylsilane (TMS) is covered in the main section.

Reaction of *cis*-1,2-Dimethoxyethylene (2) with Potassium *tert*-Butoxide.—A small Parr bomb reaction, fitted with a pressure gauge, was charged with 1.5032 g (0.01342 mol) of potassium *tert*-butoxide and 5.0325 g (0.05188 mol) of 2. The reaction was placed in a 120 ± 0.1° constant-temperature oil bath for 8 hr. The final pressure was 100 psig. The reactor was cooled to room

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temperature and vented. The reaction mixture was transferred to a 25-ml flask and the liquid portion transferred on a high vacuum system. The total recovery of solids and liquids was 95% (6.2096 g). The liquid portion was analyzed by quantitative gas chromatography. Methyl *tert*-butyl ether (4) was observed in 41% yield. The solid products (1.7989 g) were dissolved in water and titrated with standard HCl (14.5 ml of 1.00 *N* HCl). This represented 14.5 mequiv of base from the solid products.

Reaction of Bromo Acetal 7 with Potassium *tert*-Butoxide.—A Parr reaction bomb was charged with 1.1256 g (0.0101 mol) of potassium *tert*-butoxide, 6.4422 g (0.0871 mol) of *tert*-butyl alcohol, and 0.8623 g (0.0051 mol) of 7. The reactor was heated at 120 ± 0.1° for 8 hr. The final pressure reading was 30 psig. The reactor was cooled to room temperature and vented. The product mixture was transferred on a high vacuum system and the liquid products were collected in a cooled (−60°) receiver at 0.1 mm pressures. The liquid portion was analyzed by quantitative gas chromatography. The yield of ketene dimethyl acetal (6) was 52%. The total recovery of solid and liquid was 8.1359 g (97% recovery). No 4 was observed.

Registry No.—1, 24332-20-5; 2, 7062-96-6; 3, 7062-97-7; 4, 1634-04-4; 6, 922-69-0; 7, 7252-83-7; potassium *tert*-butoxide, 865-47-4; *tert*-butyl alcohol, 75-65-0.

A Convenient Synthesis of Adamantylideneadamantane[1]

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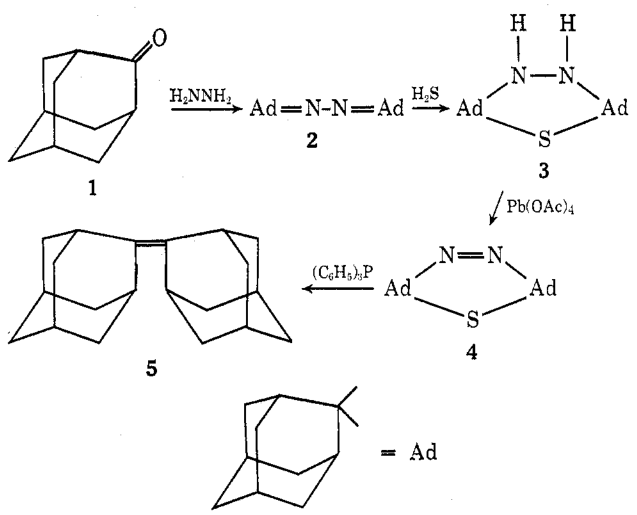
Recent investigations in this laboratory of the photooxidation of adamantylideneadamantane (5) in pinacolone solvent have provided the first direct evidence for the intermediacy of perepoxides in the addition of singlet oxygen to alkenes to form 1,2-dioxetanes.[2] Adamantylideneadamantane (5) has also been the subject of considerable interest because of the unusual stability of the 1,2-dioxetane[3] and the bromonium ion[4] obtained from this alkene.

We have found the synthesis of 5[5] *via* the carbenoid dimerization with *gem*-dibromoadamantane and zinc-copper couple to be very sensitive to the surface area and activity of the Zn-Cu couple. Reduction of the dibromide to adamantane is often the predominant reaction. We are therefore prompted to report a convenient, high-yield synthesis of 5 based on the extrusion of nitrogen and sulfur from an azo sulfide 4.[6]

Condensation of adamantanone (1) with hydrazine hydrate gives the azine 2. Addition of hydrogen sulfide to 2 yields the thiadiazolidine 3. Oxidation of 3 with lead tetraacetate affords the thiadiazine 4. Adamantylideneadamantane (5) is obtained by heating a melt of 4 and triphenylphosphine at 125°. The overall yield of 5 from 1 is 65%.



Experimental Section

Methods.—Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. The infrared spectra were measured on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model T-60 spectrometer with tetramethylsilane as internal standard. Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind.

Adamantanone Azine (2).—A solution of hydrazine hydrate (98%, 1.30 g, 26 mmol) in 15 ml of *tert*-butyl alcohol was added dropwise under nitrogen over a period of 45 min to a stirred refluxing solution of adamantanone (5.22 g, 35 mmol) in 60 ml of *tert*-butyl alcohol. After the addition was complete, the solution was refluxed for an additional 12 hr and subsequently allowed to stand at ambient temperature for 24 hr. The solvent was removed on a rotary evaporator to give an off-white crystalline mass to which was added 200 ml of water. The aqueous mixture was extracted with ether (4 × 100 ml). The combined ether extracts were washed with brine, dried ($MgSO_4$), and concentrated to give following recrystallization from hexane 5.10 g (98%) of 2: mp 313–315°; ir (KBr) 2885, 1622, and 1430 cm^{-1}; nmr ($CDCl_3$) δ 3.28 (m, 1 H), 2.62 (m, 1 H) and 1.93 (m, 12 H).

Anal. Calcd for $C_{20}H_{28}N_2$: C, 81.03; H, 9.52; N, 9.54. Found: C, 80.86; H, 9.51; N, 9.30.

Adamantanespiro-2′-(1′,3′,4′-thiadiazolidine)-5′-spiroadamantane (3).—Hydrogen sulfide was bubbled through a solution of the azine 2 (12.2 g, 41.1 mmol), and 5 mg of *p*-toluenesulfonic acid in 300 ml of 1:3 acetone–benzene at ambient temperature. Thin layer chromatography (silica gel, ethyl ether) indicated complete consumption of 2 after 12 hr. The solvent was removed on a rotary evaporator to give 12.8 g (95%) of the thiadiazolidine 3. This material was used in the subsequent step without further purification. Recrystallization from hexane afforded colorless crystals of 3: mp 300–307° dec; ir (KBr) 2880, 1705, and 1620 cm^{-1}; nmr ($CDCl_3$) δ 3.62 (br, 1 H) and 2.25–1.26 (m, 14 H).

2′,5′-Dihydroadamantanespiro-2′-(1′,3′,4′-thiadiazine)-5′-spiroadamantane (4).—To a suspension of $CaCO_3$ (20.7 g, 0.21 mol) in 300 ml of benzene at 0° was added in several portions lead tetraacetate (20.7 g, 46.7 mmol); the mixture was stirred for 20 min. A mixture of thiadiazolidine 3 (11.85 g, 35.9 mmol) and 300 ml of benzene was added dropwise with stirring over a period of 1.5 hr. After the addition was complete, the mixture was stirred at ambient temperature for 8 hr. Thin layer chromatography (silica gel, ether) indicated complete consumption of 3. Upon addition of 400 ml of water, a brown precipitate formed which was removed by filtration. The aqueous layer was separated, saturated with NaCl, and extracted with ether. The organic portions were combined, washed with brine, dried ($MgSO_4$), and concentrated to give 10.94 g (94%) of a yellow residue 4, mp 140–145°. This material was used in the subsequent step

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