To complete the characterization of **1**, it was converted at −80° to its hydrochloride, which had been prepared in a different way by Addor.[2] As described in ref 2, the hydrochloride rearranged into β-chloroethyl carbamate upon standing at room temperature.

Besides direct nucleophilic displacement on chlorine, which appears most likely, addition and elimination appears to be a possibility for the mechanism of formation of **1**.[4] It is interesting to note that a previous attempt to prepare **1** by reduction of **3** was unsuccessful.[3]

The trimerization of **1** most likely proceeds *via* ring opening to β-hydroxyethyl cyanate. Alkyl cyanates usually rearrange to isocyanates rather than trimerize, but electronegative substituents on the alkyl appear to slow down the isomerization so that trimerization can compete successfully, yielding trialkoxy-1,3,5-triazines.[5] A trimer similar to **2** was obtained upon basic treatment of 2-imino-1,3-oxathiane hydrochloride.[6]

Experimental Section

Ethylene Iminocarbonate (1). Into a 300-ml 3-neck flask fitted with Dry Ice–acetone condenser, mechanical stirrer, and gas inlet was condensed 200–250 ml of dry ammonia. To this was then added 2.5 g of sodium hydride washed 6–7 times with ether. A blue color resulted and disappeared after stirring for 6–10 hr, or upon addition of a small crystal of ferric nitrate (10–15 min. required). The mixture was cooled to −80° and 5 g of **3** were added. At −80°, the reaction proceeds to less than 50% after 2 hr. However, at −60° to −50°, it proceeds rapidly, often in a vigorously exothermic fashion. It was monitored by removing a small sample of the mixture, evaporating off the NH$_3$, triturating the residue with ice-cold pyridine and taking the nmr spectrum of the pyridine extract. The reaction was usually complete after 1 hr at −50 to −60° as evidenced by the loss of the nmr peak at δ 4.65, and the appearance of a singlet at δ 4.4. Ammonia was removed under reduced pressure (water aspirator) at −50 to −40°. The residue was triturated 3 times with ether at −20 to −30°. The ether extract was filtered and the ether removed on a rotary evaporator below 0°, leaving white crystals: mp 38–45°; yield varied from ~250 mg to 1 g (6–26%); ^{1}H nmr (acetonitrile-d_3) singlet at δ 4.4 (4 H), broad peak near δ 5.3 (1 H); ir (Nujol mull) 1700 and 3300 cm^{-1}; mass spectrum molecular ion peak at *m/e* 87, other peaks at 58, 44, and 43 (base peak) (a peak at *m/e* 58 is also seen in the mass spectrum of **3**).

2,4,6-Tris(β-hydroxyethoxy)-1,3,5-triazine (2). A. From Reaction Residue. Further extraction of the ether extracted sodamide residue with either acetonitrile or methylene chloride followed by filtration and evaporation of the solvent yielded a light yellow oil. Upon standing or triturating with acetonitrile, the oil gave white crystals, mp 113–117°. Yield 1.0–1.5 g. Analytical sample was crystallized from acetone: mp 117–120° (sintering); ^{1}H nmr (D$_2$O) A$_2$B$_2$ pattern centered at δ 3.7 and 4.2; ir (Nujol) 3300 (broad) and 1560 cm^{-1}; uv (acetonitrile) shoulder at 260 nm (ϵ 32), then strong rise in absorption but no maximum down to 205 nm; mass spectrum (electron impact ionization), no molecular ion at *m/e* 261, peaks at 244 (M$^+$ − OH, presumably bicyclic immonium ion), 231 (M$^+$ − CH$_2$O), 218, 201, 187, 174, 156, 143, 130 (base peak), 113, 87, 70; mass spectrum (chemical ionization) peak at *m/e* 262 (M$^+$ + H); high-resolution mass spectrum (Varian MAT 311, resolution 10,000), peak at nominal *m/e* 231 matched with PFK; 231.0852, for C$_8$H$_{13}$N$_3$O$_5$ calculated 231.0855.

B. From Ethylene Iminocarbonate (1). After standing at room temperature for several hours, ethylene iminocarbonate trimerized spontaneously, giving crystals of mp 114–118°, whose nmr and ir spectra were identical with those of the above-described trimer.

Ethylene Iminocarbonate Hydrochloride. Into 25 ml of dry ethylene glycol dimethyl ether (distilled from LiAlH$_4$) was placed ~20 mg of ethylene iminocarbonate. The solution was cooled to −80° (complete dissolution did not occur). A stream of dry HCl was bubbled into the mixture for 2 min. A cloudy suspension developed. The solid was collected on filter and washed with ether, giving fine white crystals: mp 73–75° (lit.[2] 77–78°); ir (Nujol mull) 1510, 1550, 1720, and a broad band at 2600–3400 cm^{-1}. Upon standing over the weekend, the hydrochloride rearranged to β-chlorethyl carbamate, mp 68–70° (lit.[2] 65–70°).

Registry No.—1, 6703-57-7; 1 HCl, 52699-47-5; 2, 891-65-6; 3, 22718-26-9.

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Ozonization of the 7-Phenylnorcaranes. Effects of Solvent and Temperature

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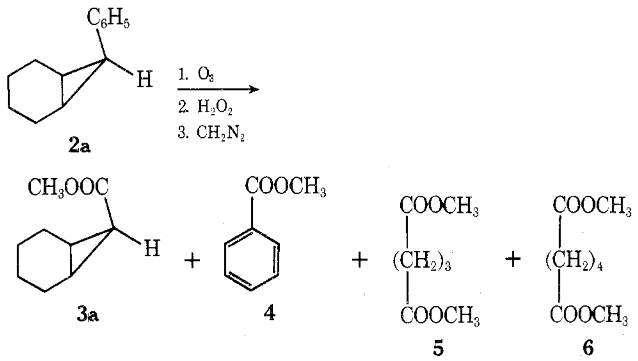
Recently we reported the first direct chemical evidence[1] supporting Closs',[2] Jensen's,[3] and Ledlie's[4] stereochemical assignments of *endo*- and *exo*-7-phenylnorcarane (**2a** and **2b**, respectively). This involved degrading **2a** and **2b** with ozone, employing the procedure of Shabarov,[5] producing the known *endo*- and *exo*-norcarane-7-carboxylic acids,[6,7] respectively, and a cyclopropane cleavage product, benzoic acid (**4**), all of which were isolated as their methyl esters. We then became interested in searching for other cleavage products and now wish to report the isolation and identification of the remaining compounds formed as **2a** and **2b** are ozonized, noting the effects of solvent and temperature on the product distribution. A modified procedure for the synthesis of **2a** is also discussed.

Jensen[3] has reported that triphenyltin hydride reduction of crude 7-chloro-7-phenylnorcarane (**1**), prepared by reaction of cyclohexene, benzal chloride, and potassium *tert*-butoxide,[8] yields, by vpc, 80% **2a**, 1% **2b**, and 19% olefin. Our observations indicate that the origin of the olefin arises not from the reduction of **1**, but occurs as a result of reduction of an olefinic product produced during the preparation of **1**. This olefinic impurity was removed with ozone. Purified **1** was then reduced with lithium aluminum hydride in diglyme furnishing a 65% yield of products which analyze (vpc) as 97% **2a**, 3% **2b**, and no olefin. Subsequent distillation of the reaction mixture yields a sample of **2a** that is 99% pure.[9]

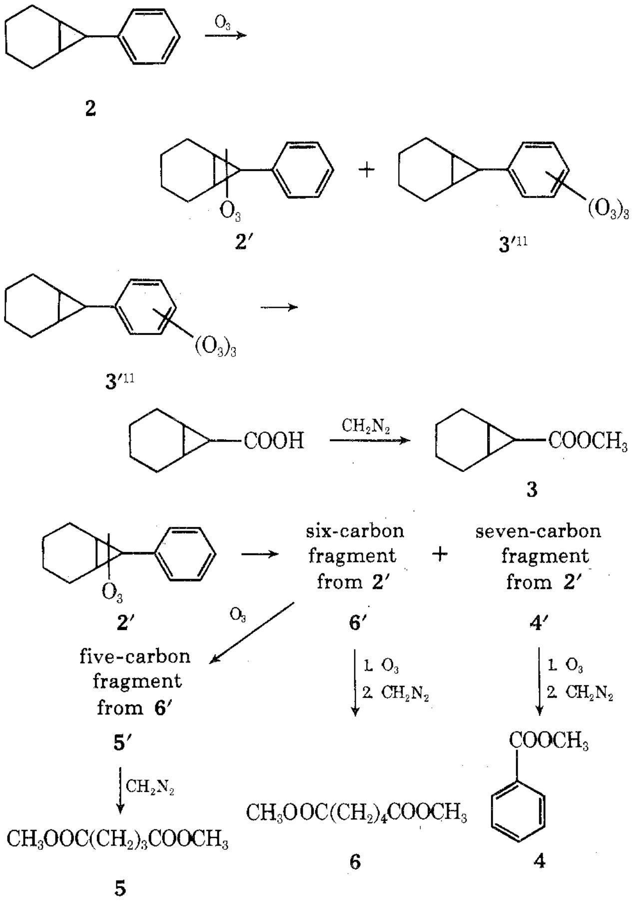
Ozonization of **2a** in 95% acetic acid at 25°, followed by treatment of the ozonized material with hydrogen peroxide and subsequent methylation of the products, furnishes a mixture containing four volatile components. These were separated by preparative gas chromatography and labeled in order of increasing elution time as **3a**, **4**, **5**, and **6**. Compounds **3a** and **4** have previously been identified as *endo*-7-carbomethoxynorcarane and methyl benzoate, respectively.[1] Compound **5** was identified as dimethyl glutarate by comparison of its ir and nmr spectra with reference spectra, correct elemental analysis, and by saponification of **5** to glutaric acid. Compound **6** furnished a correct elemental analysis for dimethyl adipate, gave ir and nmr spectra identical with authentic material, and saponification of **6** furnished adipic acid. These materials, **3a**, **4**, **5**, and **6**, were formed in 13, 16, and 9 and 8% yields, respectively,



when ozonized with a stream of 3% ozone. As expected, *exo*-7-phenylnorcarane furnished the same products (neglecting stereochemistry) when exposed to ozone. Both **2a** and **2b** consumed 8.3 mol of ozone/mol of starting compound when ozonized at 25° in 95% acetic acid.

Comparison of product ratios obtained from complete and partial ozonizations of **2b** provides some insight into these reactions. Essentially the same **3b**/**4** ratio is obtained from both of these ozonizations indicating that these two compounds result from the initial attack of ozone on **2b**. The **5**/**6** ratio was five times larger for the completely ozonized sample indicating that **5** resulted from ozone attack on **6′**. Gas chromatographic analysis of a sample of **2b** that had been treated with ozone and then diazomethane confirmed the presence of all four methyl esters, thereby demonstrating that it was the ozone and not the hydrogen proxide that was responsible for these ring opening reactions.[10] A proposed reaction scheme is given (Scheme I). Of course ozone could also react with **3′**[11] at the cyclopropane portion of the bicyclic ring system leading to the formation of **5** and **6**.

Scheme I



The effects of varying the source and concentration of ozone, temperature, and solvent upon the product distribution have been investigated. Ozonizing with ozone concentrations in the range of 3–6% in a stream of oxygen, ozonizing with a stream of 3% ozone in air, or ozonizing with oxygen-free ozone[12] in a stream of nitrogen had virtually no effect on the product distribution or total yield of the reaction. The effects of varying the temperature, employing 95% acetic acid as the solvent, afforded the most dramatic effect upon the product distribution while maintaining good overall yields. Increased reaction temperatures tend to favor attack at the bicyclic ring system, while lower temperatures tend to favor attack at the phenyl ring. When **2a** was ozonized in methylene chloride or ethyl acetate at 25°, one observes a decrease in the overall yield of the reaction as well as a reduction of the **3a**/**4** ratio when compared to the results obtained using 95% acetic acid as the solvent. Overall, there was a decrease in attack on the bicyclic ring system in the exo isomer as compared to the endo isomer, possibly due to the decreased shielding of the phenyl ring in the exo isomer. We are presently investigating the ozonization of other bicyclo[*n*.1.0] systems as a function of structure and reaction temperature.

Table I
Influence of Temperature on the Product Distribution in the Ozonization of the 7-Phenylnorcaranes

Compd	Solvent	Temp (°C)	Ozone concn (%)	% yield[a]				
				3a	3b	4	5	6
2a	95% HOAc	6	3	19		17	8	8
2a	95% HOAc	25	3	13		16	9	8
2a	95% HOAc	60	3	8		20	10	7
2a	95% HOAc	80	3	8		29	7	9
2b	95% HOAc	6	3		23	8	7	4
2b	95% HOAc	25	3		25	11	10	5
2b	95% HOAc	80	3		11	17	14	4

[a] Each reaction was performed twice with the average yield calculated for each product shown in Table I. The yield data were reproducible to within ±1%.

Experimental Section

An F&M gas chromatograph, Model 810, equipped with a 14 ft × 0.25 in. 5% Carbowax 1500 column operated at 130°, He flow rate of 100 ml/min, was employed for all analytical and preparative gas chromatography. Ir spectra were obtained using a Beckman Model 10 grating ir spectrophotometer with potassium bromide cells. Nmr spectra were recorded in carbon tetrachloride with a Varian A-60 spectrometer employing tetramethylsilane as an internal reference. A Welsbach ozonator, Model T-816, operated at a flow of 1 l./min was used for all ozonolyses. The elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Boiling points are uncorrected.

Ozonolysis of *endo*-7-Phenylnorcarane[5] (2a). A stream of 3% ozone was bubbled through a 250-ml gas wash bottle containing a magnetically stirred mixture of 1.0 g of **2a**[9] (99% pure) in 100 ml of 95% acetic acid until a test in water showed no turbidity. The time required for this reaction at 25° was 2.0 hr. After completion of the reaction, 10 ml of 30% hydrogen peroxide was added, and the solution was allowed to stir at room temperature overnight. The mixture was then heated in an oil bath at 95° for 4 hr, and the acetic acid removed *in vacuo*, furnishing a mixture of four acids. These acids were dissolved in dioxane and treated with diazomethane[13] and the resulting methyl esters separated by preparative gas chromatography employing a 14 ft × 0.25 in. column containing 5% Carbowax 1500 on Chromosorb P operated at 130°. The order of elution of the four methyl esters is **3a**, **4**, **5**, and **6**, respectively. The faster eluting compounds **3a** and **4** have previously been identified as *endo*-7-carbomethoxynorcarane and methyl benzoate, respectively.[1]

Compound **5** was proven to be dimethyl glutarate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0624 g of **5** was accomplished by refluxing with 1 ml of concentrated hydrochloric acid for 20 min, cooling, and then removing the water by placing the mixture in a vacuum desiccator along with a beaker of concentrated sulfuric acid. This procedure furnished a 59% yield of glutaric acid, mp and mmp 96.2–97.2° (lit.[14] mp 97°).

Anal. Calcd for $C_7H_{14}O_4$: C, 52.49; H, 7.55. Found: C, 52.39; H, 7.58.

Compound **6** was proven to be dimethyl adipate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0697 g of **6** *vide supra* gave adipic acid in 55% yield, mp and mmp 150.5–151.5° (lit.[15] mp 150–151°).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.94; H, 7.97.

The yields[16] of esters **3a, 4, 5,** and **6** based on **2a** were 13, 16, 9, and 8%, respectively.

Ozonization of **2a** was also carried out in 95% acetic acid at temperatures of 6, 60, and 80°, requiring 3.66, 1.5, and 1.33 hr, respectively, for completion. The yields[16] of esters **3a, 4, 5,** and **6** based on **2a** are, respectively, as follows: 19, 17, 8, and 8% for the 6° reaction; 8, 20, 10, and 7% for the 60° reaction; and 8, 29, 7, and 9% for the 80° reaction.

exo-**7-Phenylnorcarane**[2] **(2b).** To a stirred solution of 41 g of potassium *tert*-butoxide[8] and 230 ml of dry dimethyl sulfoxide (CaH_2) was added 9.6 g of **2a**[9] (99% pure) and then the mixture was heated to 100° under a nitrogen atmosphere for 25 hr. The reaction mixture was hydrolyzed and extracted with ether, and the extract washed with water and then dried over $CaCl_2$. Evaporation of the solvent and subsequent distillation of the residue, utilizing a Nester/Faust Auto Annular spinning band distillation column, resulted in 8.31 g (87% yield) of **2b** (98% pure), bp 126–127° (11 mm).

Ozonolysis of *exo*-**7-Phenylnorcarane**[5] **(2b).** Ozonolysis of **2b** (98% pure) was carried out in exactly the same manner described for **2a.** The time required for this reaction at 25° was 1.16 hr. The order of elution of the four methyl esters obtained is **4, 3b, 5,** and **6.** The faster eluting compounds, **4** and **3b,** have previously been identified as methyl benzoate and *exo*-7-carbomethoxynorcarane, respectively.[1]

Compound **5** was shown to be dimethyl glutarate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0829 g of **5** *vide supra* gave an 83% yield of glutaric acid, mp and mmp 95.7–96.7° (lit.[14] mp 97°).

Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.58; H, 7.53.

Compound **6** was proven to be dimethyl adipate by comparison of its ir and nmr spectra with reference spectra. Saponification of 0.0805 g of **6** *vide supra* furnished a 68% yield of adipic acid, mp and mmp 150.3–151.8° (lit.[15] 150–151°).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.43; H, 8.14.

The yields[16] of esters **3b, 4, 5,** and **6** based on **2b** were 25, 11, 10, and 5%, respectively.

Ozonization of **2b** was also carried out in 95% acetic acid at temperatures of 6 and 80°, requiring 1.66 and 0.83 hr, respectively, for completion. The yields[16] of esters **3b, 4, 5,** and **6** based on **2b** for the 6° reaction were 23, 8, 7, and 4%, respectively, while the yields for the 80° reaction were 11, 17, 14, and 4%, respectively.

Acknowledgment. The authors wish to acknowledge the financial support (Grant AE-361) of The Robert A. Welch Foundation.

Registry No.—**2a,** 10503-37-4; **2b,** 10503-36-3; **5,** 1119-40-0; **6,** 627-93-0.

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Oxidation of Olefins by Mercuric Salts. The Alkaline Decomposition of Oxymercurials

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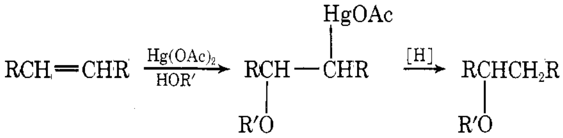
The increasing interest shown in the oxymetalation of olefins in the past few years has mirrored the fast growing field of organometallic chemistry. Among oxymetalation reactions oxymercuration occupies a position of considerable importance and the number of recent reviews is a clear testimony to this.[1–4]

The interaction of alkenes with mercuric salts yields oxymercurials which can either be reduced as typical organomercury compounds[5] or be thermally decomposed in acidic medium as in the Denigés reaction to give directly oxidized organic moieties and reduced mercury species.[6]



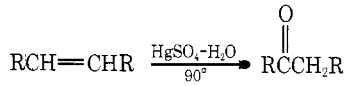
$$RCH{=}CHR \xrightarrow[HOR']{Hg(OAc)_2} \underset{R'O}{RCH}-\overset{HgOAc}{CHR} \xrightarrow{[H]} \underset{R'O}{RCHCH_2R}$$

We have studied the thermal decomposition of these organomercurials in alkaline medium and found quite a different behavior from that observed in acidic medium. Thus when basic solutions containing oxymercurials are heated, a mixture of ketone and epoxide as the oxidized organic moiety is obtained.[7]

Results and Discussion

The study was first carried out under experimental conditions analogous to the Denigés reaction[6] and then by synthesizing the desired oxymercurial and following its thermal decomposition in a chosen medium.

Aqueous Medium. The general procedure was to stir a suspension of mercuric salt in the presence of olefin. The solution obtained was then made basic and heated. At the end of the reaction, addition of hydrochloric acid regenerated the starting olefin and thus allowed an estimation of the advancement of the reaction, *i.e.*, per cent conversion.



$$RCH{=}CHR \xrightarrow[90^\circ]{HgSO_4\text{-}H_2O} R\overset{O}{\overset{\|}{C}}CH_2R$$

The results given in Table I show clearly lower yields with propene and 1-butene. This can easily be explained if one considers the possibility of allylic oxidation of α-olefins analogous to that observed in acidic medium; such oxidations generally yield α,β-unsaturated carbonyl compounds which can be expected to be unstable under the reaction conditions.[6] This was shown to be the case by introducing compounds such as acrolein or methyl vinyl ketone in the