tained with ytterbium (in threefold excess) in ammonia containing alcohol (followed by oxidation with Jones' reagent),[14] the major product formed with THF as cosolvent and no proton source was the pinacol dimer 8.[15] The presence of ytterbium enolates in these reductions is implied by the isolation of saturated ketones prior to oxidation and by analogy with lithium–ammonia reduction of similar systems.[13,16] It appears that ytterbium enolates, like their alkali metal counterparts, are stable in liquid ammonia and are appreciably less basic. However, an attempt to alkylate the ytterbium enolate from 6 with methyl iodide was not successful.[17]

Finally, the reduction of alkynes was demonstrated with diphenylacetylene and 4-octyne (THF cosolvent), affording the corresponding trans alkene (Table I). Interestingly, reduction of 1-phenylpentyne gave only a mixture of 1-phenylpentane and starting material, the proportions of which depended upon the quantity of ytterbium used. Apparently, certain double bonds can be saturated with this reagent,[18] a fact which was confirmed by the reduction of norbornadiene to bicyclo[2.2.1]heptene (eq 2) in 65% yield.[19]
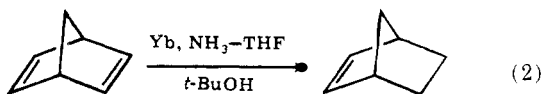
The ytterbium–ammonia system thus represents a useful reducing agent which resembles the analogous alkali metal solutions in potency. The ready availability of this lanthanide element,[20] in conjuction with its inertness to water and air (which necessitates no special precautions in its handling), and the fact that strongly basic hydroxides are avoided during workup, lends it certain advantages over the more reactive metals commonly used in electron-transfer chemistry.[21]

References and Notes

(1) Appropriately, 1978 marks the centenary of the discovery of ytterbium by Jean-Charles Galissard de Marignac at the University of Geneva; for an historical account see C. K. Jorgensen, *Chimia*, **32**, 89 (1978).

(2) A. J. Birch and G. Subba Rao in "Advances in Organic Chemistry, Methods and Results", Vol. 8, E. C. Taylor, Ed., Wiley Interscience, New York, N.Y., 1972, p 1.

(3) H. Smith "Organic Reactions in Liquid Ammonia", Interscience, New York, N.Y., 1963.

(4) The Yb^{2+} ion possesses the closed f shell electron configuration of Xe;

however, the divalent state is readily oxidized in air to Yb^{3+} ($E_{Yb^0 \to Yb^{3+}}$ is -2.27 V). The ionic radius of Yb^{2+} is intermediate between that of Li^+ and Na^+.

(5) S. Salot and J. C. Warf, *J. Am. Chem. Soc.*, **90**, 1932 (1968).

(6) The initial formation of Yb^{2+} in this process is indicated by a characteristic green color prior to workup. Addition of aqueous solutions results in the formation of a suspension of brown Yb^{3+} salts, which can be removed by filtration through Celite or may be dissolved in dilute mineral acid.

(7) All products, including those whose yields were determined by GLC, were characterized by means of their IR, NMR, and mass spectra and, where appropriate, by melting point. Comparisons with authentic samples were made where these were available, otherwise elemental composition was determined by exact mass measurement.

(8) Using a large excess of lithium and a 1:3 ratio of THF–NH₃ containing 3% *tert*-butyl alcohol, durene was reduced during 12 h to 1,2,4,5-tetramethylcyclohexa-1,4-diene in 72% yield (C. L. Kirkemo and J. D. White, unpublished observations).

(9) Cf. M. Kocor and W. K. Kotlarek, *Bull. Acad. Pol. Sci., Ser. Sci. Chem.*, **19**, 219 (1971).

(10) R. G. Harvey and K. Urbery, *J. Org. Chem.*, **33**, 2570 (1968).

(11) B. J. Magerlein and J. A. Hogg, *J. Am. Chem. Soc.*, **80**, 2220 (1958).

(12) H. L. Dryden, G. M. Webber, R. L. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

(13) D. Caine, *Org. React.*, **23**, 1 (1976).

(14) D. H. R. Barton, D. A. Ives, and B. R. Thomas, *J. Chem. Soc.*, 903 (1954).

(15) P. Bladon, J. W. Cornforth, and R. H. Jaeger, *J. Chem. Soc.*, 863 (1958).

(16) L. M. Jackman and B. C. Lange, *Tetrahedron*, **33**, 2737 (1977).

(17) See J. d'Angelo, *Tetrahedron*, **32**, 2979 (1976).

(18) G. W. Watt, *Chem. Rev.*, **46**, 325 (1950).

(19) B. R. Ortiz de Montellano, B. A. Loving, T. C. Shields, and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 3365 (1967).

(20) Ytterbium (99.9%, distilled) is available from Research Chemicals, P.O. Box 14588, Phoenix, Arizona 85063, at $0.90 per gram.

(21) This research was assisted financially by a grant (CHE77-04379) from the National Science Foundation.

(22) National Institutes of Health Research Career Development Awardee (1976–1981).

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Homoallyl–Cyclopropylcarbinyl Carbonium Ion Formation and Rearrangement under Strongly Basic Conditions

Summary: Treatment of the ethylene glycol ketal of 2,8-dibromocyclooctanone with sodium hydroxide produces the ethylene glycol ketal of 2,7-cyclooctadienone (71–76%) and a mixture of ethylene glyoxymethyl cyclohept-2-ene- and bicyclo[4.1.0]hept-7-ylorthocarboxylates (about 20%), indicating (in conjunction with the carbocation chemistry of the ethylene glycol ketal of 8-bromocyclooct-2-enone) that intermediate homoallyl–cyclopropylcarbinyl carbonium ions may be involved in the reactions leading to orthoester side products.

Sir: While the generation and reactions of carbonium ions in strongly acidic media are well documented,[1a] such is not the case for basic media.[1b,c] In this communication evidence is presented which implicates the novel formation and rearrangement of a homoallyl–cyclopropylcarbinyl carbonium ion system under *strongly alkaline conditions.*

The preparation of 2,7-cyclooctadienone is usually carried out according to the reaction sequence developed by Garbisch.[2] Cyclooctanone ethylene ketal (1) is treated with bromine to give (after recrystallization from methanol) *trans*-2,8-dibromocyclooctanone ethylene ketal (2), which is bisdehydrobrominated (with refluxing methanolic sodium hydroxide) to the diene ketal 3, which in turn is hydrolyzed to 4. It has now been discovered that there are interesting side reactions (apparently involving intermediate carbonium ions) which accompany the elimination reaction (2 → 3).

**Table I. Carbon-13 NMR Chemical Shift Assignments for Orthoesters 5–7[a,b,c]**

compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9, 10	C-11
5	47.1	133.9*	130.8*	31.3†	28.8†	27.2†	28.5†	124.8	65.7	48.8
6	28.1	14.0	23.3*	21.7*	(21.7)	(23.3)	(14.0)	122.9	65.1	49.4
7	46.1	29.1	27.4*	29.1*	(29.1)	(27.4)	(29.1)	125.7	65.6	48.7

[a] All spectra measured in benzene-d_6 with internal Me_4Si. [b] Values in parentheses are those of symmetry related atoms. [c] Chemical-shift assignments were made on general shielding parameters [J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972], relative signal intensities, and the residual splitting patterns observed with off-resonance partially decoupled spectra; pairs or groups of signals which could not be rigorously assigned to specific carbons are indicated by the symbols * and †.


1, X = H
2, X = Br

3

4
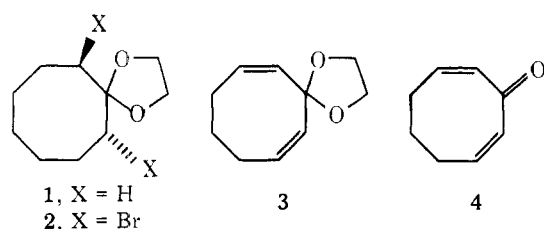
The conversion of analytically pure dibromo ketal **2** to diene ketal **3** was performed several times as described previously.[2] However, when the product was isolated by high vacuum distillation as reported[2] [65 °C (0.3 mmHg)], its purity was only about 75% (although the yield of distillate was close to 90%). On the other hand, when the rectification was conducted at higher pressure [133–135 °C (31 mmHg)] the yield was only 71–76%, but the purity of the distilled product was >95%; in addition to the distilled material, there remained a pot residue which accounted for about 20% of the material balance.[3]

Investigation of the above-mentioned residue revealed that it was composed of two major compounds which are extremely sensitive to acid hydrolysis. Utilizing a combination of spectroscopic and chemical methods, the structures of the major components were shown to be the orthoesters **5** and **6** (in the approximate ratio of 3:2). The carbon-13 NMR spectra (Table I) were particularly instructive: for **5**, the units HC=CH and $CH_3OC(OCH_2)_2CH$, as well as *four different* CH_2 groups, were established; while for **6**, the $CH_3OC(OCH_2)_2CH$ moiety, as well as *two sets of two identical* CH_2 groups and *one set of two identical* CH groups, were ascertained. Hydrogenation of **5** gave the corresponding saturated orthoester **7**, whose

7

8, R = CH_2CH_2OH
10, R = H
11, R = CH_3

9, R = CH_2CH_2OH
13, R = H
14, R = CH_2CH_3

12
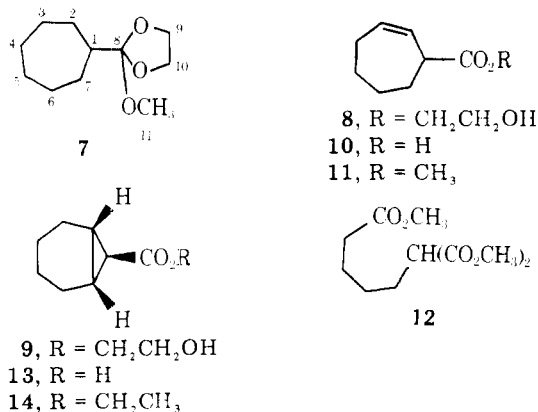
carbon-13 NMR spectrum concurred with the symmetry anticipated. Hydrolysis of orthoesters **5** and **6** gave esters **8** and **9**, whose structures were elucidated by chemical degradation (as well as consistent spectral and analytical data). Saponification of **8** gave the acid **10**, which was esterified to **11**,[4a] and subjected to the Lemieux–von Rudloff oxidative cleavage to give (after Fisher esterification) the triester **12**, whose spectral data were identical with those of authentic material prepared independently from dimethyl malonate and methyl 5-bromovalerate. Similarly, saponification of **9** gave **13**, which was
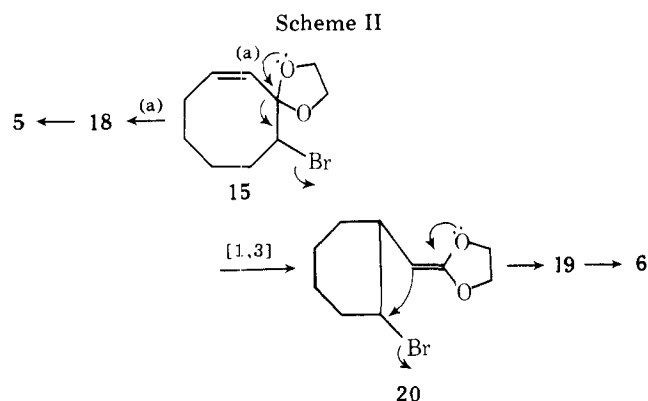
Scheme I

15

16

17

5

18

19

6
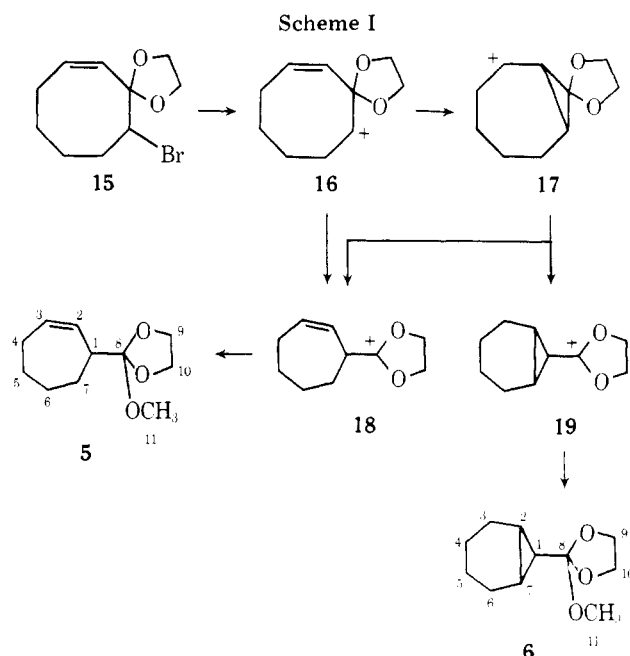
esterified to **14**,[4b] whose spectral data were identical with those of ethyl *exo*-norcarane-7-carboxylate (prepared from cyclohexene and ethyl diazocarboxylate[5]).

Having unequivocally determined the structures of the side products **5** and **6**, attention was directed to ascertaining their modes of formation. The most straightforward mechanism for the production of orthoesters **5** and **6** involves the intermediacy of the homoallyl–cyclopropylcarbinyl carbonium ions illustrated in Scheme I. Elimination of the first molecule of HBr from dibromo ketal **2** produces the homoallylic bromo ketal **15**, which under the very polar reaction conditions can ionize to the homoallylic carbonium ion **16** and its cyclopropylcarbinyl counterpart **17**. Rearrangement of ions **16** and **17** utilizing the ethylene glyoxy unit would give carbocations **18** and **19** (stabilized by the adjacent oxygen atoms), which are trapped by methoxide–methanol to give orthoesters **5** and **6**.[6]

In order to test the interpretation advanced in Scheme I, homoallylic bromide **15** was prepared (by carrying out the elimination reaction to the extent that only a small amount of diene ketal was formed) and subjected to various carbonium ion producing reactions. Thus, methanolysis of distilled **15** gave orthoester **5** *exclusively*. Likewise, treatment of methanolic **15** with aqueous silver nitrate solution gave *quantitatively* orthoester **5**, which under the reaction conditions was hydrolyzed to ester **8**.[7] These results are compatible with the intermediacy of the homoallyl carbonium ions **16** and **18**, and lend support to the hypothesis of Scheme I. The fact that no cyclopropylcarbinyl products were formed is surprising in view of the results for the acetolysis of 3-cyclooocten-1-yl brosylate (which gave bicyclo[5.1.0]octan-2-ols as the major products).[8]

An alternative mechanism not involving carbonium ion reorganizations is one related to the semibenzilic rearrange-

Scheme II

ment.[9] While such an interpretation (Scheme II) nicely accommodates the transformation of **15** to **5**, it is rather cumbersome for the conversion of **15** to **6**: a [1,3] sigmatropic shift to generate the ketene acetal **20** must precede the ejection of bromide during the formation of the three-membered ring.[11] The semibenzilic mechanism also does not account for the absence of cyclopropylcarbinyl products in the reactions of **15** with methanol or silver nitrate.

In conclusion, based on the information available, the carbonium ion pathway of Scheme I seems best suited to rationalize the formation of orthoesters **5** and **6**. This unexpected result raises questions about similar possible side reactions taking place during the preparation of ketals of 2,6-cycloheptadienone, 4,4-disubstituted cyclohexadienones, and cyclopentadienone where the constraints of smaller ring sizes enter into the picture. Work in these and other related areas is in progress.

References and Notes

(1) (a) G. A. Olah, G. Liang, K. A. Babiak, T. M. Ford, D. L. Goff, T. K. Morgan, Jr., and R. K. Murray, Jr., *J. Am. Chem. Soc.*, **100**, 1494 (1978). (b) W. H. Saunders, Jr. and A. F. Cockerill, "Mechanisms of Elimination Reactions", Wiley, New York, N.Y., 1973, pp 210, 211. In the examples cited [I. N. Feit and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **92**, 1630 (1970); A. K. Colter and D. R. McKelvey, *Can. J. Chem.*, **43**, 1282 (1965); W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Am. Chem.*

Soc., **87**, 3401 (1965); H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **76**, 455 (1954)] the maximum concentrations of the base used were approximately 1 M and the amounts of carbonium ion derived products (rearranged olefins) did not exceed 7% of the E2 reaction products. In the work described in the present report, the base concentrations were between 4.8 and 5.5 M;[2] such high concentrations would normally almost completely suppress E1 reactions. (c) Deoxidation (the reaction of alcohols with haloform in basic solution) probably involves carbonium ion intermediates; *for a review see J. T. Keating and P. S. Skell, "Carbonium Ions", G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, N.Y., 1970, pp 576, 617, and 633.*

(2) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

(3) Significantly, hydrolysis of the purer diene ketal **3** gave pure dienone **4** in yields of 92–99% after distillation, whereas hydrolysis of the less pure diene ketal gave **4** in about 75% yield (as reported[2]) along with a distillation pot residue (which was shown to consist mostly of **8** and **9**).

(4) The similarity of spectral data within each framework indicated that: (a) *no* double bond isomerization accompanied the transformation **8** to **11**; (b) no epimerization of the carboxylic group attended the conversion of **9** to **14**.

(5) E. Ciganek, *J. Am. Chem. Soc.*, **93**, 2207 (1971); H. Musso, *Chem. Ber.*, **101**, 3710 (1968).

(6) Interestingly, no ethers or alcohols derived by capture of ions **16** and **17** were found; therefore, rearrangement to the much more stable ions **18** and **19**, respectively, is very fast relative to the rate of interception by a nucleophile. Also somewhat surprising is the fact that the acids corresponding to esters **8** and **9** (which would be produced from the trapping of carbonium ions **18** and **19**, respectively, by hydroxide followed by saponification) formed to the extent of only about 2%.

(7) In contrast to this result, it was observed that both dibromo ketal **2** and its monobromo counterpart are *completely inert* to the silver nitrate reaction conditions employed with the unsaturated bromo ketal **15**; thus, the double bond of **15** is a necessary component for the rearrangement(s) observed.

(8) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959); see also E. C. Friedrich and J. D. Cooper, *Tetrahedron Lett.*, 4397 (1976); L. E. Friedrich and F. R. Wight, *J. Am. Chem. Soc.*, **92**, 1807 (1970); A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4850 (1962); A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

(9) Such a process has been found to be operative in the thermolysis of 2-bromocyclobutanone ethylene ketal (but not for its five- and six-membered homologues).[10]

(10) J. Salaun, B. Garnier, and J. M. Conia, *Tetrahedron*, **29**, 2895 (1976); see also S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

(11) While the alkylation of ketene acetals by various halides is a known reaction,[12] the ketene acetal generally has to be *unsubstituted*, although the intramolecular nature of the pathway depicted in Scheme II might permit this restriction to be circumvented. With regard to the [1,3] sigmatropic shift, cyclooctenes are isomerized to vinylcyclohexanes at rather elevated temperatures (>500 °C).[13]

(12) S. M. McElvain and F. McShane, Jr., *J. Am. Chem. Soc.*, **74**, 2662 (1952), and references cited therein.

(13) J. K. Crandall and R. J. Watkins, *J. Org. Chem.*, **36**, 913 (1971).

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