and partially *via* a singlet reaction. If either (a) or (c) holds, then the absence of piperylene quenching allows estimation of the upper limits for τ_T of **3K–7K** (Table I). On the other hand, if α cleavage occurs totally from the singlet state, then clearly efficient piperylene quenching would not be expected and nothing can be safely concluded about the τ_T values extracted from our Stern–Volmer plots.

By analogy,[7,8,9] we would expect the n,π^* triplet state of cyclic ketones **3K–7K**, if produced, to undergo α cleavage and subsequent rapid disproportionation to **3A–7A**.[7–9] Thus, for reaction to occur solely from the n,π^* singlet there would have to be little or no intersystem crossing in these ketones. This could be the case if the rate constant for α cleavage from the singlet, k_r^s, were much larger than the rate constant for intersystem crossing, k_{st}. But if $k_r^s \gg k_{st}$, then the singlet lifetimes, τ_s, will be approximately $1/k_r^s$ and hence determined primarily by k_r^s. However, we will show below that this possibility can be experimentally ruled out.

The introduction of either α-methyl substituents[9] or ring strain[7–9] in cyclic alkanones has been shown to increase the value of k_r^T. That ring strain and α substitution will similarly affect α cleavage of n,π^* singlet states seems quite reasonable. Thus, if singlet lifetimes are determined by k_r^s, then τ_s should *decrease* with increasing angle strain or α-alkyl substituents.

On the contrary, ketones **3K–7K** all have τ_s values *larger* than that of cyclopentanone, with **3K** being over four times greater. This implies that τ_s for **3K–7K** is primarily determined *not* by k_r^s, but rather by k_{st}, which for alkyl ketones *decreases* with increasing substitution of α-methyl groups.[15] *Thus, we conclude that α cleavage of the ketones* **3K–7K** *must arise, at least in part, from the n,π^* triplet state.* The lack of quenching of aldehyde formation by piperylene can then safely be used to determine the upper limits for τ_T of **3K–7K** given in Table I.

Since radiationless deactivation of alkyl ketone triplets is relatively inefficient,[16] k_r^T can be approximated by τ_T^{-1}. Thus, for ketones **3K–7K**, k_r^T must be greater than 5×10^{10} sec^{-1}. On the other hand, $1/\tau_s$ must be an upper limit for k_r^s. Since the singlet lifetimes of **3K–7K** range from 4 to 9 nsec, we conclude that $k_r^s < 2.5 \times 10^8$ sec^{-1}. Hence there is a difference of *at least* two orders of magnitude in the reactivity of the n,π^* singlet state and the n,π^* triplet state of these cyclic alkanones toward α cleavage. The source of this striking reactivity difference toward α cleavage for these cyclic alkanone singlets and triplets, which is of considerable interest, is being actively investigated.

(15) J. C. Dalton, unpublished results. See also A. C. Testa and M. O'Sullivan, Abstracts, 156th National Meeting of the American Chemical Society, Sept 1968, PHYS 166.
(16) P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966).
(17) National Institutes of Health Predoctoral Fellow, 1966–1969.
(18) National Institutes of Health Predoctoral Fellow, 1966–1969.
(19) National Institutes of Health Postdoctoral Fellow, 1968–1969.
(20) Alfred P. Sloan Fellow, 1966–1970.

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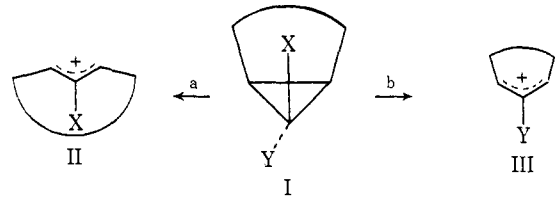
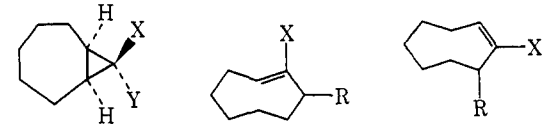
Silver Perchlorate Promoted Ring Expansion of Halocarbene Adducts of Cyclic Olefins. A Facile Synthesis of *trans*-Cyclooctene and *trans*-Cyclononene Derivatives

Sir:

The ring expansion of halocarbene adducts of cyclic olefins is now well established as a synthetic reaction of considerable utility.[1,2a] Recently, the application of the principle of orbital symmetry conservation to this reaction[3] has led to the prediction that the ring expansion of dihalocarbene adducts (I, X = halogen; Y = halogen) should follow one of two pathways (a or b, Scheme I). It then seemed likely from steric considerations[4] that pathway a, involving the *exo*-leaving group (Y) and leading to a *trans,trans*-allyl cation (II) (and hence to a *trans* olefin derivative), would be preferred unless the expanded ring were too small to accommodate a *trans* double bond. In the latter case, pathway b would be preferred. Clearly, pathway b is prohibited for *exo*-monohalocarbene adducts (I, X = H; Y = halogen) and pathway a for *endo* adducts (I, X = halogen; Y = H).



In contrast to its thermal stability[2a] we now report that when 8,8-dibromobicyclo[5.1.0]octane (IVa) was treated with an excess of silver perchlorate in anhydrous methanol solution at 20°, it was quantitatively converted *in less than 5 min* into *trans*-2-bromo-3-methoxycyclooctene[5] (Va, R = OMe) [nmr[6] τ 3.89 (dd, J = 4 and 11.5 Hz, 1 H), 6.38 (dd, 1 H), 6.81 (s, 3 H), 7.0–9.4 (m, 10 H)]. When Va (R = OMe) was heated in a nitrogen atmosphere at 170–180° for 140 min, it underwent *ca.* 75% conversion to its *cis* isomer (VIa, R = OMe) [τ 3.78 (t, J = 8.5 Hz, 1 H), 5.90 (t, J = 7.5 Hz, 1 H), 6.80 (s, 3 H), 7.6–8.8 (m, 10 H)].



IVa, X = Y = Br
b, X = Y = Cl
c, X = H; Y = Br
d, X = Br; Y = H

Va, X = Br
b, X = Cl
c, X = H

VIa, X = Br
b, X = H

(1) W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 71 (1963); W. Kirmse, "Carbene Chemistry," Academic, New York, N. Y., 1964, Chapter 8; C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic, New York, N. Y., 1968, Chapter VIII; T. Ando, H. Hosaka, H. Yamanaka, and W. Funasaka, *Bull. Chem. Soc. Jap.*, **42**, 2013 (1969).
(2) (a) M. S. Baird, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc., C*, 1173 (1969); (b) M. S. Baird and C. B. Reese, *ibid.*, 1803 (1969).
(3) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).
(4) C. H. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).
(5) Satisfactory analytical and spectroscopic data were obtained for all new compounds described.
(6) Nmr spectra of CCl_4 solutions were measured at 100 MHz with a Varian HA 100 spectrometer. Me_4Si was used as internal standard, and chemical shifts are given in parts per million on a τ scale.

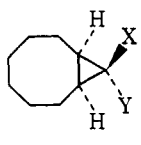
Table I. Silver Perchlorate[a] Promoted Ring Expansion of 8-Halobicyclo[5.1.0]octane Derivatives (IV)

Substrate	Solvent	Temp, °C	Reaction time, min	Product	Isolated yield,[b] %
IVa	MeOH	20	5	Va, R = OMe	82
IVa	Me_2CO–H_2O[c]	20	15	Va, R = OH	80
IVb	MeOH	45	45	Vb, R = OMe	77
IVc	MeOH	20	5	Vc, R = OMe	75
IVc	Me_2CO–H_2O	20	15	Vc, R = OH	75
IVd	MeOH	45	180	VIb, R = OMe	45
IVd	Me_2CO–H_2O	56	120	VIb, R = OH	55

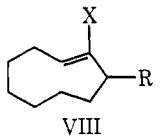
[a] Although a slight excess of $AgClO_4$ is sufficient, it is convenient to use *ca.* 2 molar equiv of it with respect to the substrate. The initial concentration of $AgClO_4$ was generally *ca.* 1 *M*. The reactions were found to proceed much more slowly in dilute solution. [b] In all reactions except those involving IVd (when some starting material remained), glpc indicated quantitative conversion to the product indicated. [c] Me_2CO–H_2O (95:5, v/v).

Similarly, 8,8-dichlorobicyclo[5.1.0]octane (IVb) was quantitatively converted into *trans*-2-chloro-3-methoxycyclooctene (Vb, R = OMe), but the reaction conditions were rather more vigorous (Table I). As anticipated,[7] *exo*-8-bromobicyclo[5.1.0]octane[9] (IVc) underwent rapid and quantitative conversion to *trans*-3-methoxycyclooctene (Vc, R = OMe) [τ 4.2–4.8 (m, 2 H), 6.36 (dt, J = 5.5 and 9 Hz, 1 H), 6.81 (s, 3 H), 7.5–9.4 (m, 10 H); ν_{max} 980 cm^{-1}] at 20°, whereas the corresponding *endo* derivative[10] IVd was more slowly converted (Table I) into the *cis* isomer (VIb, R = OMe) [τ 4.24–4.74 (m, 2 H), 6.02 (m, 1 H), 6.84 (s, 3 H), 7.7–9.0 (m, 10 H)]. We believe that this is the first reported example of a pair of *exo* and *endo* epimers each undergoing ring expansion to give a pure geometrical isomer, in the manner predicted.[3]

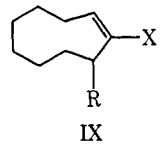
The possibility of effecting $AgClO_4$-promoted ring expansion in the presence of water was then examined. It was found that, for a particular substrate, the rate of reaction in acetone–water (95:5 v/v) was comparable to that observed in methanol solution. When IVa or IVc was treated with an excess of $AgClO_4$ in acetone–water solution at 20°, a quantitative yield of the expected alcohol (Va or Vc, R = OH) was obtained within 15 min (Table I). The conversion of *exo*-8-bromobicyclo[5.1.0]octane (IVc) into *trans*-cycloocten-3-ol (Vc, R = OH) had previously been reported by Whitham and Wright.[11] These workers effected the transformation in 60% yield by heating IVc for 28 hr in aqueous dioxane solution at 100° but found[11] that, under these reaction conditions, Ag^+ promoted the isomerization of Vc (R = OH) into VIc (R = OH). When *endo*-8-bromobicyclo[5.1.0]octane (IVd) was heated, under reflux, with $AgClO_4$ in acetone–water solution for 3 hr, *cis*-cycloocten-3-ol (VIb, R = OH) was obtained in satisfactory yield.



VII



VIII



IX

(7) *exo*-8-Tosyloxybicyclo[5.1.0]octane (IV, X = H; Y = OTs) has been shown[8] to undergo acetolysis at a much greater rate than its *endo* isomer (IV, X = OTs; Y = H).

(8) U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

(9) C. L. Osborn, T. C. Shields, B. A. Shoulders, C. G. Cardenas, and P. D. Gardner, *Chem. Ind.* (London), 766 (1965).

(10) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, 28, 703 (1963).

(11) G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967).

The seven experiments listed in Table I were repeated with the corresponding 9-halobicyclo[6.1.0]nonane derivatives (VII). In all cases, closely comparable results were obtained. Thus when 9,9-dibromobicyclo[6.1.0]nonane (VII, X = Y = Br) was treated with $AgClO_4$–MeOH at 20°, a quantitative conversion to *trans*-2-bromo-3-methoxycyclononene[12] (VIII, X = Br; R = OMe) was effected within 5 min. The nmr spectrum of this product [τ 3.80 (dd, J = 5.5 and 10.5 Hz) and 3.99 (dd, J = 5.5 and 10 Hz), 6.09 (m) and 6.55 (dd, J = 4 and 10.5 Hz), 6.72 (s) and 6.83 (s), 7.3–9.2 (m)] was unexpectedly complex inasmuch as it contained two well-separated sets of signals for the olefinic, methine, and methoxyl protons. This spectrum suggested the presence of a mixture of the two possible diastereoisomers[13] of VIII (X = Br; R = OMe) in the proportions of 5:4 (the ratio of the integrals of the pairs of olefinic, methine, and methoxyl proton signals). When this material (VIII, X = Br; R = OMe) was heated in a nitrogen atmosphere at 200° for 7 hr, 80% of the volatile products consisted of the corresponding *cis* isomer[2b] (IX, X = Br; R = OMe); when it was treated with Na–liquid NH_3, it was converted into a 60:40 mixture of *trans*- and *cis*-3-methoxycyclononenes (VIII and IX, X = H; R = OMe), in contrast to the report[16] that such reductions proceed stereospecifically with retention of configuration.

When the 3:1 mixture of diastereoisomeric alcohols (VIII, X = Br; R = OH), prepared by the action of $AgClO_4$–Me_2CO–H_2O on VII (X = Y = Br), was treated with PBr_3–petroleum ether, a 1:1 mixture of *trans*- and *cis*-2,3-dibromocyclononenes (VIII and IX, X = R = Br) was obtained. This material was separated by adsorption chromatography into the diastereoisomeric *trans* isomers VIII (X = R = Br) [τ 3.40 (dd, J = 6.5 and 10 Hz) and 3.97 (dd, J = 6 and 9 Hz),

(12) This material was contaminated with *ca.* 5% of *cis* isomer (IX, X = Br; R = OMe). However pure *trans* compound was obtained when the reaction was carried out at 0°.

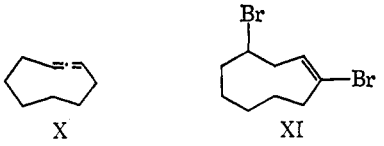
(13) The presence of two diastereoisomers is due to the chirality of the *trans*-cyclononene system[14] and of C-3. This phenomenon was not observed in the ring expansion of any of the above 8-halobicyclo[5.1.0]-octane derivatives (IV), but the two diastereoisomers of *trans*-3-methoxycyclooctene (Vc, R = OMe) have been prepared by another route.[15] It is possible that the ring-expansion reaction is stereospecific and leads to a pure diastereoisomer in both series, and that the differences observed are due to the comparative optical instability of the *trans*-cyclononene system.[14] This subject will be discussed in detail in a forthcoming publication.

(14) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. Winkler, *J. Amer. Chem. Soc.*, 87, 3644 (1965); A. C. Cope and B. A. Pawson, *ibid.*, 87, 3649 (1965).

(15) J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, 1593 (1968).

(16) H. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Amer. Chem. Soc.*, 73, 3329 (1951).

5.28 (dd) and 5.56 (dd, J = 5.5 and 10.5 Hz), 7.1–7.3 (m)] and the *cis* isomer IX (X = R = Br) [τ 3.93 (t, J = 9 Hz), 4.91 (dd, J = 5 and 12 Hz), 7.5–8.8 (m)]. The latter compound was identical with the main pyrolysis product of 9,9-dibromobicyclo[6.1.0]nonane[2b] (VII, X = Y = Br), thus suggesting that the pyrolysis conditions were too vigorous to allow the *trans* isomer VIII (X = R = Br) to be isolated.



X XI

Recently, Wedegaertner and Millam[17] reported that *trans*- and *cis*-2,3-dibromocyclononenes (VIII and IX, X = R = Br) were the products of bromine addition to cyclonona-1,2-diene (X). We have confirmed that the minor adduct (*ca.* 40%) is indeed *cis*-2,3-dibromocyclononene (IX, X = R = Br), but have shown[18] that the major adduct (*ca.* 60%) is *cis*-1,4-dibromocyclononene (XI) and not *trans*-2,3-dibromocyclononene, as previously reported.[17]

The facile $AgClO_4$-promoted ring-expansion reaction appears to be general. Furthermore, the reaction conditions described in this communication are appreciably milder than any which have previously been reported[1] for the solvolysis (in the presence or absence of Ag^+) or pyrolysis of halocarbene adducts of cyclic olefins. This has led to an increase in the synthetic potential of the ring-expansion reaction.

Acknowledgment. We thank Dr. Mark Baird for the gift of some starting materials.

(17) D. K. Wedegaertner and M. J. Millam, *J. Org. Chem.*, 33, 3943 (1968).

(18) The nmr spectrum of the major product [τ 4.17 (t, J 8.5 Hz, 1 H), 5.90 (m, 1 H), 7.1–7.7 (m, 4 H), 7.8–8.6 (m, 8 H)] corresponded closely to that reported by Wedegaertner and Millam;[17] however, it differed considerably from that of *trans*-2,3-dibromocyclononene and it seemed unlikely, both from the chemical shift (τ 5.90) and the multiplicity of its signal, that the methine proton was allylic. Double irradiation of the low-field part of the allylic region at τ 7.14 caused the triplet at τ 4.17 to collapse to a singlet and decreased the multiplicity of the signal at τ 5.90, which became virtually a triplet. These data suggested a partial structure $-CBr{=}CHCH_2CHBrCH_2-$ for this product and hence that it was either *cis*-1,4-dibromocyclononene (XI) or its *trans* isomer. The assignment of structure XI was confirmed by chemical evidence.

(19) Holder of a Science Research Council research studentship.

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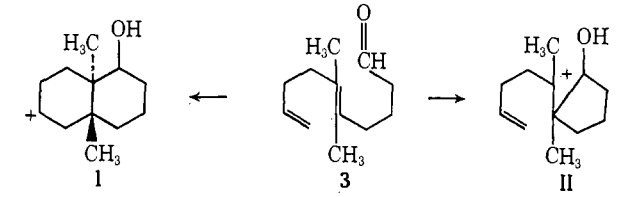
Received January 2, 1970

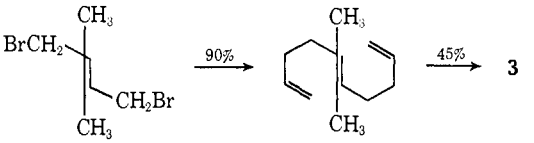
The Stereospecific Synthesis and Acid-Catalyzed Cyclization of 4,6-Dimethyl-*trans*-5,9-decadienal[1]

Sir:

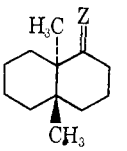
The elegant work from the laboratories of Johnson,[2a] Corey,[3] and van Tamelen[4] has reduced to laboratory practice certain aspects of the stereoselective synthesis and cyclization of squalene-like polyenes. The work of Johnson and coworkers,[2a] in particular, provides not only nonenzymic analogies that mimic the sterol biosynthetic processes but also practical synthetic procedures for the generation of *trans*-fused polycyclic systems from readily available acyclic precursors. It is the latter process that attracted our attention as a method for the generation[5] of the *trans*-13,14-dimethyl C/D ring system of such triterpenes as lanosterol and alnusenone. While such terpenoids arise in the enzymic squalene cyclization *via* a backbone rearrangement process, it appeared attractive to try to shortcut a portion of this natural process in the laboratory through the cyclization of the appropriate polyene system. Before such a synthetic program could realistically be planned, however, one further demonstration of the efficacy of the nonenzymic polyene cyclization process was necessary; namely, that the participation of an internal, tetrasubstituted double bond results in products derived from the formation of the decalin skeleton (I) in preference to those from the generation of the cyclopentane framework (II). While Johnson's work[2b,c] has shown that the cyclization of certain polyenic derivatives with internal disubstituted double bonds leads predominantly to products with the desired decalin skeleton, small amounts of cyclopentenyl derived products were also formed. In addition, these workers found that the formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate[2d] leads almost exclusively to the formation of cyclopentyl-type products as a result of the initial generation of the more stable, tertiary cyclopentyldimethyl carbonium ion. The similarity between the polyene derivatives logically desired for the triterpenoid syntheses envisaged here and the latter case above prompted an initial investigation of the mode of ring formation in the nonenzymic cyclization of a less complex model system best represented by 5,6-dimethyl-*trans*-5,9-decadienal (3).

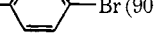


1 3 II



1 2



4, Z = β-H, α-OH (38%)
5, Z = O (82%)
6, Z = H_2 (50%)
7, Z = β-H, α-OCO—  —Br (90%)

(1) This research program was made possible by a grant (GP-7810) from the National Science Foundation. The X-ray work was supported by grants from the National Science Foundation (GB-6617X) and the National Institutes of Health (GM-12121). The authors gratefully acknowledge this support.

(2) (a) W. S. Johnson, *Accounts Chem. Res.*, 1, 1 (1968); (b) W. S. Johnson and J. K. Crandall, *J. Org. Chem.*, 30, 1785 (1965); (c) W. S. Johnson and R. B. Kinnel, *J. Amer. Chem. Soc.*, 88, 3861 (1966); (d) W. S. Johnson and R. Owyang, *ibid.*, 86, 5593 (1964).

(3) E. J. Corey, W. E. Russey, and P. R. Ortiz de Montellano, *ibid.*, 88, 4750 (1966).

(4) E. E. van Tamelen, *Accounts Chem. Res.*, 1, 111 (1968).

(5) For an alternate approach to this problem, see R. E. Ireland, D. A. Evans, D. Glover, G. M. Rubottom, and H. Young, *J. Org. Chem.*, 34, 3717 (1969).