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THE ADDITION OF BROMINE TO CYCLONONA-1,2-DIENE

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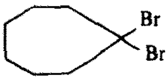
Abstract—The two isomeric dibromides, obtained by the addition of bromine to cyclonona-1,2-diene (**4**), have been identified as 2,3-dibromo-*cis*-cyclononene (**2**; R = Br) and 1,4-dibromo-*cis*-cyclononene (**5**; R = Br); these compounds were obtained in the approximate relative proportions of 40:60.

WE RECENTLY showed[1] that the main product of pyrolysis of 9,9-dibromobicyclo[6.1.0]nonane (**1**) was either *cis*- or *trans*-2,3-dibromocyclononene (**2** or **3**; R = Br). Although chemical evidence[1] favoured the *cis*-isomer (**2**; R = Br), the possibility that this product was the *trans*-isomer (**3**; R = Br), could not be excluded. However, we have since prepared the latter compound from the corresponding bromo-alcohol[2] (**3**; R = OH), and have thereby established that the main pyrolysis product of **1** was indeed 2,3-dibromo-*cis*-cyclononene (**2**; R = Br).



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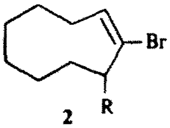

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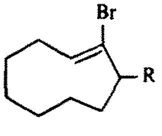

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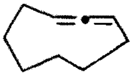

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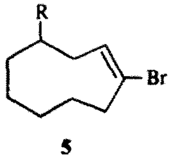

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Before we had succeeded in preparing the *trans*-isomer (**3**; R = Br), a recent report by Wedegaertner and Millam[3] came to our attention. These workers treated cyclonona-1,2-diene[4] (**4**) with an approximately stoicheiometric quantity of bromine in CCl_4 solution, and obtained two isomeric dibromides in the relative proportions of 40:60; they assigned the structures **2** (R = Br) and **3** (R = Br), respectively, to these products. A reinvestigation of this reaction has led us to the conclusion* that the minor product had been correctly formulated as 2,3-dibromo-*cis*-cyclononene (**2**; R = Br), but that the major product was 1,4-dibromo-*cis*-cyclononene (**5**; R = Br) and not **3** (R = Br) as reported previously.[3]

The mixture of isomeric dibromides was separated with difficulty by preparative GLC (Experimental). The NMR spectrum of the minor, shorter R_T component was identical to that of the pyrolysis product of **1**, 2,3-dibromo-*cis*-cyclononene[1] (**2**; R=Br). The NMR spectrum of the major, longer R_T component corresponded closely to that

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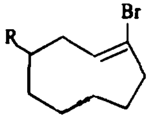
* See reference 2 for a very brief preliminary account of the results described in this paper.

reported by Wedegaertner and Millam; this spectrum was quite unlike that obtained[2] for 2,3-dibromo-*trans*-cyclononene (**3**; R = Br) and, in any case, both the chemical shift (τ 5·86) and the multiplicity of the methine signal suggested that this proton was non-allylic. Double irradiation of the lowfield part of the allylic region at τ 7·23 caused the triplet at τ 4·13 to a collapse to a singlet and decreased the multiplicity of the signal at τ 5·86, which became virtually a triplet. These data suggested that the major product of bromine addition to cyclonona-1,2-diene (**4**) had the partial structure —$CBr{=}CH{—}CH_2{—}CHBr{—}CH_2$—, and that it was either 1,4-dibromo-*cis*-cyclononene (**5**; R = Br) or its *trans*-isomer (**6**; R = Br).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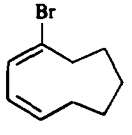
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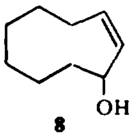
When the mixture of isomeric dibromides was treated with tri-n-butyltin hydride at 20°, it was converted solely into 1-bromo-*cis*-cyclononene[1] (**2**; R = H) in accord with the assignment of *cis*-stereochemistry to the major component;[*] when this mixture was heated with NaOMe/MeOH, under reflux, 2-bromo-3-methoxy-*cis*-cyclononene (**2**; R=OMe) and 1-bromo-*cis,cis*-cyclonona-1,3-diene (**7**) were obtained. The first compound (**2**; R=OMe) had previously been obtained[1] by the action of NaOMe/MeOH on **2** (R = Br), and the second compound (**7**) obtained as the sole product, under the same reaction conditions, from pure **5** (R = Br) (see below). When **7** was reduced with Na-liquid NH_3, *cis*-cyclononene was obtained.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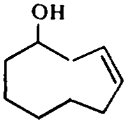
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Treatment of the mixture of isomeric dibromides with AgOAc/AcOH at 40° gave the corresponding bromo-esters (**2** and **5**; R = OAc) in good yield. The latter products were treated with NaOMe/MeOH and the resulting mixture of bromo-alcohols, which was obtained in 46% overall yield, was fractionated by adsorption chromatography to give pure 2-bromo-*cis*-cyclonon-1-en-3-ol (**2**; R = OH) and 1-bromo-*cis*-cyclonon-1-en-4-ol (**5**; R = OH). Reduction of the latter compounds with Na-liquid NH_3 gave, respectively, *cis*-cyclonon-1-en-3-ol and -4-ol (**8** and **9**), free from the corresponding *trans*-isomers. The *cis*-stereochemistry of both bromo-alcohols (**2** and **5**; R = OH) was thereby established.[†]

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[*] This evidence must be treated with some caution as reaction between 2,3-dibromo-*trans*-cyclononene[2] (**3**; R = Br) and tri-n-butyltin hydride gave[5] only 1-bromo-*cis*-cyclononene (**2**; R = H). However, it seems less likely that reduction of the non-allylic system, 1,4-dibromo-*trans*-cyclononene (**6**; R = Br) would also lead to the *cis*-product (**2**; R = H).

[†] Such reductions of acyclic systems have been reported[4] to proceed stereospecifically with retention of configuration. Treatment of 2-bromo-3-methoxy-*trans*-cyclononene (**3**; R = OMe) with Na-liquid NH_3 was stereoselective and gave[2] a 60:40 mixture of 3-methoxy-*trans*- and *cis*-cyclononenes. It therefore seems reasonable to conclude that the isomeric bromo-alcohols were both *cis* as none of the corresponding *trans*-cyclononenol was detected in the reduction products in either case.

Reaction between the tosylate ester of 1-bromo-*cis*-cyclonon-1-en-4-ol and LiBr in acetone solution gave 1,4-dibromo-*cis*-cyclononene (**5**; $R = Br$), identical to the above major bromine adduct of cyclonona-1,2-diene (**4**). As this two-step conversion of **5** ($R = OH$) into **5** ($R = Br$), which proceeded in 31% overall yield, was unlikely to have involved isomerization of the double-bond, the assignment of *cis*-stereochemistry to the latter compound (**5**; $R = Br$) is secure. Comparatively large quantities of pure 1,4-dibromo-*cis*-cyclononene may be prepared in this way. In contrast[3] to the behaviour of the mixed bromine adducts of **4**, pure **5** ($R = Br$) remained completely unchanged after it had been treated with Mg or Zn in tetrahydrofuran, or with Zn in ether at 20°.

The formation of a mixture of **2** ($R = Br$) and **5** ($R = Br$) from the addition of bromine to cyclonona-1,2-diene (**4**) can easily be rationalized. The allenic system generally appears to be attacked by halogens on its central carbon atom.[7] In the case of **4**, attack by bromine on the less-hindered side would lead to a *cis*-allylic cation,[*] which could either undergo solvolysis by bromide ion directly to give **2** ($R = Br$) or, following a 1,5-hydride shift, to give **5** ($R = Br$). Although it is well known[9] that medium-sized ring compounds undergo transannular reactions, there is surprisingly little information in the literature about the addition of bromine to medium-sized cycloalkenes and related systems. Indeed, the only well described examples[†] of such reactions in which transannular hydride shifts are involved appear to be the addition of bromine to *cis*-and *trans*-cyclodecenes.[14, 15] This area of medium-ring chemistry clearly merits a fuller investigation.

EXPERIMENTAL

NMR spectra were measured at 100 MHz with a Varian HA 100 spectrometer. Me_4Si was used as an internal standard, and chemical shifts are expressed in ppm on a τ scale. UV absorption spectra were measured with a Cary recording spectrophotometer, model 14M-50. IR spectra of liquids and solids were taken as films and Nujol mulls, respectively, with Perkin–Elmer spectrometers (models 21 and 257). Mass spectra were obtained with an AEI MS 9 spectrometer, using heated insertion. GLC was carried out with an F. & M. model 720 chromatograph with H_2 as carrier gas. Unless otherwise stated, a 6′ column containing 10% Carbowax 20 M on Chromosorb W was used.

Addition of bromine to cyclonona-1,2-diene (**4**). The procedure described by Wedegaertner and Millam[3] was followed without modification. The NMR spectrum of the mixture of dibromocyclononenes so obtained included the following signals: τ 3·89 (t, *J* 9); 4·13 (t, *J* 8·5); 4·87 (dd, *J* 5 and 12); 5·86 (m); 7·1–9·0 (m). The integrals of the τ 4·13 and 5·86 signals were *ca* 1·7 times those of the τ 3·89 and 4·87 signals.

The above mixture of dibromocyclononenes was not resolved by GLC on a 6′ Apiezon L column; however, it was separated into two components by a 6′-column containing bentone-diisodecyl phthalate (10%) on Chromosorb W. The NMR spectrum of the minor, shorter R_T component [τ 3·89 (t, *J* 9), 1H; 4·87 (dd, *J* 5 and 12), 1H: 7·5–8·8 (m), 12H] was identical to that of *cis*-2,3-dibromocyclononene.[1] The NMR spectrum of the major, longer R_T component was: τ 4·13 (t, *J* 8·5), 1H; 5·86 (m), 1H; 7·1–7·7 (m), 4H; 7·8–8·6 (m), 8H.

Reaction between dibromocyclononene mixture and tri-n-butyltin hydride. A soln of the above mixture of dibromocyclononenes (0·1 g: 0·35 mmole) and tri-n-butyltin hydride[16] (0·11 g, 0·37 mmole) was stirred for

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[*] It is unlikely that the intermediate in this reaction is a free allylic cation as the solvolysis of 2,3-dibromo-*cis*-cyclononene (**2**; $R = Br$) does not appear to involve a transannular reaction. There is also good evidence[8] that the addition of bromine to penta-2,3-diene does not involve a free allylic cation.

[†] The reaction between bromine and *cis*-cyclooctene gives solely the *trans*-1,2-adduct,[10] except at very low temperatures when transannular products have been detected;[11] the corresponding reaction with *trans*-cyclooctene follows a completely different course and even results in ring-contraction.[12] We have found[13] that the addition of bromine to *cis*-cyclononene leads to transannular products which have not yet been fully characterized; the course of addition of bromine to *trans*-cyclononene remains unclear.[14]

16 hr at 20°. GLC examination of the products revealed tri-n-butyltin-bromide, a small amount of tri-n-butyltin hydride and a third component. The latter material was isolated by GLC and shown from its NMR spectrum [τ 4·10 (t, J 8·5), 1H; 7·43 (m), 2H; 7·89 (m) 2H; 8·2–8·9 (m), 10H] to be 1-bromo-*cis*-cyclononene.[1]

Reaction between dibromocyclononene mixture and NaOMe/MeOH. A soln of the above mixture of dibromocyclononenes (1·6 g, 5·7 mmole) and NaOMe (2 g, 37 mmole) in MeOH (20 ml) was heated, under reflux, for 24 hr. The products were then concentrated and the residue partitioned between ether and water. The organic layer was washed with water, dried (MgSO$_4$) and evaporated to give an oil (1·0 g). The latter material was separated by GLC into two components. The minor component, which had the longer R_T, was shown from its NMR spectrum [τ 3·78 (t, J 9), 1H; 5·84 (dd, J 4·5 and 8·5), 1H; 6·86 (s), 3H; 7·65–8·0 (m), 2H; 8·1–9·0 (m), 10H] to be 2-bromo-3-methoxy-*cis*-cyclononene.[1]

The major component, which had the shorter R_T, was identified as *1-bromo-*cis,cis*-cyclonona-1,3-diene* [Found: C, 54·0; H, 6·25; Br, 40·0. C$_9$H$_{13}$Br requires: C, 53·75; H, 6·45; Br, 39·8%]; UV absorption (95% EtOH): λ_{max} 215 nm (ε 5,240); ν_{max}^{film} 1615 cm^{-1}; NMR spectrum: τ 3·79 (s), 1H; 4·28 (m), 2H; 7·46 (m), 2H; 7·90 (m), 2H; 8·2–8·8 (m), 6H; mass spectrum; M^+ at m/e = 200, 202 (1 : 1); base-peak at m/e = 79.

*Reduction of 1-bromo-*cis,cis*-cyclonona-1,3-diene* (7) *with* Na/*liquid* NH$_3$. A soln of 1-bromo-*cis,cis*-cyclonona-1,3-diene (1·0 g; 95% pure, contaminated with 2-bromo-3-methoxy-*cis*-cyclononene) in light petroleum (15 ml; b.p. 30–40°) was added with stirring over a period of 10 min to a soln of Na metal (2·2 g) in liquid NH$_3$ (50 ml). After a further period of 30 min NH$_4$Cl was added, the excess NH$_3$ was allowed to evaporate and water (15 ml) was added. The organic layer was separated, dried (MgSO$_4$) and carefully evaporated to leave an oil (0·3 g, 50%) which was shown from its IR spectrum and NMR spectrum [τ 4·56 (m), 2H; 7·86 (m), 4H; 8·3–8·7 (m), 10H] to be almost pure *cis*-cyclononene.[17]

Reaction between dibromocyclononene mixture and AgOAc/AcOH. A soln of the above mixture of dibromocyclononenes (0·5 g, 1·8 mmole) and AgOAc (1·0 g, 6·0 mmole) in glacial AcOH was maintained at 40° for 2 hr. The products were filtered, and the filtrate partitioned between ether and an excess of Na$_2$CO$_3$aq. The ether layer was separated, washed with water, dried (MgSO$_4$) and concentrated to a clear yellow oil. The latter material was separated by GLC into two components. The NMR spectrum of the slightly predominant, longer R_T components was: τ 4·13 (t, J 9), 1H; 5·34 (m), 1H; 7·2–7·8 (m), 4H; 8·14 (s), 3H; 8·2–8·7 (m), 8H; the NMR spectrum of the shorter R_T component was: τ 3·96 (t, J 9), 1H; 4·40 (dd, J 4 and 10), 1H; 7·7–7·9 (m), 2H; 8·09 (s), 3H; 8·1–9·0 (m), 10H.

*2-Bromo-*cis*-cyclonon-1-en-3-ol* (2; R = OH) *and 1-bromo-*cis*-cyclonon-1-en-4-ol* (5; R = OH). A soln of the crude mixture of dibromocyclononenes (25 g), obtained from the addition of Br$_2$ (14·6 g, 91 mmole) to cyclonona-1,2-diene (11·0 g, 90 mmole) at −20°, and AgOAc (15·0 g, 90 mmole) in glacial AcOH (100 ml) was maintained at 40° for 2 hr and then worked up as above. The products were distilled and a fraction (15·0 g) with b.p. 75–90°/0·4 mm was collected. A soln of the latter material in MeOH (100 ml) was treated with NaOMe (5·0 g, 92·5 mmole), and the reactants stirred at 20°. After 16 hr, the products were neutralized with TsOH/MeOH, concentrated, and the residue extracted with CHCl$_3$. The filtered extract was evaporated to give an oil (9·0 g, 46%), which was shown by GLC and TLC to consist largely of two components.

A soln of the above oil in petroleum ether (b.p. 60–80°)—benzene (95 : 5; v/v) was applied to a column (150 g) of SilicAR CC7, which was then eluted with petroleum ether containing larger proportions of benzene. The fractions eluted with petroleum ether–benzene (80 : 20) were combined and concentrated to give 2-bromo-*cis*-cyclonon-1-en-3-ol. [Found in material recrystallized from petroleum ether (b.p. 30–40°): C, 49·75; H, 6·9; Br, 36·8. C$_9$H$_{15}$BrO requires: C, 49·4; H, 6·85; Br, 36·5%] as a colourless solid (2·0 g, 10% overall yield based on cyclonona-1,2-diene), m.p. 65–68°; NMR spectrum: τ 3·96 (t, J 9), 1H; 4·48 (t, J 7), 1H; 7·7–9·2 (m), 12H; ν_{max}^{Nujol} 1635, 3260 cm^{-1}; mass spectrum: M^+ at m/e = 218, 220 (1 : 1); base-peak at m/e = 41.

The fractions eluted with light petroleum–benzene (75 : 25) were combined and concentrated to give *1-bromo-*cis*-cyclonon-1-en-4-ol* [Found: C, 49·7; H, 6·8; Br, 36·7. C$_9$H$_{15}$BrO requires: C, 49·4; H, 6·85; Br, 36·5%] as a slightly discoloured viscous oil (3·5 g, 18% overall yield based on cyclonona-1,2-diene); NMR spectrum: τ 4·08 (t, J 8·8), 1H; 5·91 (s), 1H; 6·25 (m), 1H; 7·2–7·8 (m), 4H; 8·1–8·9 (m): ν_{max}^{film} 1635, 3340 cm^{-1}; mass spectrum: M^+ at m/e=218, 220 (1 : 1); base peak at m/e=57.

*Reduction of 2-bromo-*cis*-cyclonon-1-en-3-ol* (2; R = OH) *with* Na/*liquid* NH$_3$. A soln of 2-bromo-*cis*-cyclonon-1-en-3-ol (0·5 g, 2.3 mmole) in light petroleum (10 ml; b.p. 30–40°) was added with stirring over a period of 10 min to a soln of Na metal (1·0 g, 43 mmole) in liquid NH$_3$ (25 ml). After a further period of 30 min, the products were worked up as above (see reduction of 1-bromo-*cis,cis*-cyclonona-1,3-diene).

Evaporation of the dried ($MgSO_4$) organic layer gave an oil (> 95% pure by GLC and TLC) which was characterized as cis-*cyclonon-1-en-3-ol* [Found: C, 77·2; H, 11·1. $C_9H_{16}O$ requires: C, 77·1; H, 11·4%]; yield, 0·275 g (85%); NMR spectrum (at 60 MHz): τ 4·49 (m), 2H; 5·45 (m), 1H; 6·57 (s), 1H; 7·5–8·9 (m), 12H; ν_{max}^{film} 1645, 3340 cm^{-1}; mass spectrum: M^+ at $m/e = 140$; base-peak at $m/e = 83$.

Reduction of 1*-bromo-*cis*-cyclonon-1-en-4-ol* (**5**; R = OH) *with* Na/*liquid* NH_3. 1-Bromo-*cis*-cyclonon-1-en-4-ol (0·75 g, 3·4 mmole) was reduced with Na metal (1·6 g, 70 mmole) in liquid NH_3 (50 ml) by the procedure described above for its isomer. Thus cis-*cyclonon-1-en-4-ol* [Found: C, 76·95; H, 11·3. $C_9H_{16}O$ requires: C, 77·1; H, 11·4%] was obtained as an oil (95% pure by GLC and TLC): yield *ca* 0·5 g: NMR spectrum; τ 4·3–4·8 (m), 2H; 6·30 (m), 1H; 6·43 (s), 1H; 7·5–8·1 (m), 4H; 8·2–9·0 (m), 8H; ν_{max}^{film} 1020, 1645, 3340 cm^{-1}: mass spectrum: M^+ at $m/e = 140$; base-peak at $m/e = 55$.

1,4-*Dibromo-*cis*-cyclononene* (**5**; R = Br). Toluene-*p*-sulphonyl chloride (1·3 g, 6·8 mmole) was added to a soln of 1-bromo-*cis*-cyclonon-1-en-4-ol (1·0 g, 4.6 mmole) in anhyd pyridine (10 ml) at 0°. After 48 hr at 0°, the products were poured onto an ice-water mixture (50 g) and the oil obtained extracted with ether. The dried ($MgSO_4$) organic layer was evaporated, and the residue (TLC homogeneous) dissolved in acetone (10 ml). LiBr (0·8 g, 9·2 mmole) was added to this soln, and the reactants were allowed to stand at 20° for 24 hr and were then heated, under reflux, for 1 hr. The cooled products were evaporated and the residue partitioned between ether and water. The ether layer was separated, dried ($MgSO_4$) and concentrated.

A soln of the residue in light petroleum (b.p. 30–40°) was applied to a column of SilicAR CC7 (25 g), which was then eluted with light petroleum. The appropriate fractions were combined and evaporated to give 1,4-*dibromo-*cis*-cyclononene* [Found: C, 38·5; H, 4·9; Br, 56·5. $C_9H_{14}Br_2$ requires: C, 38·3; H, 5·0; Br, 56·7%] as an oil; yield 0·40 g (31%, based on 1-bromo-*cis*-cyclonon-1-en-4-ol); ν_{max}^{film} 1635 cm^{-1}; mass spectrum: M^+ at $m/e = 280, 282, 284$ (1 : 2 : 1); base-peak at $m/e = 28$; NMR spectrum: τ 4·13 (t, *J* 8·5), 1H; 5·86 (m), 1H; 7·1–7·7 (m), 4H; 7·8–8·6 (m), 8H. Double-irradiation at τ 7·23 caused the triplet at τ 4·13 to collapse to a singlet and decreased the multiplicity of the signal at τ 5·86, which became virtually a triplet.

The major bromine adduct of cyclonona-1,2-diene (see above) and 1,4-dibromo-*cis*-cyclononene had identical mass, IR and NMR spectra, and identical chromatographic properties (GLC and TLC).

Reaction between 1,4*-dibromo-*cis*-cyclononene* (**5**; R = Br) *and* NaOMe/MeOH. A soln of 1,4-dibromo-*cis*-cyclononene (0·15 g, 0·53 mmole) and NaOMe (0·20 g, 3·7 mmole) in MeOH (5 ml) was heated, under reflux, for 16 hr. The products were worked up as in the similar experiment with the mixed bromine adducts of cyclonona-1,2-diene (see above), to give a yellow oil (0·09 g). The latter material was GLC homogeneous; its R_T and IR spectrum were identical to those of 1-bromo-*cis, cis*-cyclonona-1,3-diene.

*Reaction between mixed bromine adducts of cyclonona-*1,2*-diene* (**4**) *and Mg metal/tetrahydrofuran.* Mg ribbon (0·3 g) and a crystal of I_2 were added to a soln of the above mixture of bromine adducts (0·1 g) in anhyd THF (5 ml) at 20°. After 16 hr, GLC revealed that all the starting materials had been consumed and that the sole volatile product had the same R_T as cyclonona-1,2-diene.

Pure 1,4-dibromo-*cis*-cyclononene remained completely unreacted after the same treatment: it was also unaffected after similar treatment with Zn metal in ether or tetrahydrofuran.

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REFERENCES

[1] M. S. Baird and C. B. Reese, *J. Chem. Soc.* (C), 1803 (1969)

[2] C. B. Reese and A. Shaw, *J. Am. Chem. Soc.* **92**, 2566 (1970)

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

[4] W. R. Moore and H. R. Ward, *Ibid.* **25**, 2073 (1960)

[5] C. B. Reese and A. Shaw, unpublished observations

[6] H. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Am. Chem. Soc.* **73**, 3329 (1951)

[7] H. Fischer, *The Chemistry of Alkenes*, Ed. S. Patai, p. 1074 *et seq.*; Wiley, New York, 1964; D. R. Taylor, *Chem. Rev.* **67**, 338 (1967)

[8] W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Am. Chem. Soc.* **90**, 6741 (1968)

[9] A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* **20**, 119 (1966)

[10] G. Wittig and H.-L. Dorsch, *Liebigs Ann.* **711**, 46 (1968)

[11] P. W. Henniger, L. J. Dukker, and E. Havinga, *Rec. Trav. Chim.* **85**, 1177 (1966)

[12] N. L. Allinger and L. A. Tushaus, *Tetrahedron* **23**, 2051 (1967)

[13] M. S. Baird and C. B. Reese, unpublished observations

[14] J. Sicher, J. Závada, and M. Svoboda, *Coll. Czech. Chem. Commun.* **27**, 1927 (1962)

[15] M. Havel, M. Svoboda, and J. Sicher. *Ibid.* **34**, 340 (1969)

[16] G. J. M. Van Der Kerk, J. G. Noltes, and J. G. H. Luiften, *J. Appl. Chem.* **7**, 366 (1957)

[17] A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.* **74**, 3643 (1952)