least-squares treatment was repeated until no negative values were obtained.

Later the mass spectral parent peaks were added to the data base to obtain eq 10-15 in which the P's are peak

$$M_{0y}M_{x0} = P_{88}/\sum_P \qquad (10)$$

$$M_{0y}M_{x1} + M_{1y}M_{x0} = P_{89}/\sum_P \qquad (11)$$

$$M_{0y}M_{x2} + M_{1y}M_{x1} + M_{2y}M_{x0} = P_{90}/\sum_P \qquad (12)$$

$$M_{0y}M_{x3} + M_{1y}M_{x2} + M_{2y}M_{x1} = P_{91}/\sum_P \qquad (13)$$

$$M_{1y}M_{x3} + M_{2y}M_{x2} = P_{92}/\sum_P \qquad (14)$$

$$M_{2y}M_{x3} = P_{93}/\sum_P \qquad (15)$$

heights and $\sum_P$ is the sum of the corrected (for ^{18}O and ^{13}C) heights of the parent peaks. In this case the results obtained using nine equations were the first approximation used in the nonlinear least-squares treatment involving 19 equations.

The deuterium contents at various times throughout the reaction that were thus obtained were then fit to a given mechanistic scheme. The methods of Rodaguin and Rodaquina[18] were used to obtain eq 16-22 from Scheme III and eq 23-27 from Scheme V with k_{20} set equal to zero.

$$M_{x3} = M_{x3}°E_3 \qquad (16)$$

$$M_{x2} = 3M_{x3}°(E_2 - E_3) + M_{x2}°E_2 \qquad (17)$$

$$M_{x1} = 3M_x°(E_1 - E_2 + E_3) + 2M_{x2}°(E_1 - E_2) + M_{x1}°E_1 \qquad (18)$$

$$M_{x0} = 1 - M_{x3} - M_{x2} - M_{x1} \qquad (19)$$

$$E_3 = \exp(-3kt) \qquad (20)$$

$$E_2 = \exp(-2kt) \qquad (21)$$

$$E_1 = \exp(-kt) \qquad (22)$$

$$M_{2x} = M_{2x}°F_2 \qquad (23)$$

$$M_{1x} = 2M_{2x}°(F_1 - F_2) + M_{1x}°F_1 \qquad (24)$$

$$M_{0x} = 1 - M_{2x} - M_{1x} \qquad (25)$$

$$F_2 = \exp(-kt) \qquad (26)$$

$$F_1 = \exp(-kt/2) \qquad (27)$$

For Schemes IV, VI, and V when k_{20} was one parameter to be determined, the differential reaction method was used in which the total reaction time was divided into increments and the changes in concentration calculated for each separate increment.[1b] The time increments were shortened by factors of 2 until the values of the parameter obtained changed by less than 0.1%.

The k_P values were estimated essentially by the methods used before for other ketones.[3,5,7,8] Catalysis constants were determined for hydrogen ions (always negligible under the conditions of the present study), hydroxide ions, and four tertiary amines.[9] The points for three of these amines, trimethylamine, *N*-methylpyrrolidine, and *N*-methylmorpholine, give good Brøsted plots for both methylene and methyl exchange. The point for triethylamine lies below these lines, presumably because of steric hindrance. The methylene plot has a slope of 0.68 and the methyl plot a slope of 0.59. Simple basic catalysis by the tertiary amino group of 3DP was assumed to take place at a rate that agreed with these lines. As previously, the primary amino group was assumed to be only one-seventh as reactive. These assumptions and the micro pK_a values determined earlier for 3DP give k values of 5.01×10^{-3} M^{-1} s^{-1} and 1.26×10^{-3} M^{-1} s^{-1} for removal of deuterons from the CD_3 and CD_2 groups, respectively, by the tertiary amino group of 3DP. The molecule as a whole would then be $^8/_7$ this reactive. It was assumed that the Brønsted line for monocationic amines lies 0.44 log units above the one for uncharged amines. On this basis, $Me_2NCH_2CH_2CH_2NH_3^+$ was estimated to have rate constants of 1.51×10^{-3} M^{-1} s^{-1} and 3.19×10^{-5} M^{-1} s^{-1} for dedeuteration of the CD_3 and CD_2 groups, respectively.

For DTN a pK_{HTP} value of 9.32 was assumed, since this is the value estimated earlier for 3-*endo*-((dimethylamino)methyl)-2-*endo*-norbornamine,[19] whose structure merely lacks the carbon-bound methyl groups of DTN and whose pK values (6.82 and 9.78) are near those of DTN (6.59 and 9.84). This assumption leads to estimates of 30%, 38%, and 32% for the percent of monoprotonated diamine that is tertiary protonated, primary protonated, and internally hydrogen bonded. Rate constants of 5.25×10^{-3} M^{-1} s^{-1} and 1.28×10^{-3} M^{-1} s^{-1} for attack on the CD_3 and CD_2 groups by DTN and 6.28×10^{-4} and 9.14×10^{-5} M^{-1} s^{-1} for monoprotonated DTN were then calculated.

Registry No. $MeOCD_2C(O)CD_3$, 89922-02-1; 3DP, 109-55-7; DTN, 56310-23-7.

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[18] Rodaguin, N. M.; Rodaguina, E. N. "Consecutive Chemical Reactions"; English Translation, Schneider, R. F., Ed.; D. van Nostrand: Princeton, NJ, 1964.

[19] Hine, J.; Li, W.-S. *J. Org. Chem.* **1975**, *40*, 1795-1800.

Chlorocyanoketene. Synthesis and Cycloadditions to Alkenes

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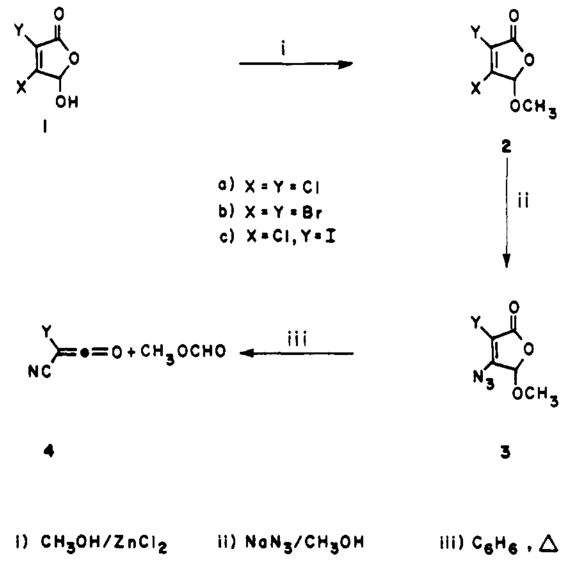
Details for two syntheses of chlorocyanoketene (CCK) are provided. These involve the thermolysis (103 °C) of 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone as well as generation of the ketene at ambient temperature upon treatment of 3,4-dichlorocyclobutenedione with sodium azide in acetonitrile. In addition, the previously unreported cycloadditions of CCK to alkenes are described. These give good yields of the corresponding cyclobutanones and include additions to di-, tri-, and tetrasubstituted alkenes.

In preliminary accounts, we have shown that chloro-, bromo-, and iodocyanoketene can be conveniently generated from the corresponding 4-azido-3-halo-2(5H)-furanones (**2a-c**) upon thermolysis in refluxing benzene.[1,2]

0022-3263/84/1949-2190$01.50/0

Scheme I



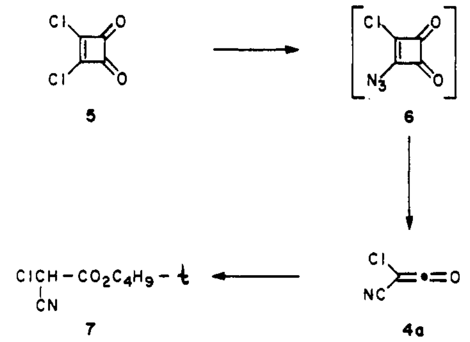
In order to provide more information regarding the synthetic utility of these unusual electron-deficient ketenes, a study of the cycloadditions of chlorocyanoketene to alkenes is described in this manuscript.

Synthesis of Chlorocyanoketene (CCK). Two general methods have been reported for the synthesis of cyanoketenes; these involve the thermolyses of either 2,5-diazido-1,4-benzoquinones[3] or 4-azido-2-furanones.[1,2] Perhaps the most widely employed of these is the former which is particularly useful for the synthesis of alkyl- or arylcyanoketenes. However, attempts to utilize this for the generation of chlorocyanoketene met with failure due to the insolubility of the diazidoquinone precursor. This problem was circumvented by the latter method which employs 4-azido-3-chloro-5-methoxy-2(5H)-furanone (**3a**), a vinyl azide which is easily prepared and readily cleaves to CCK and methylformate in refluxing benzene or toluene (Scheme I).[4]

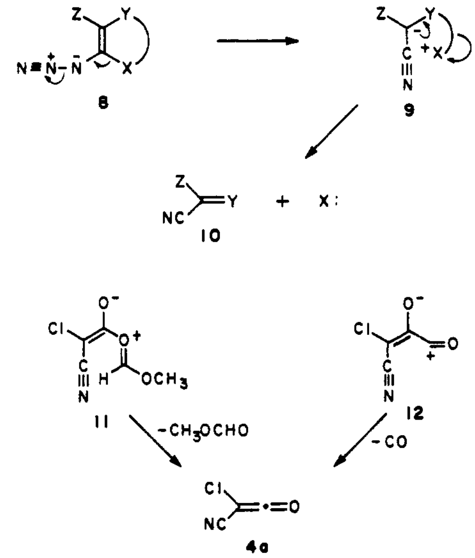
A brief summary of the above synthesis of halocyanoketenes along with a previously unreported route to CCK employing 3,4-dichlorocyclobutenedione are given below. The azidofuranone method starts with mucohalic acid (**1**) which is converted to its pseudomethyl ester **2**, and this, in turn, gives the azidofuranone **3** in high yield upon treatment with sodium azide in methanol. The ketene is then generated upon thermolysis of **3** as mentioned above. However, since halocyanoketenes are exceptionally reactive and thus undergo facile self-condensation, they must be generated in situ in order to explore their synthetic utility.[5]

A most interesting alternative route to CCK was observed upon treatment of an acetonitrile solution of 3,4-dichlorocyclobutenedione (**5**) with sodium azide (Scheme II).[6] When this was accomplished at ambient temperature in the presence of excess *tert*-butyl alcohol the corresponding ester, **7**, was obtained in 77% yield.

Scheme II



Scheme III



The above two routes to CCK are anticipated to be complimentary. That is, the furanone **3a** provides CCK at 80 °C while the cyclobutenedione **5** gives it at ambient temperatures. Thus, CCK syntheses, as outlined here, are now available which will allow comparison studies to be made of the ketene's reactivity as a function of temperature.

The formation of chlorocyanoketene from either the azidofuranone **3a** or the proposed azidocyclobutenedione **6** most likely follows a common mechanistic pathway which we have previously generalized to encompass a variety of appropriately substituted vinyl azides.[7] These transformations are viewed as proceeding via the mechanism outlined in Scheme III. For example, when Y is a carbonyl group, cleavage of the cyclic vinyl azide **8** to the zwitterion **9** followed by subsequent fragmentation would lead to **10**, a cyanoketene. As specifically applied to the examples described here, the zwitterionic intermediates, **11** and **12**, would arise from, respectively, the furanone **3a** and the cyclobutenedione **6** and both intermediates would then give CCK upon fragmentation.

If one reasonably assumes **6** to be the penultimate precursor to CCK when **5** is treated with sodium azide, then the observation that it undergoes facile cleavage to **12** at ambient temperature provides significant mechanistic information for the above two CCK syntheses as well as for the generalized vinyl azide cleavage outline in Scheme III. Specifically, since both **6** and **3a** are 3-azido-2-chloro enones and the former decomposes rapidly at ambient temperature while the latter requires >80 °C, then release of strain energy must be an important factor in the

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[1] Kunert, D.; Chambers, R.; Mercer, F.; Hernandez, L.; Moore, H. W. *Tetrahedron Lett.* **1978**, 929.

[2] Moore, H. W.; Hernandez, L.; Sing, A. *J. Am. Chem. Soc.* **1976**, *98*, 3728.

[3] Moore, H. W.; Gheorghiu, M. D. *Chem. Soc. Rev.* **1981**, *10*, 289.

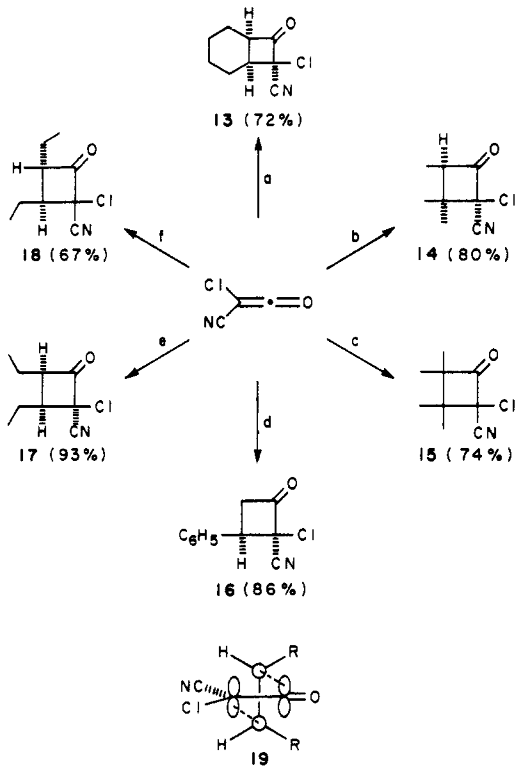
[4] Moore, H. W.; Hernandez, L.; Kunert, D. M.; Mercer, F.; Sing, A. *J. Am. Chem. Soc.* **1981**, *103*, 1769.

[5] *tert*-Butylcyanoketene is an exception; it is stable for an extended period of time when kept in solution (benzene).

[6] The synthesis of chlorocyanoketene by this route (unpublished) was provided by Dr. R. C. De Selms (Eastman Kodak) and is in complete analogy to his previously reported synthesis of phenylcyanoketene. See: De Selms, R. C. *Tetrahedron Lett.* **1969**, 1179.

[7] Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

Scheme IV[a]



[a] a, Cyclohexene; b, 2-methyl-2-butene; c, 2,3-dimethyl-2-butene; d, styrene; e, *cis*-3-hexene; f, *trans*-3-hexene.

cleavage of **6**. Thus, loss of nitrogen must be synchronous with C–C bond ionization. As a result, nitrenes and/or azirines are unlikely intermediates in the thermolyses of **3a**, **6**, or the appropriately substituted vinyl azides **8**, since all presumably proceed via a common mechanistic pathway.

Cycloadditions of Chlorocyanoketene to Alkenes. Haloketenes have found extensive use in the synthesis of cyclobutanones and related products, and dichloroketene is of particular note.[8,9] It has been shown to cycloadd to a number of alkenes, including those which are normally unreactive ketenophiles such as tri- and tetraalkyl-substituted examples. Chlorocyanoketene would be more electrophilic and sterically less hindered than dichloroketene. Thus, its ability to undergo analogous cycloadditions should equal or even surpass that of the dichloro analogue. In addition, the syntheses of CCK, as outlined here, do not involve reagents such as tertiary amines, activated zinc, or phosphorous oxychloride as are used in the available dichloroketene syntheses. As a result, the possible influence of such reagents on the course of the cycloadditions are avoided. Also, the unsymmetrical nature of CCK provides a stereochemical consequence to its cycloadditions which is, of course, absent for those of dichloroketene. Finally, it is noted that the resulting 2-chloro-2-cyanocyclobutanones would be activated toward facile ring-opening reactions, i.e., secoalkylation reactions.[10] For these reasons, it was of interest to investigate the cycloadditions of CCK to a variety of alkenes.

It was observed that CCK is indeed similar to dichloroketene in its ability to cycloadd to most alkenes (Scheme IV). In addition, the results are in complete accord with a concerted $2\pi_s + 2\pi_a$ mechanism. For example, CCK expresses high reactivity as evidenced by the fact that it adds to the di-, tri-, and tetrasubstituted alkenes, cyclohexene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene, to give respectively the cyclobutanones, **13**, **14**, and **15** in very good isolated yields. Furthermore, the cyclobutanones, **13**, **14**, and **16** were obtained by a highly stereoselective route since only one diastereomer of the cyclohexene adduct, **13**, and of the 2-methyl-2-butene adduct, **14**, could be detected by spectral analysis (^{1}H NMR and ^{13}C NMR) and a diastereiometric ratio of 98:2 (GLC and ^{13}C NMR) was observed for the styrene adduct **16**. In addition, the cycloadducts **17** and **18** illustrate that the cycloadditions also proceed with preservation of the stereochemistry of the alkene. For example, **17** was obtained in 93% yield as a single diastereomer from *cis*-3-hexene; the cis relationship of the methine protons was established from their observed coupling constant (J = 10.9 Hz).[11] Analogously, **18** obtained from *trans*-3-hexene, revealed a trans relationship of the methine protons (J = 9.9 Hz). However, both the 2,3-Z and 2,3-E diastereomers of **18** were obtained in a 65:35 ratio as shown by the ^{1}H NMR and ^{13}C NMR spectra of the crude product. Finally, it was observed that the cis alkene reacts faster than the trans isomer. For example, when 3.8 equiv of a 1:1 mixture of the *cis*- and *trans*-3-hexenes was treated with 1 equiv of CCK at 103 °C, the only product observed was **17**.

The complete relative stereochemistries of the adducts **13**, **14**, and **16** were not established but are reasonably assumed to be as indicated on the basis of mechanistic considerations. That is, the reactions most probably proceed via a concerted $2\pi_s + 2\pi_a$ mechanism involving the transition state represented by the generalized structure **19**.[12] All of the results presented thus far are in agreement with such a mechanism. Of particular importance in this regard is the observation that *cis*-3-hexene gave **17** as a single diastereomer, and the trans isomer gave a 65:35 mixture of diastereomers. As mentioned above, both diastereomers obtained from the trans alkene were shown to have an 3,4-E configuration. The major isomer was shown to have the 2,3-Z configuration on the basis of its NMR spectral data. Specifically, the absorption of the methine proton at C-3 was more deshielded (2.59) in the major diastereomer than in the minor (2.34). Since it is known that a cyano group deshields a cis more than a trans disposed vicinal proton in cyclobutanones, the above structural assignment is reasonable.[13] Analogously, the chemical shift of the methine proton at position 3 of **17** is even more deshielded (3.03) than the corresponding absorption in **18** (2.59). Thus, the 2,3-Z configuration of **17** is most likely.

When the alkenic ketenophile becomes progressively more nucleophilic, the reactions appear to become dipolar in nature. For example, treatment of cyclopentadiene with CCK gave a 55:45 mixture of the diastereomers of **20** (30%). Such a result would not be anticipated for a concerted reaction since, on the basis of the results observed with cyclohexene, the addition of this ketene to a cyclic cis alkene would be expected to give a single diastereomer. Even more dramatic, was the result obtained when dihydropyran was treated with the ketene. Here, the only isolable product was **21** (32%), a product most

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[8] Brady, W. T. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; pp 279–308.

[9] Brady, W. T. *Tetrahedron* **1981**, *37*, 2949.

[10] Trost, B. M.; Bogdanowicz, M. J.; Frazee, W. J.; Salzmann, T. N. *J. Am. Chem. Soc.* **1978**, *100*, 5512.

[11] Braillon, B.; Salaun, J.; Gore, J.; Conia, J. M. *Bull. Soc. Chim. Fr.* **1964**, 1981.

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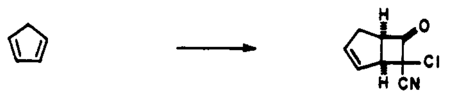
[13] Weyler, W.; Byrd, L.; Caserio, M. C.; Moore, H. W. *J. Am. Chem. Soc.* **1972**, *94*, 1027.



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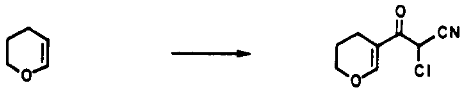

21

likely arising from a proton-transfer process involving a zwitterionic intermediate.

The above cycloadditions were all accomplished by slowly adding the azidofuranone **3a** (1 equiv) to hot (103 °C) toluene containing an excess of the alkene (1.9 equiv). Such conditions, in general, often give excellent results for CCK cycloadditions since a low concentration of the ketene is maintained during the course of the reaction, and thus ketene polymerization products are minimized. In comparison, when cyclohexene, at ambient temperature, was treated with CCK as generated from **5**, a complex mixture of products resulted and little or no cyclobutanone **13** was detected. Under these conditions the ketene is formed rapidly and its self-condensation and/or reaction with azide ion presumably effectively compete with its ability to cycloadd to the alkene.

Experimental Section

All reagents and solvents were purified and dried according to the prescribed methods.[14] Unless otherwise stated, all reactions were carried out in flame-dried glassware under an atmosphere of argon. Melting points were obtained on a Laboratory Device Meltemp capillary melting point apparatus. Mass spectral data were obtained on a Finnigan Model 4000 GCMS spectrograph. Isobutane was used as the ionizing gas for all spectra obtained under CI conditions. Unless specified, IR spectra were obtained on a Perkin Elmer 283 Spectrophotometer in carbon tetrachloride. All NMR data were obtained on a Varian FT-80 or a Brucker WM-250 spectrometer. Deuteriochloroform was employed as the solvent and tetramethylsilane was used as the internal standard. All spectral data are in strict agreement with the assigned structures.

***tert*-Butyl Chlorocyanoacetate (7).** To a solution of 0.93 mL (0.73 g, 9.9 mmol) of *tert*-butyl alcohol in 130 mL of toluene at 103 °C was added 1.00 g (5.3 mmol) of **3a** in 10 mL of toluene over a period of 5 min. After 1 h and 45 min the reaction solution was cooled and the solvent removed in vacuo. The resulting light yellow liquid was purified by flash column chromatography (silica gel Super-60, hexane:ethyl acetate 9:1) to give 0.80 g (86%) of **7** as a colorless liquid.

Anal. Calcd for $C_7H_{10}O_2Cl$: C, 47.87; H, 5.74. Found: C, 48.11; H, 5.62.

The ester **7** was also prepared from 3,4-dichlorocyclobutenedione (**5**) as follows. To a suspension of 0.35 g (5.4 mmol) of NaN_3 in 5.0 mL (3.9 g, 52.8 mmol) of *tert*-butyl alchol was added 0.80 g (5.3 mmol) of **5** in 0.5 mL of acetonitrile over a period of 20 min. After 2 h and 45 min 50 mL of dichloromethane was added and the mixture was washed three times with 15-mL portions of brine. The aqueous layers were combined, 10 mL of 5% HCl was added, and the solution was washed once with 25 mL of diethyl ether. The organic layers were combined and dried with magnesium sulfate, and the solvent was removed in vacuo. The resulting light yellow oil was purified by flash column chromatography to give 0.72 g (77%) of **7** as a colorless liquid. The spectral properties of this product were identical with those obtained from **7** prepared as described above.

7-Chloro-7-cyanobicyclo[4.2.0]octan-8-one (13). To a solution of 1.0 mL (0.81 g, 9.5 mmol) of cyclohexene in 130 mL of toluene at 103 °C was added 1.0 g (5.3 mmol) of **3a** in 10 mL of toluene over a period of 5 min. After 1 h and 45 min the reaction solution was cooled and the solvent removed in vacuo. The crude solid was then recrystallized from petroleum ether to give 710 mg (73%) of **13** as a white crystalline solid, mp 39.5–40.5 °C.

Anal. Calcd for $C_9H_{10}NOCl$: C, 58.87; H, 5.49. Found: C, 58.58; H, 5.71.

2-Chloro-2-cyano-3,3,4-trimethylcyclobutanone (14). The title compound was prepared by the procedure outlined above by using 2-methyl-2-butene to give **14** as a light yellow oil. The pure compound, 720 mg (80%), was obtained as a colorless oil after Kugelrohr distillation.

Anal. Calcd for $C_8H_{10}NOCl$: C, 55.99; H, 6.29. Found: C, 55.86; H, 5.99.

2-Chloro-2-cyano-3,3,4,4-tetramethylcyclobutanone (15). The title compound was prepared by the procedure outlined above using 2,3-dimethyl-2-butene to give **15** as a light yellow oil. After Kugelrohr distillation, **15** was obtained in 74% yield (720 mg) as a white semisolid.

Anal. Calcd for $C_9H_{12}NOCl$: C, 58.23: H, 6.62. Found: C, 58.01, H, 6.66.

2-Chloro-2-cyano-(*Z*)-3,4-diethylcyclobutanone (17). The title compound was prepared by the procedure outlined above by using (*Z*)-3-hexene to give 1.0 g of an orange oil which was purified by Kugelrohr distillation to give 920 mg (93%) of **17** as a colorless liquid: ^1H NMR 3.69 (t of d, J = 10.9 Hz, J = 7.2 Hz, 1), 3.03 (t of d, J = 10.8 Hz, J = 6.7 Hz, 1), 1.73 (overlapping q of d, J = 7.2 Hz, J = 6.7 Hz, 4), 1.07 (m, 6).

Anal. Calcd for $C_9H_{12}NOCl$: C, 58.23; H, 6.62. Found: C, 58.16; H, 6.59.

2-Chloro-2-cyano-(*E*)-3,4-diethylcyclobutanone (18). The title compound was prepared in 67% yield as a 65:35 mixture of diastereomers (^1H NMR analysis) by the method outlined above: colorless liquid; ^1H NMR 3.43 (t of d, J = 10.0 Hz, J = 7.2 Hz, 0.65), 3.26 (t of d, J = 10.0 Hz, J = 6.9 Hz, 0.35), 2.59 (d of d of d, J = 10.0 Hz, J = 6.5 Hz, J = 5.4 Hz, 0.65), 2.34 (d of d of d, J = 9.8 Hz, J = 7.1 Hz, J = 4.5 Hz, 0.35), 1.87 (m, 4), 1.10 (m, 6); ^{13}C NMR 191.0, 190.8, 114.0, 112.6, 65.7, 64.6, 62.7, 62.2, 49.1, 45.7 25.6, 23.7, 22.6, 22.3, 11.9, 11.8, 11.2, 11.1; MS (EI) 116 (18), 70 (100).

Anal. Calcd for $C_9H_{12}NOCl$: C, 58.23; H, 6.62. Found: C, 58.22; H, 6.35.

2-Chloro-2-cyano-3-phenylcyclobutanone (16). The title compound was prepared in 86% yield by the procedure outlined above: colorless oil; ^1H NMR 7.32 (m, 5), 4.33 (m, 1), 3.76 (m, 2); ^{13}C NMR 187.27, 133.16, 128.92, 128.63, 128.48, 114.08, 65.80, 49.57, 43.02. A minor diastereomeric isomer was revealed by the appearance of small shoulders on the peaks given above. This ratio was established to be 98:2 by GLC analysis of the reaction mixture.

Anal. Calcd for $C_{11}H_8NOCl$: C, 64.25; H, 3.92. Found: C, 63.95; H, 3.98.

3-(Chlorocyanoacetyl)-5,6-dihydro-4*H*-pyran (21). Employing the procedure as outlined above using dihydropyran gave 1.0 g of a viscous dark orange oil. This was purified by flash column chromatography (silica gel 60; 7/3 hexane–ethyl acetate) to give 310 mg (32%) of **21** as a clear oil.

Anal. Calcd for $C_9H_8NO_2Cl$: C, 51.77; H, 4.34. Found: C, 51.64; H, 4.29.

7-Chloro-7-cyano-6-oxobicyclo[3.2.0]hept-2-ene (20). The title compound was synthesized as a 55:45 mixture of the 2,3-*Z* and 2,3-*E* diastereomers, respectively (^1H NMR), by the procedure outlined above by using 1.25 equiv of cyclopentadiene. Kugelrohr distillation of the crude product gave a 30% yield of **20** as a white semisolid: ^1H NMR 6.19 (m, 0.55), 6.10 (m, 0.45), 5.92 (m, 0.55), 5.73 (m, 0.45), 4.52 (m, 0.45), 4.39 (m, 0.55), 4.20 (m, 0.55), 3.86 (m, 0.45), 2.77 (m, 2); ^{13}C NMR 193.29, 192.93, 138.89, 138.13, 127.10, 126.50, 114.59, 112.07, 65.07, 63.79, 62.15, 61.28, 53.82, 51.98, 36.41, 35.96.

Anal. Calcd for C_8H_6NOCl: C, 57.33; H, 3.61. Found: C, 57.60; H, 3.93.

Acknowledgment. We wish to thank the National Science Foundation for financial support of this work (CHE-8025567).

Registry No. **3a**, 60010-88-0; **5**, 2892-63-9; **7**, 89937-14-4; **13**, 89937-15-5; **14**, 89937-16-6; **15**, 89937-17-7; **16**, 89937-19-9; **17**,

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(14) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: New York, 1980.

89937-18-8; **18** (isomer 1), 90024-43-4; **18** (isomer 2), 90024-44-5; **20** (isomer 1), 89937-21-3; **20** (isomer 2), 90024-45-6; **21**, 89937-20-2; Cl(CN)C=C=O, 60010-89-1; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; (*Z*)-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; styrene, 100-42-5; cyclopentadiene, 542-92-7; 3,4-dihydro-2*H*-pyran, 110-87-2.

Supplementary Material Available: Spectral data and further experimental details (7 pages). Ordering information is given on any current masthead page.

Factors Conducive to the Cascade Rearrangement of Sterically Congested and Geometrically Restricted Three-Membered Rings. Facile Synthesis of a Topologically Nonplanar Heterocycle

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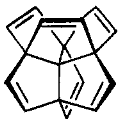
The two triepoxide stereoisomers of 2,8,9-trimethylene[3.3.3]propellane rearrange under the influence of Lewis acids or heat to the topologically nonplanar trioxahexaquinane **3**. The same involvement of the ensemble of three-membered rings in diepoxides **12** and monoepoxide **13** has not been realized. Whereas the former lead to a myriad of unidentified products under a variety of conditions, **13** was found to isomerize cleanly to aldehyde **14** in the presence of anhydrous zinc chloride. Although these developments signaled that cyclopropane rings are less prone to engage in the necessary cationic cascade, it proved possible to induce hydrative threefold cyclopropane ring cleavage in **9** by means of trifluoromethanesulfonic acid in dichloromethane solution with formation of an alcohol provisionally formulated as **15**. Mechanistic considerations are presented where relevant.

Some time ago, we called attention to the maximally unsaturated hydrocarbon **1** to which the name C_{17}-hexaquinacene was assigned.[1] This molecule compresses the structural elements of [3.3.3]propellatriene and triquinacene into a highly compact spherical construction. Furthermore, the unusual connectivity in **1** causes it to be topologically nonplanar,[2,3] an unusual three-dimensional property that brings into being a new kind of isomerism.[4] Since the rare structural characteristic in question is molecularly based, the perhydrohexaquinane **2** and heterocyclic derivatives such as **3** also cannot be depicted in two dimensions without intercepting bonds. In addition, **3** is noninterconvertible with its mirror image. Since this group of molecules represents one of the simplest examples of topological nonplanarity,[5] synthetic efforts were directed to their acquisition.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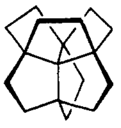
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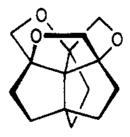
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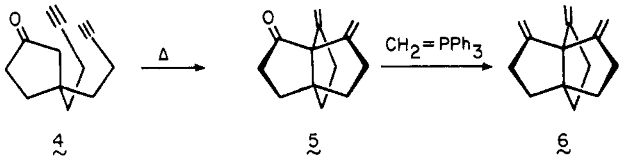
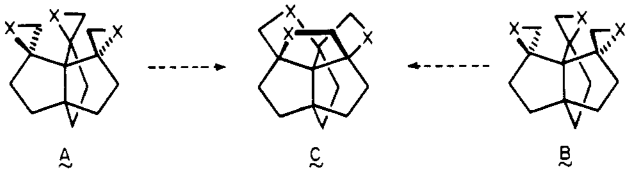
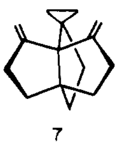
To this end, we were attracted to developments emanating from Conia's laboratory which showed that access to ring-functionalized [3.3.3]propellanes (e.g., **5** and **6**) could be gained by twofold ene cyclization of cyclopentanone **4** at elevated temperatures.[6] Particularly intriguing to us was the possibility that homologation of these molecules as in A or B might subsequently set the stage for reorganization of the three-membered rings under proper reaction conditions to give C. At this point in time, Professor Conia informed us of his successful conversion of **6** to a mixture of **7**–**9** by means of the Simmons–Smith reaction.[7] Importantly, the acquisition of **9** demonstrated that steric factors would not preclude access to highly strained hexacyclic molecules of this type.



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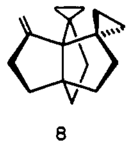
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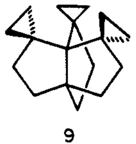
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(1) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* 1978, *100*, 1600.

(2) (a) Balaban, A. T. "Chemical Applications of Graph Theory"; Academic Press: New York, 1976; p 84. (b) Harary, F. "Graph Theory"; Addison-Wesley: Reading, MA, 1969.

(3) In the terms of graph theory, a graph is classified as *planar* if upon drawing it on a plane no two edges meet except at a vertex. If this is not possible, the graph is considered to be *nonplanar*.

(4) Fox, G. L. *Chem. Eng. News* 1982, 21.

(5) A second, more elaborate example is the Möbius strip molecule tris(THYME): Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* 1982, *104*, 3219.

(6) Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron Lett.* 1975, 4053; *Tetrahedron* 1980, *36*, 1203.

(7) Drouin, J. Ph.D. Thesis, Université de Paris Sud, Centre d'Orsay, 1976.

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