Peroxy Acid Oxidation of Cycloalkynes and the Decomposition of 2-Diazocycloalkanones[1]

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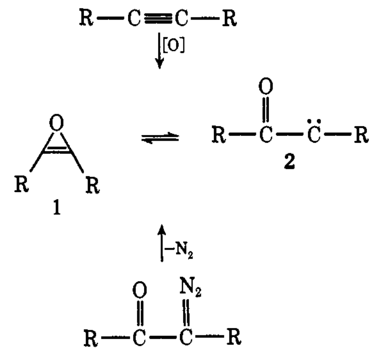
Abstract: Cyclooctyne (**3**), cyclononyne (**7**), cyclodecyne (**12**), and cyclododecyne (**17**) were oxidized with *m*-chloroperoxybenzoic acid (MCPBA) in methylene chloride. Cyclononyne and cyclodecyne afforded cis-bicyclic ketones **9** and **14** as major products, whereas cyclooctyne and cyclododecyne led predominantly to α,β-unsaturated ketones **6** and **19**, in addition to significant amounts of ring-contracted ketones **4** and **18**. Oxidation of **12** with tetralin hydroperoxide–cyclohexyl metaborate (THPO–CHMB) or peroxybenzimidic acid afforded results similar to those with MCPBA. Since an oxocarbene $\rightleftharpoons$ oxirene equilibrium can formally be reached from α-diazo ketones as well as acetylenes, the corresponding 2-diazocycloalkanones **24, 26, 28,** and **30** were decomposed in refluxing benzene. In each case an α,β-unsaturated ketone and a ring-contracted polymethyleneketene were major products. The decomposition of 2-diazocyclodecanone (**28**) with glacial acetic acid, 70% perchloric acid, or boron trifluoride ethyl ether afforded 2-cyclodecen-1-one (**16**) as the major product. The relevance of oxirenes and α-ketocarbenes as intermediates in the oxidation of acetylenes and the decomposition of α-diazo ketones is discussed.

Oxirenes (**1**) are of theoretical and experimental interest as potential 4π antiaromatic systems[3] and have been postulated as intermediates in various thermal and photochemical reactions.[4] Isotopic labeling studies have indeed supported the intermediacy of oxirenes in the photochemical decomposition of α-diazo ketones[5] and ketene,[6a] and in the reaction of singlet methylene with carbon monoxide.[6b] Similarly, product analysis of the thermal and photochemical decomposition of unsymmetrically substituted α-diazo ketones supports the intervention of oxirenes.[7] Interestingly, theoretical calculations indicate that oxocarbenes (**2**) are thermodynamically more stable than oxirenes (**1**).[5b] The addition of oxygen[8] and sulfur atoms[9] to acetylenes has also provided evidence for oxirenes and thiirenes.

The intermediacy of oxirenes has been proposed in the peroxy acid oxidation of acetylenes, but no compelling evidence has been presented.[10] In theory, the apparent oxocarbene $\rightleftharpoons$ oxirene equilibrium can be attained from acetylenes and the corresponding α-diazo ketones as shown in Scheme I. In this account we wish to report the results of our studies on the peroxy acid oxidation of the C_8, C_9, C_{10}, and C_{12} cycloalkynes and the decomposition of the corresponding 2-diazocycloalkanones.

Scheme I



Results and Discussion

Cycloalkyne Oxidations. Cyclooctyne (**3**), cyclononyne (**7**), cyclodecyne (**12**), and cyclododecyne (**17**) were each allowed to react with 1.1 equiv of *m*-chloroperoxybenzoic acid (MCPBA) in methylene chloride at room temperature, and the residual oils after aqueous work-up were analyzed by glpc. The oxidation products are presented in Table I. In all cases structures were established by direct spectral and/or glpc comparison with authentic samples. The oxidation of cyclooctyne (**3**) afforded cycloheptanone (**4**, 22%),[11] *cis*-bicyclo[3.3.0]octan-2-one (**5**, 29%),[12] and *cis*-2-cycloocten-

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[1] Abstracted from the Ph.D. Thesis of P. W. Concannon, Brown University, 1972.

[2] National Science Foundation Trainee, 1969–1971.

[3] (a) R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968), and previous publications cited therein; (b) D. T. Clark, *Theor. Chim. Acta*, **15**, 225 (1969), and references cited therein.

[4] Despite several incorrect claims to the contrary in the earlier literature, oxirenes have never been isolated or detected. For a summary, see V. Franzen, *Justus Liebigs Ann. Chem.*, 614, 31 (1958).

[5] (a) I. G. Csizmadia, J. Font, and O. P. Strausz, *J. Amer. Chem. Soc.*, 90, 7360 (1968); (b) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970); (c) G. Frater and O. P. Strausz, *ibid.*, **92**, 6654 (1970); (d) K.-P. Zeller, H. Meier, H. Kolshorn, and E. Müller, *Chem. Ber.*, **105**, 1875 (1972).

(5e) Note Added in Proof. After submission of our original manuscript two papers recently appeared on the mechanism of the Wolff rearrangement: J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Amer. Chem. Soc.*, **95**, 124 (1973); I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and O. P. Strausz, *ibid.*, **95**, 133 (1973).

[6] (a) R. L. Russell and F. S. Rowland, *ibid.*, **92**, 7508 (1970). These authors question the participation of oxirenes in the photochemical Wolff rearrangement of α-diazo ketones on the basis of evidence which supports the intervention of oxirene in the photolysis of ketene. (b) D. C. Montague and F. S. Rowland, *ibid.*, **93**, 5381 (1971).

[7] S. A. Matlin and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 11 (1972).

[8] (a) I. Haller and G. C. Pimentel, *J. Amer. Chem. Soc.*, **84**, 2855 (1962); (b) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, 43, 525 (1965).

[9] A much greater stability of thiirenes relative to oxirenes is predicted:[3b] O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 4805 (1967).

[10] (a) V. Franzen, *Chem. Ber.*, **88**, 717 (1955), and previous papers; (b) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **86**, 4866 (1964); (c) J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964); (d) E. W. Byrnes, Ph.D. Thesis, University of New Hampshire, 1964; *Diss. Abstr.*, **25**, 4401 (1965); (e) J. Ciabattoni, R. A. Campbell, C. A. Renner, and P. W. Concannon, *J. Amer. Chem. Soc.*, **92**, 3826 (1970).

[11] Commercially available from the Aldrich Chemical Co., Milwaukee, Wis.

[12] A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, 74, 5884 (1952); A. C. Cope, H.-H. Lee, and H. E. Petree, *ibid.*, **80**, 2849 (1958); R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

1-one (**6**, 49%).[13] Cyclononyne (**7**) gave cyclooctanone (**8**, 1%),[11] *cis*-bicyclo[4.3.0]nonan-2-one (**9**, 68%),[14] *cis*-bicyclo[4.3.0]nonan-7-one (**10**, 16%),[15] and *cis*-2-cyclononen-1-one (**11**, 15%).[16] Reaction of cyclodecyne (**12**) with MCPBA yielded cyclononanone[11] (**13**, <1%), *cis*-bicyclo[5.3.0]decan-2-one (**14**, 67%),[17] *cis*-bicyclo[4.4.0]decan-2-one (**15**, 12%),[18] and *cis*-2-cyclodecen-1-one (**16**, 21%).[19] Finally, cyclododecyne (**17**) afforded cycloundecanone (**18**, 15%),[11] *cis*-2-cyclododecen-1-one (**19**, 66%),[20] and *trans*-2-cyclododecen-1-one (**20**, 19%).[20]

The formation of ring-contracted ketones **4**, **8**, **13**, and **18** involves the formal loss of a carbon atom, presumably as carbon dioxide, from the oxidation of cycloalkynes **3**, **7**, **12**, and **17**, respectively. These ketones are undoubtedly secondary products derived from the known oxidative cleavage of the initially formed polymethyleneketene intermediates **25**, **27**, **29**, and **31**, respectively (*vide infra*).[21] The major if not exclusive formation of cis bicyclic ketones and cis enones in the oxidation of cycloalkynes is the result of kinetically controlled reactions. Supporting evidence was provided by the cyclodecyne and cyclododecyne results. In the former case only cis-fused bicyclic ketones **14** and **15** were formed in spite of the fact that the corresponding trans isomers are thermodynamically more stable. The relative stabilities of some cis and trans bicyclic ketones are indicated in Table II. Similarly, in all cases, cis enones were the major if not exclusive isomers regardless of thermodynamic stability. Only in the cyclododecyne (**17**) case was trans enone detected. However, it is uncertain whether **20**, the more stable isomer, is a direct oxidation product or an indirect product arising from partial isomerization of the cis isomer **19** which reportedly occurs at room temperature.[20]

Table I. MCPBA Oxidation of Cycloalkynes

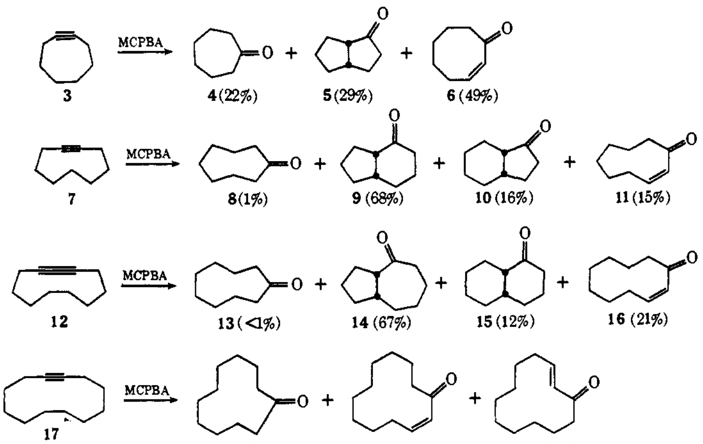
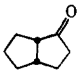
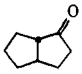
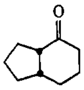
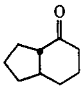
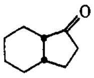
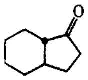
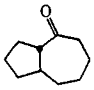
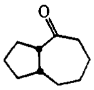
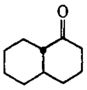
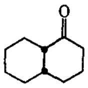
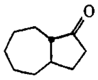
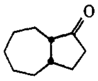
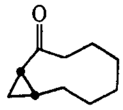


Table II. Relative Thermodynamic Stability of Cis and Trans Bicyclic Ketones

More stable	Less stable	Ref
		*a*
		*b*
		*c*
		*d*
		*e*
		*f*

[a] A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 946 (1934). [b] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964). [c] H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 31 (1963). [d] H. L. Goering, A. C. Olson, and H. H. Espy, *J. Amer. Chem. Soc.*, **78**, 5371 (1956). [e] C. D. Gutsche and H. H. Peter, *ibid.*, **77**, 5971 (1955). [f] E. Negishi, private communication; see H. C. Brown and E. Negishi, *Chem. Commun.*, 594 (1968).

The results are consistent with the intervention of α-ketocarbenes as depicted in Scheme II for cyclodecyne (**12**). Cis bicyclic ketones **14** and **15** arise *via* 1,5- and 1,6-transannular C–H insertion reactions, respectively, of ketocarbene **21**.[22] The possible 1,3-transannular insertion product, namely *cis*-bicyclo[7.1.0]decan-2-one (**22**),[23] was demonstrated to be absent by glpc comparison of the product mixture with an authentic sample. Unfortunately, the presence or absence of *cis*-bicyclo[5.3.0]decan-8-one (**23**),[24] a potential 1,5-transannular insertion product, could not be established since its glpc retention time was very similar to that of **16**. However, if present, the yield of **23** must be very minor since the yield of **16** as determined by nmr (18%) is in close agreement with the



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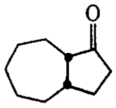

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[13] A. C. Cope and L. L. Estes, Jr., *J. Amer. Chem. Soc.*, **72**, 1128 (1950); N. Heap and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966).

[14] D. M. Bailey, J. E. Bowers, and C. D. Gutsche, *J. Org. Chem.*, **28**, 610 (1963). We are indebted to Professor Gutsche for a gift of authentic **9**.

[15] H. O. House and G. H. Rasmusson, *ibid.*, **28**, 31 (1963). We are grateful to Professor House for providing us with an authentic sample of **10** and its trans isomer.

[16] M. Regitz and J. Rüter, *Chem. Ber.*, **102**, 3877 (1969).

[17] (a) H. E. Holmquist, H. S. Rothrock, C. W. Theobald, and B. E. Englund, *J. Amer. Chem. Soc.*, **78**, 5339 (1956); (b) A. C. Cope and G. Holzman, *ibid.*, **72**, 3062 (1950); (c) H. L. Goering, A. C. Olson, and H. H. Espy, *ibid.*, **78**, 5371 (1956).

[18] (a) A. I. Meyers, W. Beverung, and G. Garcia-Munoz, *J. Org. Chem.*, **29**, 3427 (1964); (b) C. D. Gutsche and H. H. Peter, *J. Amer. Chem. Soc.*, **77**, 5971 (1955); (c) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 422 (1953).

[19] (a) R. G. Carlson and J. H. Bateman, *Tetrahedron Lett.*, 4151 (1967); (b) R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, **32**, 1608 (1967). We are grateful to Professor Carlson for providing us with an authentic sample of **16** as well as infrared and nmr data of both **16** and its trans isomer.

[20] H. Nozaki, T. Mori, and R. Noyori, *Tetrahedron*, **22**, 1207 (1966).

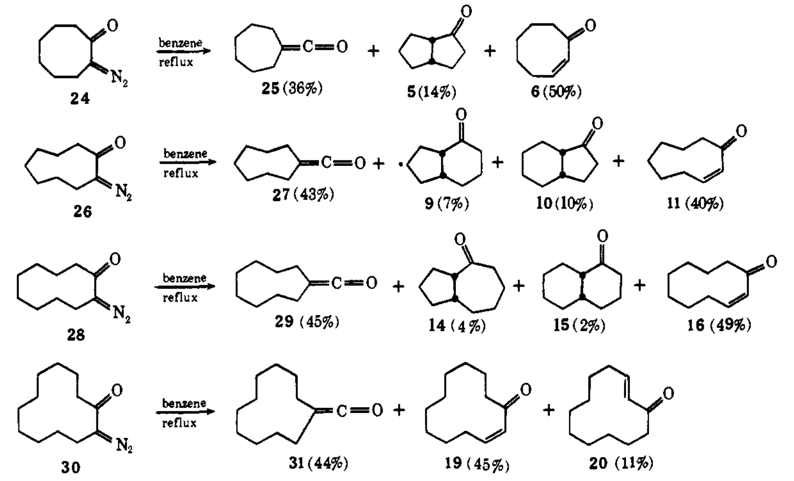
[21] J. K. Crandall and S. A. Sojka, *Tetrahedron Lett.*, 1641 (1972).

[22] For a review of transannular carbene reactions in medium-sized rings, see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev., Chem. Soc.*, **20**, 119 (1966).

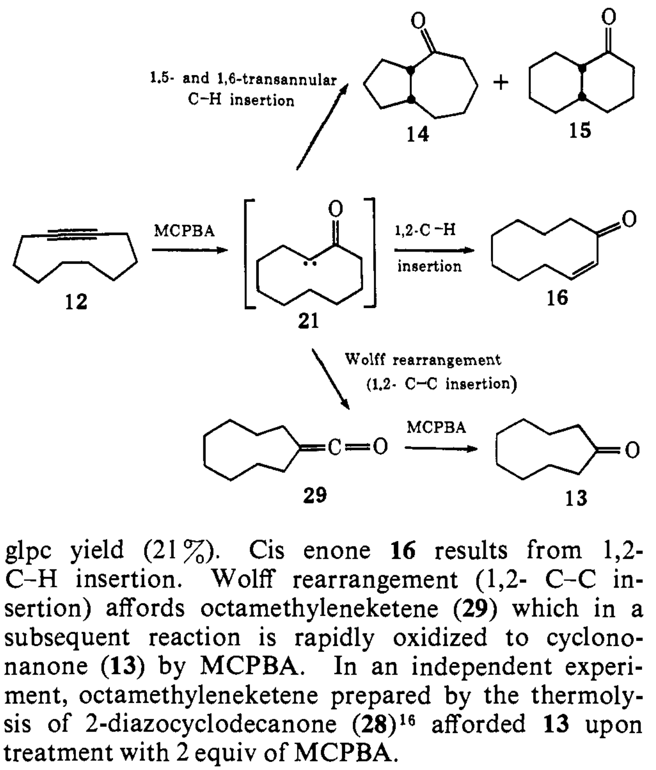
[23] C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 6892 (1969). We are grateful to Professor C. S. Foote for kindly sending us an authentic sample of **22**.

[24] N. Jones, H. T. Taylor, and E. Rudd, *J. Chem. Soc.*, 1342 (1961); N. Jones and H. T. Taylor, *ibid.*, 4017 (1959); C. D. Gutsche, I. Y. C. Tao, and J. Kozma, *J. Org. Chem.*, **32**, 1782 (1967).

Table III. Thermal Decomposition of 2-Diazocycloalkanones



Scheme II



glpc yield (21%). Cis enone **16** results from 1,2-C–H insertion. Wolff rearrangement (1,2- C–C insertion) affords octamethyleneketene (**29**) which in a subsequent reaction is rapidly oxidized to cyclononanone (**13**) by MCPBA. In an independent experiment, octamethyleneketene prepared by the thermolysis of 2-diazocyclodecanone (**28**)[16] afforded **13** upon treatment with 2 equiv of MCPBA.

Some interesting trends are evident in Table I, the most striking of which is the similarity of product distributions obtained from cyclononyne and cyclodecyne. In both cases the major product is a bicyclic ketone derived from 1,5-transannular insertion (*i.e.*, **9** and **14**, respectively). In the C_9 and C_{10} cycloalkyne cases transannular reactions account for 84 and 79% of the products, respectively. This is not surprising since transannular reactions are induced by proximity effects which are most pronounced in cyclononyne and cyclodecyne. Significant amounts (**11**, 15% and **16**, 21%) of cis enones, but only very minor amounts (~1%) of ring-contracted ketones **8** and **13**, were formed. The product distributions obtained from cyclooctyne and cyclododecyne were similar to each other only to the extent that enones **6**, **19**, and **20** were the major oxidation products (49 and 85%, respectively) and ring-contracted ketones **4** and **18** were present in significant amounts (22 and 15%, respectively). The major expected difference between the C_8 and C_{12} cycloalkyne cases was the extent of transannular insertion reactions. Cyclooctyne afforded 29% of 1,5-transannular insertion product **5**, whereas no transannular products were detected in the cyclododecyne case.

2-Diazocycloalkanone Decompositions. The corresponding diazo ketones, namely, 2-diazocyclooctanone (**24**), 2-diazocyclononanone (**26**), 2-diazocyclodecanone (**28**), and 2-diazocyclododecanone (**30**), were each decomposed in anhydrous refluxing benzene under nitrogen, and the resulting solutions were analyzed by glpc. As before in the cycloalkyne studies, product structures were established by spectral and/or glpc comparison with authentic samples. The results are presented in Table III. The thermolysis of 2-diazocyclooctanone (**24**) afforded hexamethyleneketene (**25**, 36%), *cis*-bicyclo[3.3.0]octan-2-one (**5**, 14%), and *cis*-2-cycloocten-1-one (**6**, 50%). The decomposition of 2-diazocyclononanone (**26**) gave heptamethyleneketene (**27**, 43%), *cis*-bicyclo[4.3.0]nonan-2-one (**9**, 7%), *cis*-bicyclo[4.3.0]nonan-7-one (**10**, 10%), and *cis*-2-cyclononen-1-one (**11**, 40%). The products derived from 2-diazocyclodecanone (**28**) were identified as octamethyleneketene (**29**, 45%), *cis*-bicyclo[5.3.0]decan-2-one (**14**, 4%), *cis*-bicyclo[4.4.0]decan-2-one (**15**, 2%), and *cis*-2-cyclodecen-1-one (**16**, 49%). Finally, 2-diazocyclododecanone (**30**) yielded decamethyleneketene (**31**, 44%), *cis*-2-cyclododecen-1-one (**19**, 45%), and *trans*-2-cyclododecen-1-one (**20**, 11%). The yellow polymethyleneketenes **25**, **27**, **29**, and **31** were collected on a preparative SE-30 glpc column, and their structures were established on the basis of characteristic intense infrared absorption at 2100 cm^{-1}. These ketenes undergo facile air oxidation to the corresponding cycloalkanones.[25] As in the cyclododecyne oxidation, it could not be established whether *trans*-2-cyclododecen-1-one (**20**) was a primary product or a secondary product derived from partial isomerization of the cis isomer **19**.

Upon examination of Tables I and III, striking similarities and differences between the cycloalkyne and

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[25] See C. D. Gutsche and J. W. Baum, *J. Amer. Chem. Soc.*, 90, 5862 (1968), and references cited therein.

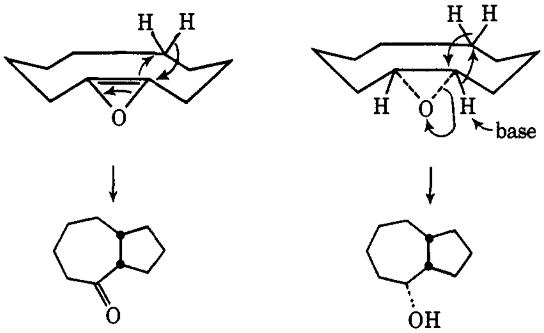
2-diazocycloalkanone reactions are evident. Identical products and stereochemistry were observed in both cases. The assumption is made that polymethyleneketenes **25**, **27**, **29**, and **31** are primary products of the cycloalkyne oxidations and precursors to the observed cycloalkanones **4**, **8**, **13**, and **18**, respectively (*vide supra*). The corresponding product distributions, however, were different, most dramatically in the C_9 and C_{10} diazo ketone decompositions in comparison with the C_9 and C_{10} acetylene oxidations. Diazo ketones **26** and **28** afforded only 17 and 6% transannular insertion products, respectively, as compared with 84 and 79% transannular insertion from cycloalkynes **7** and **12**, respectively. Similarly, **26** and **28** gave 43 and 45% ketene, respectively, whereas **7** and **12** provided only about 1% ketene.

Solvent and temperature effects were excluded as a rationalization for the differences in product distribution in the two reactions by the appropriate control experiments. Oxidation of cyclodecyne (**12**) with MCPBA in refluxing benzene or glacial acetic acid at room temperature did not significantly alter the product distribution. Furthermore, the oxidation of cyclodecyne with other known peroxidic epoxidizing agents such as tetralin hydroperoxide–cyclohexyl metaborate (THPO–CHMB)[26] in refluxing cyclohexane or peroxybenzimidic acid[27] in aqueous methanol gave similar results. The decomposition of 2-diazocyclodecanone (**28**) in glacial acetic acid, boron trifluoride ethyl ether, and perchloric acid afforded *cis*-2-cyclodecen-1-one (**16**) as the major product in 60, 97, and 80% yield, respectively.

The results of this study are consistent with the intervention of α-ketocarbene intermediates or α-ketocarbenoid transition states in the peroxy acid oxidation of acetylenes and the thermal aprotic decomposition of α-diazo ketones. However, a major question is raised: Why do these two reactions afford identical products but in different distribution? As pointed out earlier, solvent and temperature effects do not provide a rationalization on the basis of suitable control experiments (*vide supra*). We believe that the mechanisms of these two related reactions are similar but not identical.

One rationalization involves the initial conversion of the acetylene to an oxirene which owing to its low stability rapidly isomerizes to an α-ketocarbene. The related α-diazo ketone might not decompose to a free ketocarbene; that is, nitrogen departure may be concerted with product formation.[28] An alternative possibility is that both reactions produce α-ketocarbene intermediates which differ in conformation and energy. This, of course, assumes that intramolecular reaction can compete with collisional deactivation and conformational equilibration. Since the conformations of the cycloalkynes are more rigid and proximity effects more pronounced than in the corresponding 2-diazocycloalkanones, this would explain the high yield of transannular insertion in the C_9 and C_{10} cycloalkyne oxidations in contrast to the respective C_9 and C_{10} diazo ketone decompositions. A third possible explanation involves a direct intramolecular trapping of the oxirene intermediate in the cycloalkyne oxidations in contrast to the α-diazo ketone decompositions, which may not involve oxirenes as the product forming intermediates. For example, transannular insertion may be concerted with oxirene ring opening. Cope has demonstrated that the formation of bicyclic alcohols from medium-ring epoxides and strong nonnucleophilic bases proceeds *via* an α elimination–carbenoid insertion mechanism.[22,29] The analogy between the proposed direct transannular insertion of the oxirene derived from cyclodecyne and the base-induced α elimination–carbenoid insertion of *cis*-cyclodecene oxide is depicted in Scheme III.

Scheme III



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Finally, the concurrent operation of two or more mechanistic pathways in either or both the cycloalkyne oxidations and 2-diazocycloalkanone decompositions cannot be excluded.

Experimental Section

Melting points were determined on a Kofler Micro Heating Stage and are uncorrected. Infrared and nmr spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and a Varian A-60A spectrometer, respectively. Analytical glpc was performed on an Aerograph Model A-200 gas chromatograph equipped with a flame ionization detector. Preparative gas chromatography was accomplished on a Varian Aerograph Model A-90-P gas chromatograph fitted with a thermal conductivity detector. Quantitative determinations were obtained by integration of the chromatograms with a Honeywell Electronik 19 recorder equipped with a Model 215 Disc chart integrator.

Cycloalkynes. Cyclooctyne (**3**), cyclononyne (**7**), cyclodecyne (**12**), and cyclododecyne (**17**) were prepared by the mercuric oxide oxidation of the dihydrazones of 1,2-cyclooctanedione (suberil),[30] 1,2-cyclononanedione (azelil),[31] 1,2-cyclodecanedione (sebacil),[32] and 1,2-cyclododecanedione,[33] respectively. Cyclooctyne was also prepared by the dehydrobromination of 1-bromocyclooctene.[34]

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[26] P. F. Wolf and R. K. Barnes, *J. Org. Chem.*, 34, 3441 (1969).

[27] G. B. Payne, *Tetrahedron*, **18**, 763 (1962).

[28] (a) F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, **88**, 950 (1966); (b) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969, p 77; (c) W. Kirmse, "Carbene Chemistry," Vol. I, 2nd ed, Academic Press, New York, N. Y., 1971, pp 475–493.

[29] (a) A. C. Cope, M. Brown, and H.-H. Lee, *J. Amer. Chem. Soc.*, **80**, 2855 (1958); (b) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6370 (1960); (c) see also G. Wittig and J. J. Hutchison, *Justus Liebigs Ann. Chem.*, **741**, 79 (1970).

[30] (a) A. T. Blomquist and L. H. Liu, *J. Amer. Chem. Soc.*, **75**, 2153 (1953); (b) G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3260 (1961). Suberil was prepared by the selenium dioxide oxidation[30b] of cyclooctanone rather than *via* the acyloin condensation of dimethyl suberate.

[31] (a) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Amer. Chem. Soc.*, 74, 3643 (1952); (b) V. Prelog, K. Schenker, and W. Küng, *Helv. Chim. Acta*, **36**, 471 (1953).

[32] (a) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952); (b) V. Prelog, K. Schenker, and H. H. Günthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (c) A. T. Blomquist and A. Goldstein, *Org. Syn.*, **36**, 77 (1956).

[33] V. Prelog and M. Speck, *Helv. Chim. Acta*, **38**, 1786 (1955). The procedure of Wittig and Krebs[30b] was adapted for the synthesis of 1,2-cyclododecanedione.

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

The alternative synthesis of cyclododecyne from *cis*-cyclododecene by the procedure of Nozaki and Noyori[35] resulted in a contaminated product which could not be purified by distillation.

2-Diazocycloalkanones. The preparation of 2-diazocyclononanone (**26**), 2-diazocyclodecanone (**28**), and 2-diazocyclododecanone (**30**) was effected by base treatment of the corresponding 1,2-cycloalkanedione monotosylhydrazones.[36] The alternative formyl–diazo interchange method was also employed to produce 2-diazocyclooctanone (**24**) and **26**.[37] This general procedure involves reaction of the corresponding 2-hydroxymethylenecycloalkanone and triethylamine with tosyl azide.[37b]

Peroxy Acid Oxidation of Cycloalkynes. The oxidation of cyclodecyne was typical. To a stirred solution of 0.25 g (1.83 mmol) of cyclodecyne (**12**) in 7 ml of methylene chloride was added in one portion under nitrogen 0.41 g (2.01 mmol) of 85% *m*-chloroperoxybenzoic acid (MCPBA)[11] in 8 ml of methylene chloride. Reaction was evidenced by the gradual precipitation of *m*-chlorobenzoic acid from solution. After stirring for 2 hr at room temperature, the reaction mixture was diluted with 50 ml of methylene chloride and extracted with two 50-ml portions of 5% sodium sulfite solution, two 50-ml portions of 5% sodium carbonate solution, and 50 ml of saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation to afford 0.25 g of a fragrant colorless oil which exhibited strong carbonyl absorption near 1700 $\mathrm{cm^{-1}}$ and weak olefinic absorption at 1630 $\mathrm{cm^{-1}}$ in the infrared. The nmr spectrum indicated a mixture of compounds. The vinyl region (δ 5–7) was identical with that of an authentic sample of *cis*-2-cyclodecen-1-one (**16**).[19] The absence of *trans*-2-cyclodecen-1-one was similarly demonstrated by the absence of its characteristic nmr vinyl proton splitting pattern.[19] Integration of the spectrum indicated that the mixture was composed of approximately 18% of **16**. Treatment of the product mixture with 2,4-dinitrophenylhydrazine reagent afforded an orange 2,4-dinitrophenylhydrazone, mp 164.5–165.5° (1:3 ethyl acetate–95% ethanol), the infrared spectrum of which was found to be identical with that of an authentic sample of *cis*-bicyclo[5.3.0]decan-2-one 2,4-dinitrophenylhydrazone, lit.[17c,38] mp 160–163°. Similarly, a crystalline oxime of **14** was isolated, mp 117–118.5° (lit.[39] mp 119°). Glpc analysis of the product mixture *vs.* authentic samples on a 0.02 in. × 50 ft SCOT Carbowax 20M capillary column (130°, 4 cc/min) confirmed the presence of *cis*-bicyclo[5.3.0]decan-2-one (**14**, 67%) and *cis*-2-cyclodecen-1-one (**16**, 21%). A third component was readily identified as *cis*-bicyclo[4.4.0]decan-2-one (*cis*-α-decalone) (**15**, 12%). Finally, a very minor component was identified as cyclononanone (**13**, <1%). The following bicyclic ketones were shown to be absent by glpc analysis: *cis*-bicyclo[7.1.0]decan-2-one (**22**),[23] *trans*-bicyclo[5.3.0]decan-8-one,[40] *trans*-bicyclo[5.3.0]decan-2-one,[17c] and *trans*-bicyclo[4.4.0]decan-2-one (*trans*-α-decalone).[18b]

Tetralin Hydroperoxide–Cyclohexyl Metaborate (THPO–CHMB) Oxidation of Cyclodecyne. The oxidation was performed by adapting the method of Wolf and Barnes[26] for the epoxidation of olefins with THPO–CHMB. A mixture of 0.25 g (1.83 mmol) of cyclodecyne, 0.205 g (1.25 mmol) of THPO, and 0.158 g (1.25 mmol) of CHMB in 20 ml of cyclohexane was refluxed under nitrogen for 24 hr (*ca.* 80% reacted). The reaction mixture was washed with 50 ml of 5% sodium sulfite solution, 50 ml of water, and dried over anhydrous magnesium sulfate. Removal of solvent afforded an oil which was analyzed by glpc and shown to contain **14** (47%), **15** (23%), and **16** (31%).

Peroxybenzimidic Acid Oxidation of Cyclodecyne. A mixture of 0.25 g (1.83 mmol) of cyclodecyne, 0.174 g (1.53 mmol) of 30% hydrogen peroxide solution, 0.159 g (1.53 mmol) of freshly distilled benzonitrile, 0.031 g (0.31 mmol) of anhydrous potassium bicarbonate, and 5 ml of methanol[27] was stirred at room temperature under nitrogen for 4 days (<50% reacted). Water (10 ml) was added, the aqueous solution was extracted with three 10-ml portions of chloroform, and the combined organic layers were dried over anhydrous magnesium sulfate. Concentration gave 1 ml of solution, dilution of which with 5 ml of hexane resulted in the precipitation of 0.055 g (30%) of benzamide, mp 128–128.5°. Glpc analysis of the mother liquor revealed the presence of **14** (69%, includes 18% of trans isomer which probably arises from the epimerization of **14**), **15** (23%, includes 8% of the trans isomer), and **16** (8%).

Thermal Decomposition of 2-Diazocycloalkanones. A typical procedure for 2-diazocyclodecanone (**28**) is described. A solution of 0.5 g of **28** in 0.5 ml of dry benzene was refluxed under nitrogen for 1 hr, after which nitrogen evolution had ceased. The infrared spectrum exhibited ketene absorption at about 2100 $\mathrm{cm^{-1}}$ in addition to absorption in the carbonyl (1700–1800 $\mathrm{cm^{-1}}$) and olefinic regions (1630 $\mathrm{cm^{-1}}$). Glpc analysis of the product mixture required the use of two columns. Octamethyleneketene (**29**) was analyzed on a $^1/_8$ in. × 5 ft stainless steel column packed with 5% Silicone Gum Rubber (SE-30) on Chromosorb W, 60–80 mesh (140°, 25 cc/min). The other carbonyl components were analyzed on a 0.02 in. × 50 ft SCOT Carbowax 20M capillary column (140°, 4 cc/min). The product distribution is given in Table III.[41]

Octamethyleneketene (29). Preparative glpc was used to isolate this air-sensitive compound. A 20-mg sample of 2-diazocyclodecanone dissolved in a minimum amount of methylene chloride was decomposed in the injection port (220°) of the gas chromatograph. Collection of the major component on a 0.25 in. × 10 ft aluminum column packed with 15% Silicone Gum Rubber (SE-30) on silanized (DMCS), acid-washed Chromosorb W, 80–100 mesh (220°, 50 cc/min) afforded a yellow pungent liquid which exhibited intense absorption in the infrared [2095 $\mathrm{cm^{-1}}$ ($\mathrm{CCl_4}$); lit.[16] 2105 $\mathrm{cm^{-1}}$ (mesitylene)]. The polymethyleneketenes undergo rapid air oxidation to the corresponding cycloalkanones.[25]

MCPBA Oxidation of 29. A solution of 96 mg (0.53 mmol) of 2-diazocyclodecanone (**28**) in 2 ml of benzene was heated to reflux under nitrogen for 1 hr, after which infrared examination showed the presence of octamethyleneketene and the absence of the α-diazo ketone. A solution of 0.239 g (1.18 mmol) of 85% MCPBA in 2 ml of benzene was added in one portion, and an immediate evolution of gas and discharge of the yellow color of the ketene occurred. Infrared analysis after 5 min showed the complete absence of the absorption band at 2100 $\mathrm{cm^{-1}}$ and an increase in the absorption band at 1700 $\mathrm{cm^{-1}}$. Glpc analysis confirmed that the oxidation product was cyclononanone.

Decomposition of 2-Diazocyclodecanone (28) in Acetic Acid. Compound **28** (0.200 g) was dissolved in 5 ml of glacial acetic acid and stirred at room temperature for 5 min. The evolution of nitrogen was rapid and the solution became colorless. The mixture was poured into 25 ml of water, the aqueous solution was extracted with two 30-ml portions of ether, and the combined ether layers were washed with two 30-ml portions of water, three 50-ml portions of 5% sodium bicarbonate solution, and 50 ml of saturated salt solution. The organic phase was dried and concentrated to give 0.16 g of a yellowish oil. Glpc analysis showed that the major product was *cis*-2-cyclodecen-1-one (**16**, 60%). The nmr spectrum gave evidence for the presence of three acetates (three methyl signals at δ 2.08, 2.00, and 1.97) two of which have been tentatively identified as 2-acetoxycyclodecanone[19b] and 6-acetoxycyclodecanone[17b,19b] by nmr and glpc comparison with authentic samples. The third acetate may be 5-acetoxycyclodecanone.

Decomposition of 28 by Perchloric Acid. To a stirred solution of 0.166 g of **28** in 3 ml of dry ether was added 1 drop of 70% perchloric acid. Decomposition was instantaneous with vigorous nitrogen evolution. The colorless solution was diluted with 30 ml of ether and washed with 50 ml of water, two 50-ml portions of 5% sodium bicarbonate solution, and 50 ml of saturated salt solution. The ethereal phase was dried and concentrated to a yellow oil, analysis of which by glpc indicated the presence of *cis*-2-cyclodecen-1-one (**16**) as the major product (~80%), in addition to other unidentified minor products.

Decomposition of 28 by Boron Trifluoride Ethyl Ether. To a solution of 0.136 g (7.5 mmol) of **28** in 2 ml of dry ether was added in one portion 0.103 g (7.5 mmol) of freshly purified boron trifluoride ethyl ether. Vigorous nitrogen evolution occurred, and after stirring for 5 min, the solution became colorless. The mixture was diluted with 30 ml of ether and washed with three 50-ml portions of saturated salt solution. The organic phase was dried and

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(36) A. T. Blomquist and F. W. Schlaefer, *J. Amer. Chem. Soc.*, **83**, 4547 (1961).

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(38) We are indebted to Professor H. L. Goering for sending us an authentic sample of the 2,4-DNP and infrared spectrum of **14**.[17c]

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(41) Apparently, Regitz and Rüter[16] overlooked **10** and **14** as minor products from the decomposition of **26** and **28**, respectively.

concentrated to a yellow oil which was shown to be almost exclusively (97%) *cis*-2-cyclodecen-1-one (**16**) by glpc and nmr.

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Structure and Thermal Isomerization Reactions of Protonated Cyclohepta-3,5-dienones in Superacids. A Convenient Preparation of Cyclohepta-2,4-dienone[1,2]

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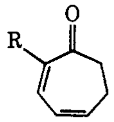
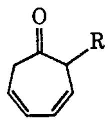
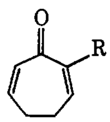
Abstract: An attractive synthetic route has been developed for the conversion of cyclohepta-3,5-dienone (**2a**) to cyclohepta-2,4-dienone (**1a**). The procedure is based upon the quantitative rearrangement of protonated **2a** to protonated **1a** in FSO_3H. Dependence of the rate of isomerization upon the acidity of the superacid medium suggests that the reaction proceeds through a dication intermediate. In more weakly acidic media, *e.g.*, 96% H_2SO_4, deuterium incorporation studies implicate a deprotonation–reprotonation mechanism. This change in mechanism is accompanied by the formation of some protonated cyclohepta-2,6-dienone (**3a**). The structures of these hydroxy cations, the mechanisms of the isomerizations, and extension of these reactions to 2-substituted systems are discussed.

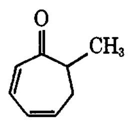
In the course of our studies on the photochemistry of monocyclic dienones in acidic media[3] we had need of cyclohepta-2,4-dienone (**1a**) and its 2-methyl derivative **1b**. Although the preparation of **1a** has been described by van Tammelen and Hildahl,[4] their synthesis, albeit effective, is lengthy and not suited to the convenient preparation of large quantities. Moreover, the synthesis of 2-alkyl substituted derivatives by this route did not appear particularly attractive.

As cyclohepta-3,5-dienone (**2a**) and its 2-substituted derivatives can be readily obtained from tropone, it would seem with a suitable means of isomerization that these could serve as suitable precursors for **1**.[5] Furthermore, an alternative isomerization of **2a** would be to give the cross-conjugated dienone **3a** and cyclohepta-2,5-dienone. While **3a** can be obtained by the procedures of Garbisch,[6] or Birch,[7] this potential rearrangement could again provide access to the 2-substituted 2,6-dienones.


1a, R = H
b, R = Me


2a, R = H
b, R = Me


3a, R = H
b, R = Me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Thermal interconversion of **1a** with **2a**[8] and **1b** with **2b**[9] has been reported to take place in solution at temperatures greater than 60°. As the isomerization of **2a** proceeds by way of a 1,5-hydride shift, no cross-conjugated dienone, **3a**, was detected as a product. At 80° an equilibrium was reached which consisted of 35% **1a** and 65% **2a**. The thermal isomerization of **2b** produced not only **1b** in the equilibrium mixture but also **4**.[10]

Although the material balance in these isomerizations was good, the separation of the mixtures was found to be difficult. The most effective method, preparative glpc, was severely limited, not only in terms of the quantities obtainable, but by the extreme ease of the thermal interconversion of these compounds.

If the cyclohepta-3,5-dienones (**2**) are to be viable synthetic precursors of their 2,4 isomers, then the isomerization has to be made either essentially quantitative, or to give at least no other volatile products. Clearly, irrespective of the manner in which isomerization of **2** to **1** is accomplished, if thermodynamic equilibrium between the two ketones is reached, the separation problem will remain.

A possible solution to these problems, is to so structurally modify **1** and **2** that the equilibrium position

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(1) This work was supported by the National Research Council of Canada and the Research Board of the Science and Engineering Division, McMaster University.

(2) Part VI of a series entitled "The Chemistry of Cycloheptadienones."[3] Preliminary accounts of part of this work have been presented earlier.[3a]

(3) For earlier parts of this series, see (a) K. E. Hine and R. F. Childs, Abstracts, 55th Chemical Conference of the Chemical Institute of Canada, Quebec, June 1972, No. 63; K. E. Hine and R. F. Childs, *J. Chem. Soc., Chem. Commun.*, 144 (1972); (b) K. E. Hine and R. F. Childs, *ibid.*, 145 (1972); K. E. Hine and R. F. Childs, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. 120; K. E. Hine and R. F. Childs, *J. Amer. Chem. Soc.*, **93**, 2323 (1971).

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(10) A systematic study of the thermal isomerizations of **2b** has not been reported. Preliminary results in our laboratory show that **2b** is converted to an equilibrium mixture of **1b**, **4**, and **2b** in solution at 80° or in the gas phase between 170 and 360°. In each case **1b** is the predominant isomer.