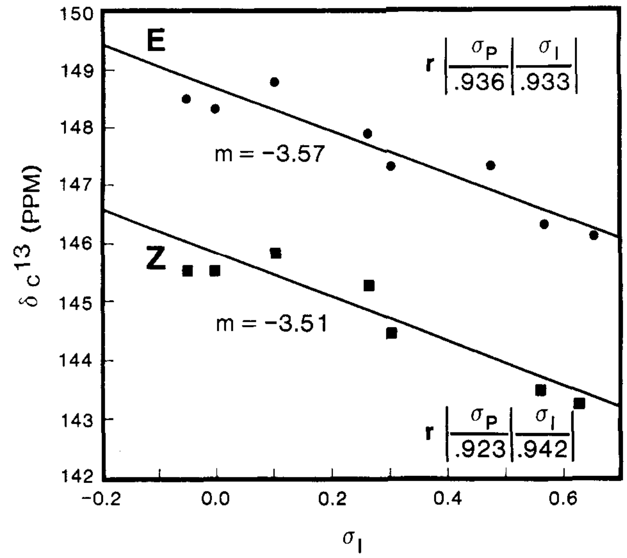

Figure 5. Plot of the iminyl carbon chemical shifts of *E* and *Z* isomers of oxime methyl ethers vs. the Hammett substituent constant, σ_I.

resonance is of reduced importance.

Oxime Methyl Ethers. One may note the same general trend as above with both *E* and *Z* isomers with respect to the chemical shifts. The *Z* isomers are consistently upfield from the *E* isomers. This is analogous to olefinic systems in which the ^{13}C chemical shifts of the cis isomers are consistently upfield from the trans isomers.[24] In the Hammett plot (Figure 5) one should note the intermediate magnitude of the slope revealing an intermediate sensitivity of the oxime methyl ethers as compared to the hydrazones and oximes. The σ_p and σ_I values correlated equally well. This suggests that resonance is of some importance when compared to the hydrazones and phenylhydrazones but of greater importance when compared to the oximes. This is consistent with the relative resonance-derived electron-donating abilities of the substituents on the iminyl nitrogen. The non-iminyl nitrogen of the hydrazones and phenylhydrazones are more able to donate electrons by resonance than the hydroxyl group of the oximes or the methoxy group of the oxime methyl ethers. Also, the methoxy group would be expected to be better able to donate electrons than the hydroxyl group (several hyperconjugated structures can be drawn for the methoxy moiety).

In summary, on one end of the scale the hydrazones have the greatest negative slope indicative of the greater sensitivity of this class to the substituent effect, and the ^{13}C chemical shifts correlate best using the σ_p values showing that resonance is of importance in this system. On the other end of the scale, the oximes have the smallest negative slope indicative of the low sensitivity of this class to the substituent effect, and the σ_I value correlates best demonstrating that the inductive effect predominates in this class of compounds. The phenylhydrazone and oxime methyl ether iminyl carbon displayed behavior intermediate between these two extremes.

Registry No. PhCH=NNH$_2$, 5281-18-5; 4-CH$_3$C$_6$H$_4$CH=NNH$_2$, 52693-87-5; 4-MeO$_2$CC$_6$H$_4$CH=NNH$_2$, 50466-15-4; 4-NCC$_6$H$_4$CH=NNH$_2$, 87829-00-3; 4-CH$_3$OC$_6$H$_4$CH=NNH$_2$, 5953-85-5; 4-O$_2$NC$_6$H$_4$CH=NNH$_2$, 6310-10-7; PhCH=NNHPh, 588-64-7; 4-CH$_3$C$_6$H$_4$CH=NNHPh, 2829-25-6; 4-MeO$_2$CC$_6$H$_4$CH=NNHPh, 87829-01-4; 4-Me$_2$NC$_6$H$_4$CH=NNHPh, 2829-28-9; 4-MeOC$_6$H$_4$CH=NNHPh, 622-73-1; 4-ClC$_6$H$_4$CH=NNHPh, 2829-26-7; 4-O$_2$NC$_6$H$_4$CH=NNHPh, 2829-27-8; (*Z*)-PhCH=NOH, 622-32-2; (*Z*)-4-MeO$_2$CC$_6$H$_4$CH=NOH, 87829-02-5; (*Z*)-4-MeOC$_6$H$_4$CH=NOH, 3717-22-4; (*Z*)-4-ClC$_6$H$_4$CH=NOH, 3717-23-5; (*E*)-PhCH=NOH, 622-31-1; (*E*)-4-CH$_3$C$_6$H$_4$CH=NOH, 3717-15-5; (*E*)-4-MeOC$_6$H$_4$CH=NOH, 3717-21-3; (*E*)-4-ClC$_6$H$_4$CH=NOH, 3717-24-6; (*E*)-PhCH=NOMe, 10229-53-5; (*E*)-4-CH$_3$C$_6$H$_4$CH=NOMe, 70286-36-1; (*E*)-4-MeO$_2$CC$_6$H$_4$CH=NOMe, 87829-03-6; (*E*)-4-NCC$_6$H$_4$CH=NOMe, 87861-01-6; (*E*)-4-Me$_2$NC$_6$H$_4$CH=NOMe, 87829-04-7; (*E*)-4-MeOC$_6$H$_4$CH=NOMe, 70286-37-2; (*E*)-4-ClC$_6$H$_4$CH=NOMe, 54615-09-7; (*E*)-4-O$_2$NC$_6$H$_4$CH=NOMe, 54615-10-0; (*Z*)-PhCH=NOMe, 10229-54-6; (*Z*)-4-CH$_3$C$_6$H$_4$CH=NOMe, 87861-02-7; (*Z*)-4-MeO$_2$CC$_6$H$_4$CH=NOMe, 87829-05-8; (*Z*)-4-NCC$_6$H$_4$CH=NOMe, 87861-03-8; (*Z*)-4-Me$_2$NC$_6$H$_4$CH=NOMe, 87829-06-9; (*Z*)-4-MeOC$_6$H$_4$CH=NOMe, 87861-04-9; (*Z*)-4-ClC$_6$H$_4$CH=NOMe, 87861-05-0.

Thermochemistry of Phenyl-Substituted Benzobicyclo[3.1.0]hex-2-enes. Evidence for Carbenes as Intermediates

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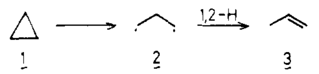
Received March 15, 1983

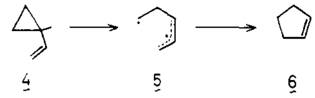
The thermal rearrangements of benzobicyclo[3.1.0]hex-2-ene (**21**) and its phenyl-substituted analogues **22**–**25** (Scheme V) as models of sterically constrained phenylcyclopropanes have been studied by means of flash vacuum pyrolysis. In most cases the major pathway was cleavage of the "internal" C(1)–C(5) cyclopropane bond followed by a 1,2-hydrogen or a 1,2-phenyl shift in the resulting biradical. For 6-phenylbenzobicyclo[3.1.0]hex-2-ene (**25**), substantial cleavage of the "external" C(1)–C(6) cyclopropane bond was observed, the phenyl substitution pattern being favorable for stabilization of the resulting biradical **62**. Phenyl-substituted 1,2-dihydronaphthalenes **44**, **47**, **51**, and **55** are among the major products. Comparison of the plots of the pyrolysis product composition of the 1,2-dihydronaphthalenes vs. pyrolysis temperature with similar plots of the title compounds (**22**–**25**) suggested that some of the minor products, viz., the 1,2-divinylbenzenes **31**, **42**, and **49**, are formed via carbenes **30**, **41**, **50**, **57**, and **61** rather than via biradicals. Especially at higher pyrolysis temperatures, a large amount of an oxidation product, viz., 1- or 2-phenylnaphthalene (**48** or **54**), is formed.

Thermal rearrangements of cyclopropanes have aroused considerable interest because of the intriguing theoretical problems involved.[1] At high temperatures cyclopropane (**1**) undergoes isomerization to propene (**3**), and the singlet

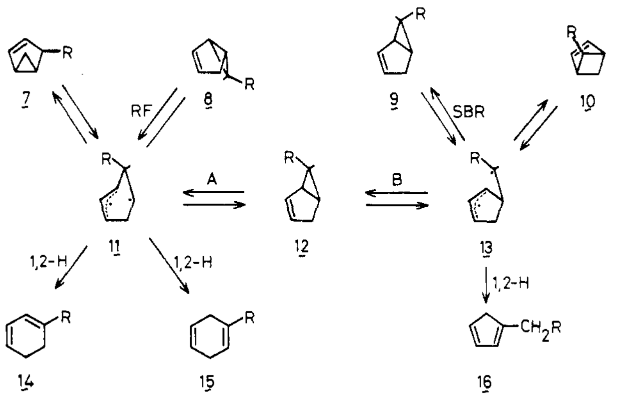
Scheme I



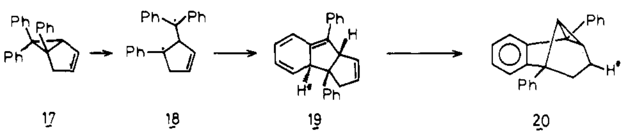
Scheme II



Scheme III



Scheme IV



trimethylene biradical (2) has been postulated as an intermediate in this reaction[2] (Scheme I). Substituents have a large influence on the activation energy for ring opening, and, sometimes, they lead to new reaction paths, e.g., in the conversion of vinylcyclopropanes 4 into cyclopentenes 6 (Scheme II).[3] Bicyclo[3.1.0]hex-2-enes 12 constitute a special class of vinylcyclopropanes because two modes of cyclopropane ring opening are possible:[4-7] cleavage of the "internal" C(1)–C(5) bond (A) leading to biradical 11 or cleavage of the "external" C(1)–C(6) bond (B) leading to biradical 13 (Scheme III). Both biradicals may lead to a variety of end products via 1,2-H shifts and via ring-flipping (RF) or single-bond rotation (SBR) followed by reclosure. However, at higher temperatures bicyclo[3.1.0]hex-2-enes 12 generally rearrange to 1,3- and 1,4-cyclohexadienes 14 and 15, products that can only arise from process A via 1,2-hydrogen shifts.[8] Even for bicyclo[3.1.0]hex-2-enes that epimerized via process B, only rearrangement products resulting from process A were observed.[9]

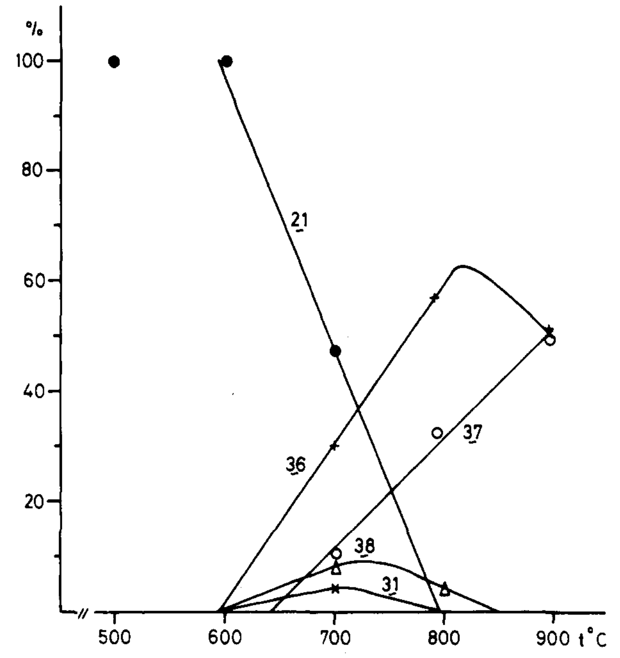
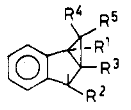


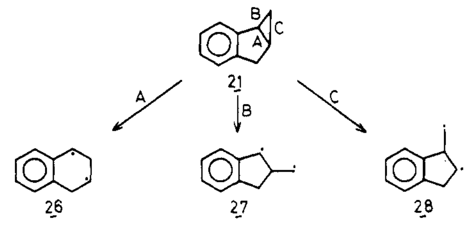
Figure 1. Product composition vs. pyrolysis temperature for FVP of benzobicyclo[3.1.0]hex-2-ene (**21**).

Scheme V



	R^1	R^2	R^3	R^4	R^5
21	H	H	H	H	H
22	Ph	H	H	H	H
exo-23	H	Ph	H	H	H
24	H	H	Ph	H	H
endo-25	H	H	H	Ph	H
exo-25	H	H	H	H	Ph

Scheme VI



Recently, a remarkable rearrangement of a phenyl-substituted bicyclo[3.1.0]hex-2-ene (17) has been reported.[10] After cleavage of the C(5)–C(6) cyclopropane bond, intermediate 19 is formed (Scheme IV). The position of the hydrogen atom carrying as asterisk is geometrically suited for a suprafacial 1,5-hydrogen migration, restoring aromaticity in concert with ring formation that leads to 20 as the only observed end product. This paper deals with the thermal rearrangements in benzobicyclo[3.1.0]hex-2-ene (21) and its phenyl substitution products 22–25 (Scheme V). Reaction pathways shown in Scheme III that would lead to permanent disruption of the aromatic moiety are unlikely in these compounds. Comparison of the results may lead to insight into the influence of phenyl substitution in various positions on the course of the reaction. Scheme VI shows the a priori possibilities for ring opening of benzobicyclo[3.1.0]hex-2-ene (21) expected on

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(1) For a recent review, see J. A. Berson, *Annu. Rev. Phys. Chem.*, **28**, 111 (1977).

(2) (a) W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **96**, 1168 (1974); (b) J. A. Berson, L. D. Petersen, and B. K. Carpenter, *ibid.*, **98**, 122 (1976); (c) M. R. Willcott, R. L. Cargill, and A. B. Sears in "Progress in Physical Organic Chemistry", Vol. 9, A. Streitwieser, Jr., and R. W. Taft, Eds., Wiley, New York, 1972, pp 25–98.

(3) E. M. Milvitskaya, A. V. Tarakanova, and A. F. Plate, *Russ. Chem. Rev.*, **45**, 469 (1976).

(4) J. J. Gajewski in "Mechanisms of Molecular Migrations", Vol. 4, B. S. Thyagarajan, Ed., Wiley, New York, 1971, pp 1–53.

(5) R. S. Cooke and U. H. Andrews, *J. Am. Chem. Soc.* **96**, 2974 (1974).

(6) J. S. Swenton and A. Wexler, *J. Am. Chem. Soc.*, **93**, 3066 (1971).

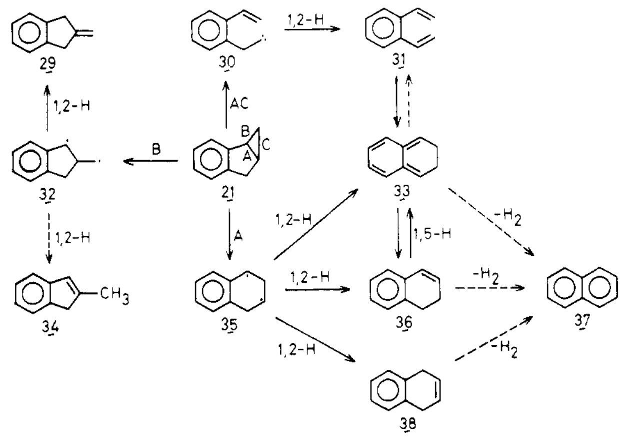
(7) J. E. Baldwin and K. E. Gilbert, *J. Am. Chem. Soc.*, **98**, 8283 (1976).

(8) R. J. Ellis and H. M. Frey, *J. Chem. Soc. A*, 553 (1966).

(9) (a) D. L. Garin, *Tetrahedron Lett.* 3035 (1977); (b) D. L. Garin and J. S. Chickos, *J. Org. Chem.*, **45**, 2721 (1980).

(10) S. Weigl and J. Warkentin, *Can. J. Chem.*, **58**, 210 (1980).

Scheme VII



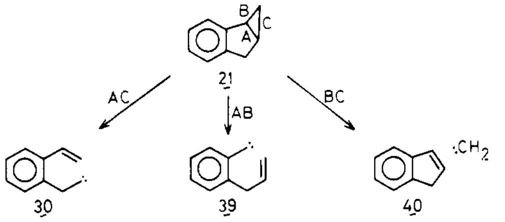
the basis of Scheme I. Internal ring opening (A) leads to biradical **26**, one radical site of which is at a benzylic and the other at a secondary carbon atom. There are two different possibilities of external ring opening (B, C). One of them (B) leads to biradical **27** with a benzylic and a primary alkyl radical site. The other (C) yields a biradical (**28**) without benzylic radical sites. Considering the stability of the various radical sites, it is expected that in the unsubstituted benzobicyclo[3.1.0]hex-2-ene internal ring opening A is the most favorable pathway. Route B is slightly less favorable, and C will probably be of minor importance. Phenyl substitution in various positions of **21** can modify, however, the order of preference.

Results and Discussion

Benzobicyclo[3.1.0]hex-2-ene (21). Figure 1 shows a plot of the product composition vs. the pyrolysis temperature for flash vacuum pyrolisis (FVP) of **21**. Rearrangement starts at about 595 °C, and the plot shows a rapid linear decrease of the starting compound **21** with increasing temperature and a linear increase of the amount of the main primary product 1,2-dihydronaphthalene (**36**).[11] Two minor primary products are 1,2-divinylbenzene (**31**)[12] and 1,4-dihydronaphthalene (**38**).[13] The percentages of **31** and **38** reach maxima around 725 °C and then decrease again. A maximum in the curve of **36** is found at 810 °C. The maxima in the curves corresponding to **36**, **38**, and **31** seem to be connected with the appearance of a secondary product from 640 °C on, viz., naphthalene[14] (**37**). 2-Methyleneindan[15] (**29**) was present in very small amounts as judged by the NMR spectra of product mixtures. Its occurrence was estimated at less than 2% at every temperature, and therefore it is not plotted in Figure 1.

In Scheme VII the products observed in FVP of **21** are explained in relation to the possibilities discussed in Scheme VI; 1,2- and 1,4-dihydronaphthalene (**36** and **38**) can be formed via ring-opening A, leading to **35**, followed by a 1,2-hydrogen shift. The amount of **36** is continuously higher than that of **38** because the conjugation between the aromatic and olefinic moieties in **36** is not present in **38**. Consequently, **36** is energetically favored over **38**. An indirect route from **35** to **36** is also possible; viz., via a 1,2-H shift in **35** leading to a biradical with two benzylic radical sites that corresponds to 2,3-dihydronaphthalene (**33**) followed by a sigmatropic 1,5-H shift.[16] Compound **31** might then arise via electrocyclic ring opening (ER) from **33**. External ring opening (B) should lead to biradical **32**. A 1,2-H shift in **32** can result in either 2-methyleneindan (**29**) or 2-methyl-1*H*-indene (**34**). Indeed, **29** is observed, though in very small amounts, but **34** could not be detected. The NMR signals of **34** might be obscured by those of other components. As expected, no products of route C are observed.

Scheme VIII



The presence of naphthalene (**37**) can readily be explained by dehydrogenation of **36**, **38**, and **33**. It is well-known that concerted dehydrogenation occurs easily in dihydrobenzenes.[8,17] When all products are explained through mechanisms A and B (Scheme VI), we must assume that in **33** electrocyclic ring opening leading to **31** and 1,5-H migration leading to **36** are competitive reactions because at lower temperatures **31** and **36** are observed simultaneously.

From evidence that will be presented below, it was concluded that the conversion of **35** into **36** via **33** is probably at least as important as the direct route. In both reactions **33** → **36** and **33** → **31** the driving force is restoration of the aromatic system, but for the 1,5-H shift a special conformation of **33** is required to bring the migration termini together.[18] There is no such requirement for the electrocyclic ring opening. Compound **36** must have a greater thermodynamic stability than **31** since the latter compound is converted into **36** at higher temperatures. This was demonstrated experimentally by subjecting *trans*-2-vinylstilbene (*trans*-**49**, Scheme X) to FVP at 900 °C. The results of this experiment will be discussed below.

From evidence that will also be given below, we believe that electrocyclic ring opening of **33** is actually not the pathway leading to **31**. We assume that an intramolecular carbene elimination in **21** leading to **30** and followed by or accompanied with a 1,2-H migration is the main route leading to **31**. 1,2-Hydrogen migrations are very commonly observed as deactivation routes for carbenes.[19] At these high temperatures a vibrational mode can be envisaged consisting of simultaneous lengthening of the A and C bonds and resulting in carbene-like state prone to undergo a 1,2-H shift. The driving force for this reaction would be relief of ring strain in the bicyclo[3.1.0]hex-2-ene system.

The question remains why only this carbene elimination (AC) takes place and not the alternatives AB and BC, which are theoretically possible (Scheme VIII). Com-

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[11] (a) References 11–15 contain NMR data of the compounds **36**, **31**, **38**, **37**, and **29** mentioned in Scheme VII; (b) E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, **36**, 971 (1971).

[12] M. Pomerantz and G. W. Gruber, *J. Am. Chem. Soc.*, **93**, 6615 (1971).

[13] M. I. Terekhova, L. N. Kurkuvskaya, E. S. Petrov, N. N. Shapetko, and A. I. Shatenstein, *J. Org. Chem. USSR*, **6**, 2370 (1970).

[14] R. W. Crecely and J. H. Goldstein, *Org. Magn. Reson.* **2**, 613 (1970).

[15] F. Scully, T. Nylund, F. Palensky, and H. Morrison, *J. Am. Chem. Soc.*, **100**, 7352 (1978).

[16] J. J. M. Lamberts and W. H. Laarhoven, *J. Org. Chem.*, **48**, 2202 (1983).

[17] I. Fleming and E. Wildsmith, *J. Chem. Soc., Chem. Commun.*, 223 (1970).

[18] J. R. de Dobbelaere, E. L. van Zeeventer, J. W. de Haan, and H. M. Buck, *Theor. Chim. Acta*, **38**, 241 (1975).

[19] C. Wentrup, "Reaktive Zwischenstufen", Thieme Verlag, Stuttgart, 1979, and references therein.

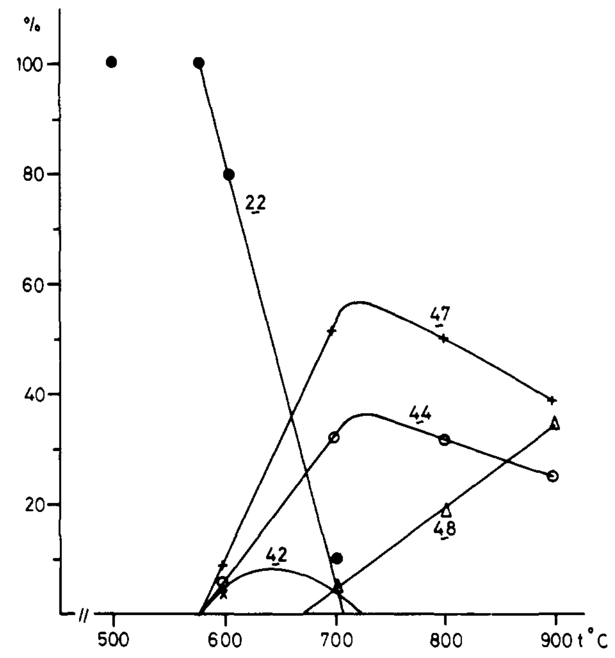
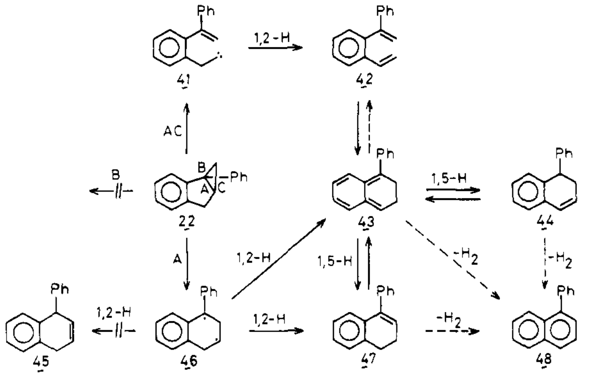


Figure 2. Product composition vs. pyrolysis temperature for FVP of 1-phenylbenzobicyclo[3.1.0]hex-2-ene (**22**).

Scheme IX



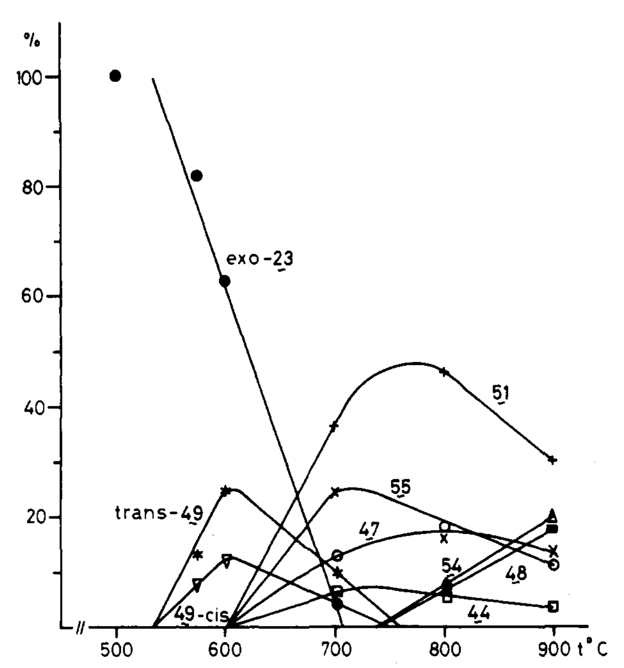
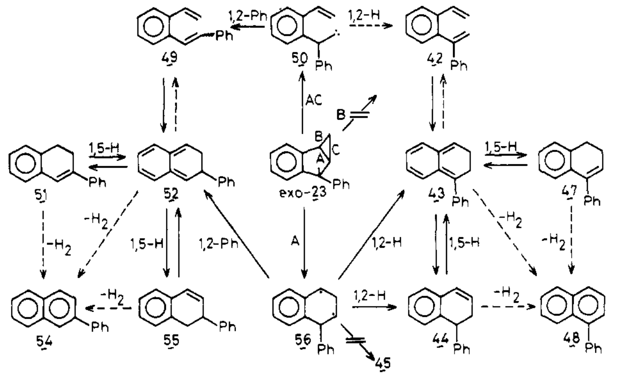


Figure 3. Product composition vs. pyrolysis temperature for FVP of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**23**).

Scheme X



parison of structures **30**, **39**, and **40** shows that **30** is the only carbene to which the deactivation route of a 1,2-H shift is open because there are hydrogen atoms available on the neighboring carbon. Carbenes **39** and **40** might also be formed, but the only deactivation route available to them is readdition to the double bond. Furthermore, we have reason to believe that no fully developed carbene is involved in the formation of **31** but rather a carbene-like state. The argument is given in the next section.

1-Phenylbenzobicyclo[3.1.0]hex-2-ene (22). In the FVP of 1-phenylbenzobicyclo[3.1.0]hex-2-ene (**22**) (Figure 2, Scheme IX), three primary products are observed, starting from 575 °C; viz., 4-phenyl-1,2-dihydronaphthalene (**47**), 1-phenyl-1,2-dihydronaphthalene (**44**), and, in smaller amounts, 1′-phenyl-1,2-divinylbenzene (**42**).[20] 1-Phenyl-1,4-dihydronaphthalene (**45**)[21] and products corresponding to route B were not found. 1-Phenylnaphthalene (**48**) appeared at temperatures above 675 °C. The presence of **44** can only be explained by the intermediacy of 1-phenyl-2,3-dihydronaphthalene (**43**). One of the main arguments for the carbene route to **42** (AC) comes from comparison of the FVP plot of **22** with those of **47** and **44**. In the FVP of **22**, compound **42** is found up to 725 °C, whereas in the FVP plot of **44** and **47**, **42** is never observed, although interconversion of **44** and **47** begins at 640 and 680 °C, respectively. This reaction requires intermediacy of **43**. If **42** is a product of electrocyclic ring opening in **43**, then it should be observed in the FVP plot of **44** and **47**. This result supports the occurrence of the carbene elimination route leading to the 1,2-divinylbenzene.

***exo*-4-Phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-23).** Upon FVP of *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**23**), a lot of products were observed (Figure 3 and Scheme X). The formation of **44** and **47** can be explained in analogy to their formation from **22** (see right half of Scheme X). The simultaneous formation of **55** and **51**, even in higher amounts, suggests, however, that the biradical **56** undergoes a 1,2-phenyl shift leading to 2-phenyl-2,3-dihydronaphthalene (**52**) as well as 1,2-H shifts leading to **43** and **44**. At lower temperatures (540–600 °C), *cis*- and *trans*-2-vinylstilbene[22] (*cis*- and *trans*-**49**) are found as the only products in rather large amounts. The observation that **55** and **51** are found in higher concentrations than **44** and **47** may be caused by their formation directly from **52** as well as from primary formed *cis*- and *trans*-**49** via ring closure above 600 °C. Comparison of the plots for FVP of *exo*-**23** with FVP of **55** shows that **55** does

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[20] See the Experimental Section.

[21] W. Carruthers and G. E. Hall, *J. Chem. Soc. B*, 861 (1966).

[22] M. Sindler-Kulyk and W. H. Laarhoven, *J. Am. Chem. Soc.*, **100**, 3819 (1978).

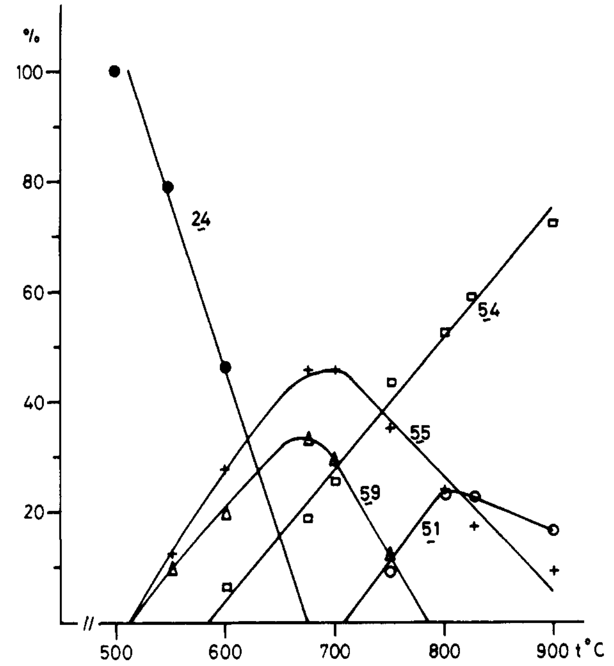


Figure 4. Product composition vs. pyrolysis temperature for FVP of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (24).

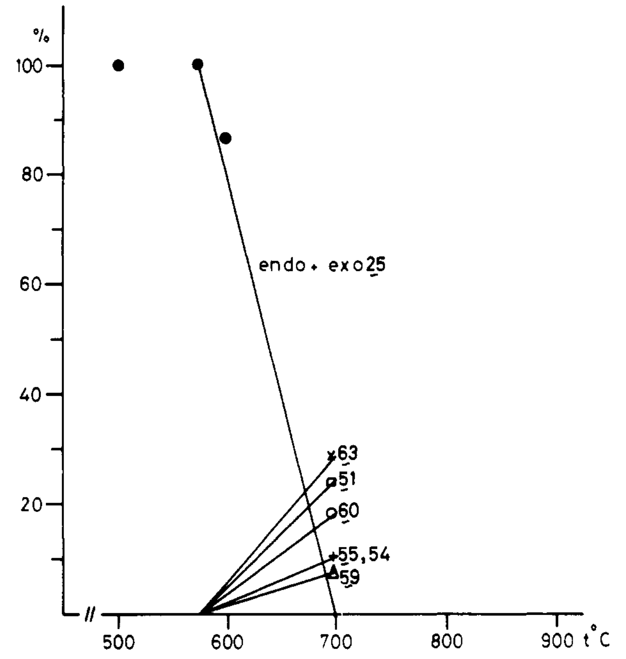
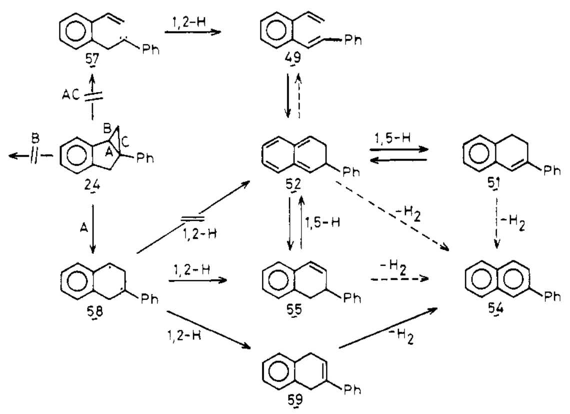
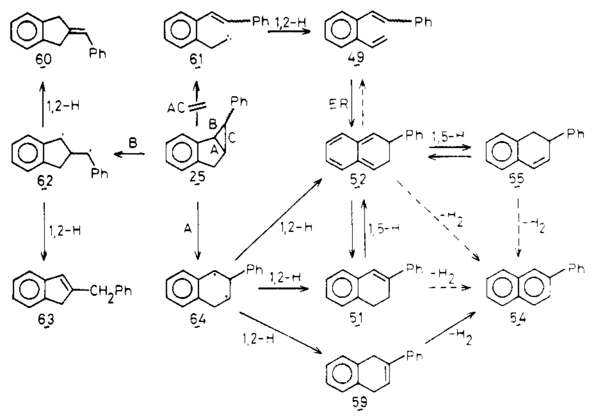


Figure 5. Product composition vs. pyrolysis temperature for FVP of 6-phenylbenzobicyclo[3.1.0]hex-2-ene (25).

Scheme XI



Scheme XII

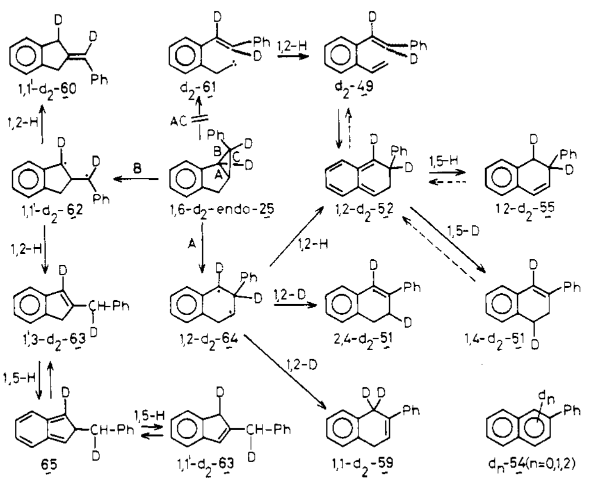


not lead to *cis*- and *trans*-**49** at temperatures where they are observed in FVP of *exo*-**23**. These findings are again in favor of the carbene mechanism, but they cut off the intermediacy of a fully developed carbene because a migratory aptitude of H > Ph > alkyl was established for carbenes in cases where no special conformational restrictions are imposed.[19] This means that in *exo*-**23** the phenyl group is in an especially favorable position with respect to the developing empty p orbital of the carbene. Most authors consider the position of the migrating group gauche to the methine hydrogen of the carbene the optimum conformation.[19] It is not difficult to imagine that at some instant during the vibrational motion at which C(5) has gained considerable carbene character, the phenyl substituent at C(4) will be gauche with respect to H(5) and consequently in a favorable position for a 1,2-phenyl migration. No trace of **42**, which would be the product of a 1,2-H shift from **50**, was observed, and, therefore, the 1,2-phenyl shift is apparently the main deactivation route of the carbene. *trans*-2-Vinylstilbene (*trans*-**49**) was pyrolyzed at 900 °C to investigate the cause of its disappearance at higher temperatures. The products observed were **51** (50%), **55** (19%), and **54** (31%), proving that **49** undergoes ring closure to 2-phenyl-2,3-dihydronaphthalene (**52**). Again in the FVP of *exo*-**23** neither products of route B (Scheme VI) nor **45** were observed.

5-Phenylbenzobicyclo[3.1.0]hex-2-ene (24). FVP of 5-phenylbenzobicyclo[3.1.0]hex-2-ene (**24**) shows a different behavior compared to the other phenyl-substituted benzobicyclo[3.1.0]hex-2-enes (Figure 4 and Scheme XI). The primary products are 2-phenyl-1,2-and 2-phenyl-1,4-dihydronaphthalene (**55** and **59**). They can originate from 1,2-H shifts in **58**, the biradical from internal ring opening (A). Biradical **58** is well stabilized because it has two benzylic radical sites. Its stability is reflected in the low temperature (510 °C) at which rearrangement starts, and in the absence of **51** among the products between 500 and 700 °C. The formation of **51** starts only when **24** has already completely disappeared and is apparently caused by rearrangement of **55** through two subsequent 1,5-H shifts (via **52**). 2-Vinylstilbenes (*cis*- or *trans*-**49**) are not observed. Apparently the presence of the 5-phenyl substituent lowers the transition state along the A route, and the competition of the carbene route (AC) as observed in FVP of **21**, **22**, and *exo*-**23** does not occur. Dehydrogenation begins at 590 °C, reflecting the readiness of 1,4-dihydronaphthalenes **59** to undergo elimination of hydrogen.[17] Again, no products corresponding to external ring opening (route B) are observed.

6-Phenylbenzobicyclo[3.1.0]hex-2-ene (25). Figure 5 and Scheme XII show the results of FVP of a mixture

Scheme XIII



of 37% *endo*- and 63% *exo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (*endo*- and *exo*-**25**). Products of external ring opening (route B) constitute a large part of the product mixture. The external ring opening leads to biradical **62**, and 1,2-H shifts in **62** produce 2-benzylideneindan[16] (**60**) and 2-benzyl-1*H*-indene (**63**).[23] Both radical sites in **62** are benzylic, and, therefore, it will be favored over the biradical **64** produced from internal ring opening (route A) in which only one of the radical sites is benzylic. Nevertheless, the products of path A (**55**, **51**, and **59**) still make up a substantial portion of the total amount of product: it seems that interal ring opening in these bicyclic compounds is intrinsically more favorable than external ring opening, a phenomenon that was already observed in FVP of the parent compound **21**. The plots in Figure 5 end at 700 °C. Above this temperature at least seven products were detected by GLC. Independent FVP of 2-benzyl-1*H*-indene (**63**) at temperatures of 700 °C and higher led to the same product mixture as FVP of **25** except for **55**, **51**, and **54**. Consequently, it is very likely that most components observed above 700 °C in FVP of **25** are actually secondary products due to rearrangement of **63**. These products were not identified. In a sample pyrolyzed at 500 °C, a temperature where no skeletal rearrangements of **25** take place, epimerization was observed and the composition of the mixture changed to 17% *endo*-**25** and 83% *exo*-**25**. After we had succeeded in separating a mixture of *endo*- and *exo*-**25**,[24] these compounds were pyrolyzed separately at 700 °C. The product mixtures from FVP of the epimers proved to be identical. This is in accordance with literature data showing that epimerization is several times faster than structural isomerization.[1] In the irradiation experiments described in an earlier paper,[24] a sample of 1,6-dideuterio-*endo*-6-phenylbenzobicyclo[3.1.0]hex-2-ene (1,6-d_2-*endo*-**25**) was isolated and this enabled us to check the mechanism of the rearrangement of **25**. Compound 1,6-d_2-*endo*-**25** was pyrolyzed at 700 °C, and a ^{1}H NMR spectrum was taken. The signals observed in this spectrum corresponded with the deuterium distribution expected on the basis of Scheme XII (Scheme XIII) with only one exception: at the position of the olefinic proton of **63** a large intensity was found. It can be accounted for by the well-known sigmatropic 1,5-H shifts always found in indenes[25] at high temperatures, and leading here from 1',3-d_2-**63** to 1,1'-d_2-**63** via the isoindene **65**. Other noteable features of the NMR spectrum of the product mixture were the complete absence of signals corresponding to H(1) in **54** (1-*d*-**54**) and H(4) in **51** (2,4-d_2-**51** and 1,4-d_2-**51**). Furthermore, protons H(4) and H(3) of **55** were visible as an AB pattern with $J_{3,4}$ = 9.7 Hz, demonstrating that there must be deuterium at C(2) because $J_{2,3}$ has disappeared. Since C(3) and C(4) are occupied by hydrogen, the other deuterium must be at C(1) (1,2-d_2-**55**). The temperature of 700 °C is too low for substantial interconversions of d_2-**55** and d_2-**51** species by 1,5-H migrations. The quintet of the olefinic proton of **59** has become a triplet, which is in accordance with the structure 1,1-d_2-**59**. The olefinic proton of **60** has completely disappeared, and the single broad line corresponding to the methylenic protons shows an integration equivalent to three protons, in accordance with 1,1'-d_2-**60**.

The systematic investigation of the thermochemistry of the phenyl-substituted benzobicyclo[3.1.0]hex-2-enes can be summarized in three main points: (1) The mode of ring opening is largely dependent on the substitution pattern. (2) Favored reaction pathways are predictable by consideration of the stability of intermediate structures and the major deactivation routes available to them. (3) Comparison with the results of thermal rearrangements in phenyl-substituted dihydronaphthalenes shows that carbene-like intermediates play a role in the pathways leading to 1,2-divinylbenzenes. Carbene formation from the phenyl-substituted benzobicyclo[3.1.0]hex-2-ene and 1,2-H or 1,2-Ph shifts must take place in concert.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WH 90 spectrometer in CDCl$_3$. δ values are reported in ppm relative to Me$_4$Si as internal standard and J values are expressed in hertz. For column chromatography, silica gel, (Merck, Kieselgel 60) was used. Gas chromatography (GLC) was performed on either a Varian Aerograph Sseries 1200 or a Hewlett-Packard 5710 A instrument fitted with a 10% w/w SE-30 column on Chromosorb WHP with dimensions 6 × 118 in. o.d. and a flame ionization detector.

The syntheses of the starting compounds **21**–**25** have been described in an earlier paper,[16] which also contains the syntheses and physical data of 1-phenyl-1,4-dihydronaphthalene (**45**), 2-phenyl-1,4-dihydronaphthalene (**59**), 2-benzyl-1*H*-indene (**63**), and 2-benzylideneindan (**60**). The products 1,2-dihydronaphthalene (**36**), 1,2-divinylbenzene (**31**), 1,4-dihydronaphthalene (**38**), naphthalene (**37**), and 2-vinylstilbene (**49**) were identified by comparison of spectroscopic data with those from literature. 2-Phenylnaphthalene (**54**) was identified by comparison with an authentic sample purchased from Fluka AG and 1-phenylnaphthalene (**48**) by comparison with a sample synthesized by oxidation of 4-phenyl-1,2-dihydronaphthalene (**47**) with DDQ.

1'-Phenyl-1,2-divinylbenzene (42). An authentic sample for identification was synthesized from 2-methylbenzophenone, which was converted into a Wittig reagent by bromination with *N*-bromosuccinimide followed by treatment with triphenylphosphine. A Wittig reaction with formaldehyde led to 2-vinylbenzophenone, which was converted into **42** by a second Wittig reaction with methyltriphenylphosphonium bromide. In accordance with the photochemistry of other 1,2-divinylbenzene,[22,26] irradiation of **42** gave **22**: ^{1}H NMR (CDCl$_3$) δ 5.06 and 5.62 (2 H, two d of d, terminal olefinic protons of C(H)=CH$_2$, J_{trans} = 17.5 Hz, J_{cis} = 11.0 and J_{gem} = 1.4), 5.20 and 5.83 (2 H, two d, C(Ph) = CH$_2$, J_{gem} = 1.4 Hz), 6.7–7.5 (m, 10 H).

2-Phenyl-1,4-dihydronaphthalene (59). This compound was isolated from the mixture of **54**, **55**, and **59**, obtained after pyrolysis of **24** at 700 °C (Figure 4). Compound **55** could be removed by column chromatography on silica gel using hexane as eluent.

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Thin-layer chromatography of the remaining mixture of **59** and **54** (silica gel/hexane) leads then to the isolation of a small amount of pure **59**. The physical data of **59** were given previously.[16]

For the pyrolysis experiments, samples of about 50 mg per run were subjected to flash vacuum pyrolysis at temperatures ranging from 500 to 900 °C at a pressure of 0.1 torr. In general, the product composition determined from GLC and NMR corresponded well and the results from GLC analysis were only used as a check on the values calculated from NMR integration. Some discrepancies between GLC and NMR data could be ascribed to interconversions on the GLC column: *endo*- and *exo*-**25** epimerize on the GLC column, the divinyl benzenes **31**, **42**, and *cis*- and *trans*-**49** and the 1,4-dihydronaphthalenes **38**, **45**, and **59** appeared to be thermolabile under GLC conditions.

Registry No. **21**, 15677-15-3; **22**, 82645-20-3; *exo*-**23**, 85803-90-3; **24**, 85803-91-4; *endo*-**25**, 67504-58-9; *exo*-**25**, 67504-57-8; **42**, 87729-00-8; **59**, 40650-73-5.

Supplementary Material Available: Tables of the results of the analyses of the pyrolysis mixtures from which the plots of Figures 1–5 have been constructed (2 pages). Ordering information is given on any current masthead page.

Substituent Effects and Mechanism in the Micellar Hydrolysis of Hydroxamic Acids[1]

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The rates of hydrolysis of octanohydroxamic and *N*-methyloctanohydroxamic acids under acidic conditions with sodium 1-dodecanesulfonate as surfactant and under alkaline conditions with cetyltrimethylammonium bromide as surfactant have been measured. Normal reaction rate orders were obtained except for the alkaline hydrolysis of octanohydroxamic acid above the critical micelle concentration of the surfactant. The latter yielded the novel result of pseudo-zero-order kinetics. The rates of acidic hydrolysis of a series of meta- and para-substituted benzohydroxamic acids in aqueous solution with sodium 1-dodecanesulfonate as surfactant were also measured. The substituent effects indicate specific micellar influences on the rates and a difference in mechanism between the bulk aqueous phase and the micellar phase.

Micellar enhancement of reaction rates of bimolecular reactions could result from one or both of two factors: the concentration of reactants by the micellar phase and the relative stabilization of transition states and/or destabilization of reactant states by the micellar environment relative to the bulk aqueous phase.[2,3] We report in this paper evidence that the latter factor has a significant role in the micellar catalysis of hydroxamic acid hydrolysis.

Results and Discussion

Equation 1, derived by Romsted,[4] is applicable to bimolecular reactions in which one reactant is an ion. The

$$k_2 = \frac{k_m'\,\beta S K_a(C_t - \text{cmc})}{[K_a(C_t - \text{cmc}) + 1][I_t + X_t K_I]} + \frac{k_w'}{K_a(C_t - \text{cmc}) + 1} \quad (1)$$

overall second-order rate constant and the rate constants in the aqueous and micellar phases are k_2, k_w', and k_m', respectively, β is the degree of counterion binding to the Stern layer, S the molar density of the micellar phase, K_a the association constant of the organic substrate with the micellar phase, C_t the total surfactant concentration, cmc the critical micelle concentration, I_t the total concentration of the hydrophilic reactant ion, X_t the total concentration of the surfactant counterion, and K_I is the ion exchange constant given by eq 2 in which the subscripts ω and m refer to the aqueous and micellar phases, respectively.

$$K_I = \frac{I_\omega X_m}{I_m X_\omega} \quad (2)$$

Table I. Kinetic Data for Acidic Hydrolysis in 0.09279 N HCl at 50.0 ± 0.11 °C as a Function of Sodium 1-Dodecanesulfonate Concentration

10^3C_t	octanohydroxamic acid, 10^5k_{obsd}, s^{-1}	*N*-methyloctanohydroxamic acid, 10^5k_{obsd}, s^{-1}
0.0	2.07	4.94
0.060	1.99	4.85
0.485	2.06	4.99
3.01	5.69	12.5
4.996	11.5	22.0
7.996	17.4	31.0
9.990	21.9	34.4
11.99	23.3	37.1
15.00	26.2	39.2
20.40	29.6	42.6
30.01	32.5	44.4
40.00	34.7	44.3
60.07	34.2	44.2

The constants of eq 1 (with $k_m'\beta S$ considered as one constant) may be estimated as follows. In the absence of added common ions, $X_t = C_t$. In the range $(C_t - \text{cmc}) \simeq C_t$, eq 1 may be treated after the manner of Martinek et al.[5] to yield eq 3,

$$\frac{C_t}{k_{obsd} - k_\omega} = \frac{k_2 C_t^2 q}{k_{obsd} - k_\omega} + \frac{k_2 C_t p}{k_{obsd} - k_\omega} + r \quad (3)$$

in which $k_{obsd} = k_2 I_t$, $k_\omega = k_\omega' I_t$, and p, q, and r are constants which are functions of the constants in eq 1. At sufficiently low enough values of C_t, the C_t^2 term is negligible and a graph of the left side of eq 3 vs.

$$k_2 C_t/(k_{obsd} - k_\omega)$$

will yield values for p and r. At the rate maximum eq 4

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