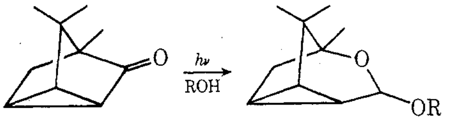
Photochemical Ring Expansion of Cyclic Ketones via Cyclic Oxacarbenes

Peter Yates* and Rafik O. Loutfy

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

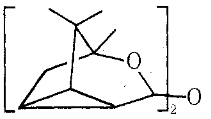
Received July 22, 1974

In 1964 Yates and Kilmurry[1] reported a new type of photochemical reaction of cyclic ketones in solution. Irradiation of cyclocamphanone (**1**) in methanol or ethanol gave the ring-expanded cyclic acetals **2a** and **2b**,[2] respectively. In aqueous solution, **1** was converted to the ether **3**, which was considered to arise from the hemiacetal **2c**. Irradiation of **1** in the presence of air gave the lactone **4**. The parent tricyclic ketone, nortricyclanone (**5**), underwent analogous reactions.[3,4]

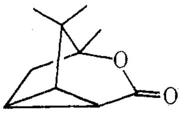


1

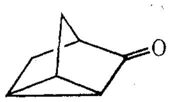
2a, R = CH_3
b, R = C_2H_5
c, R = H



3

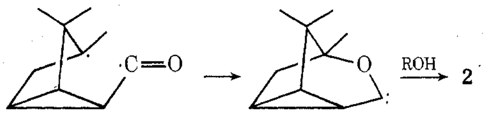


4



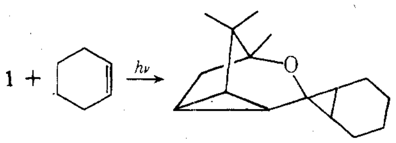
5

Consideration of these transformations in the context of previous investigations of the photochemistry of cyclic ketones[4] led to postulation of a reaction sequence in which excitation of **1** is followed by α cleavage (Norrish type 1 reaction) to give the biradical **6**, which rebonds at oxygen to give the oxacarbene **7**, which in turn reacts with solvent to give **2**.



6 7

This postulate was corroborated by demonstration that irradiation of **1** in cyclohexene gave **8**, the product anticipated from addition of the oxacarbene **7** to cyclohexene.[5]

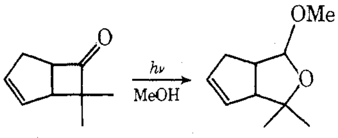


8

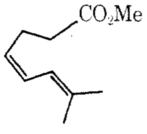
Following the original report, many other examples of this type of reaction came to light. However, the structural requirements for its occurrence are stringent. The present Account reviews these developments, in both their structural and their mechanistic aspects.[6]

Structural Aspects

By far the largest group of cyclic ketones found to undergo photochemical ring expansion to cyclic acetals consists of the cyclobutanones.[7-21] Hostettler[7] first observed the reaction in the case of the bicyclic ketone **9**, which gave the acetal **10** and the ester **11**. Subsequently, Hostettler[8] and Turro and coworkers[9-11] demonstrated that corresponding ring-expan-



9 10



11

Peter Yates received his B.Sc. degree from Queen Mary College, University of London, his M.Sc. degree from Dalhousie University, Halifax, Nova Scotia, and his Ph.D. degree from Yale. After postdoctoral work with R. B. Woodward at Harvard and a year as Instructor at Yale, he was Instructor and then Assistant Professor at Harvard from 1952 until 1960, when he moved to the University of Toronto as Professor of Chemistry.

Rafik Omar Loutfy received his Ph.D. degree from the University of Western Ontario in 1972, did postdoctoral work at the National Research Council in Ottawa and at the University of Toronto, and is now with the Xerox Research Centre of Canada, Mississauga, Ontario.

---

[1] P. Yates and L. Kilmurry, *Tetrahedron Lett.*, 1739 (1964).

[2] In many cases of cyclic acetal formation by ring expansion, two anomeric acetals are formed; since the relative configurations of the anomers often have not been determined and since this question is not relevant to the present discussion, all such anomeric mixtures are represented in this Account by a single structure without designation of configuration at the anomeric carbon atom.

[3] L. Kilmurry, Ph.D. Thesis, University of Toronto, 1966.

[4] P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

[5] P. Yates and L. Kilmurry, *J. Am. Chem. Soc.*, **88**, 1563 (1966).

[6] For recent related reviews, see (a) W.-D. Stohrer, P. Jacobs, K. H. Kaiser, G. Wiech, and G. Quinkert, *Fortschr. Chem. Forsch.*, **46**, 181 (1974); (b) N. J. Turro and D. R. Morton, *Adv. Photochem.*, **9**, 197 (1974).

[7] H. U. Hostettler, *Tetrahedron Lett.*, 687 (1965).

[8] H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).

[9] N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967).

[10] D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 4349 (1970).

[11] N. J. Turro and D. R. Morton, *J. Am. Chem. Soc.*, **93**, 2569 (1971); D. R. Morton and N. J. Turro, *ibid.*, **95**, 3947 (1973).

[12] G. Quinkert, G. Cimballek, and G. Buhr, *Tetrahedron Lett.*, 4573 (1966).

[13] G. Quinkert, P. Jacobs, and W.-D. Stohrer, *Angew. Chem., Int. Ed. Engl.*, **13**, 197 (1974); G. Quinkert and P. Jacobs, *Chem. Ber.*, **107**, 2473 (1974).

[14] N. J. Turro and D. M. McDaniel, *J. Am. Chem. Soc.*, **92**, 5727 (1970); D. M. McDaniel and N. J. Turro, *Tetrahedron Lett.*, 3035 (1972).

[15] Cf. also ref 8.

[16] H. A. Staab and J. Ipaktschi, *Tetrahedron Lett.*, 583 (1966); *Chem. Ber.*, **101**, 1457 (1968).

[17] Cf. R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, 169 (1966); O. L. Chapman, C. L. McIntosh, and L. L. Barber, *J. Chem. Soc. D*, 1162 (1971).

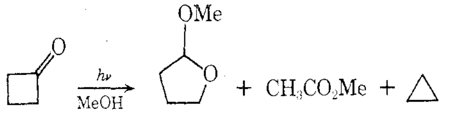
[18] N. J. Turro, E. Lee-Ruff, D. R. Morton, and J. M. Conia, *Tetrahedron Lett.*, 2991 (1969).

[19] R. G. R. Hagens, Ph.D. Thesis, University of Toronto, 1970.

[20] J. C. Tam, Ph.D. Thesis, University of Toronto, 1974.

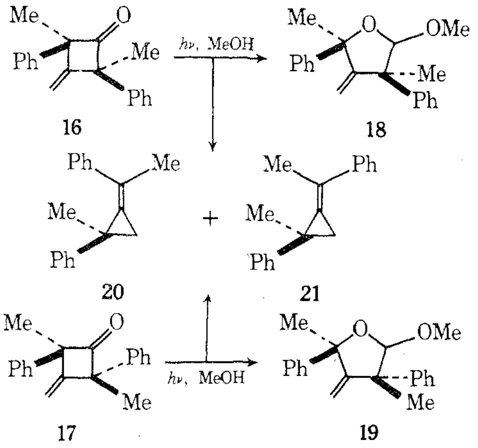
[21] For other examples, see W. F. Erman, *J. Am. Chem. Soc.*, **89**, 3828 (1967); J. G. Pacifici and C. Diebert, *ibid.*, **91**, 4595 (1969); N. J. Turro, D. R. Morton, E. Hedaya, M. E. Kent, P. D'Angelo, and P. Schissel, *Tetrahedron Lett.*, 2535 (1971); H. D. Scharf and W. Küsters, *Chem. Ber.*, **104**, 3016 (1971); H. W. Yeung, Ph.D. Thesis, University of Toronto, 1971; J. M. Denis and J. M. Conia, *Tetrahedron Lett.*, 461 (1973); K. Kimura, M. Takamura, A. Kunai, and Y. Odaira, *J. Chem. Soc., Chem. Commun.*, 685 (1974).

sion reactions occur in the case of monocyclic cyclobutanones, together with decarbonylation and cycloelimination reactions. These processes are illustrated by the photoconversion of cyclobutanone (**12**) itself to compounds **13**–**15**.[9,10] As in the case of **1**, lactone formation can occur in the presence of air.[9]

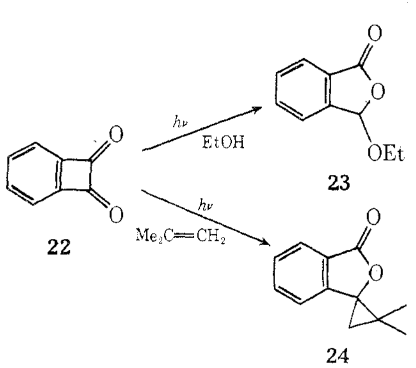


12 **13** **14** **15**

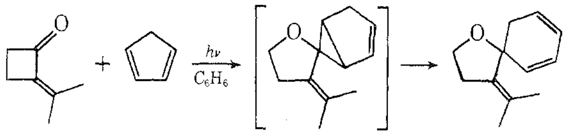
Several features of the ring expansion of cyclobutanones are noteworthy. First, acetal formation normally occurs with high regioselectivity in the case of unsymmetrical cyclobutanones; such selectivity has frequently been observed in the α cleavage of cyclic ketones and can be interpreted in terms of selective cleavage of the weaker α bond or selective formation of the more stable alkyl radical. Second, increased α-alkyl substitution in cyclobutanones favors acetal formation relative to ester and cyclopropane formation.[9-11] Third, Quinkert[12,13] and Turro[14] and coworkers have observed in several cases that the ring expansion of cyclobutanones with chiral α-carbon atoms proceeds with retention of configuration. Thus the diastereomeric 3-methylenecyclobutanones **16** and **17** give the acetals **18** and **19**, respectively.[13] Further it is noteworthy that both **16** and **17** give cyclopropanes **20** and **21** with allylic rearrangement while **18** and **19** are formed without such rearrangement.[13,15]



Trapping of an oxacarbene intermediate with alkenes has rarely been accomplished in the case of cyclobutanones. Staab and Ipaktschi[16] in their investigation of the photochemistry of benzocyclobutenedione (**22**)[17] found that irradiation in ethanol gave the acetal **23** among the products, while irradiation in the presence of alkenes gave cyclopropanes of type **24**.



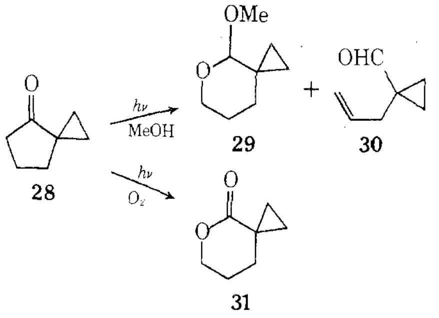
Turro and Morton[11] have observed that irradiation of 2-isopropylidenecyclobutanone (**25**) in benzene in the presence of cyclopentadiene gives the spiro ether **27** and have interpreted its formation as involving rearrangement of an initially formed adduct, **26**.



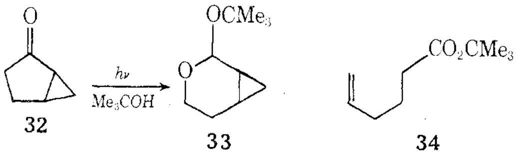
25 **26** **27**

No five-membered *monocarbocyclic* ketone has been observed to undergo photochemical ring expansion to an acetal. Such acetal formation from cyclopentanones is observed only when there is a cyclopropyl ring joined at the α position or where the cyclopentanone ring forms part of a 2-norbornanone system.

Two cases of the first kind have been reported. Irradiation of the spiro ketone **28** in methanol gives the acetal **29**;[10,22] also formed are the unsaturated aldehyde **30** and its dimethyl ketal.[23,24] Irradiation in benzene in the presence of air gives the lactone **31**.



The second case involves a cyclopentanone with a cyclopropyl group fused adjacent to the carbonyl group: irradiation of bicyclo[3.1.0]hexan-2-one (**32**) in *tert*-butyl alcohol gives the acetal **33** together with the unsaturated ester **34**.[25]



Some bicyclo[2.2.1]heptan-2-ones give photochemical ring expansion products, and some do not. The parent member of the series, norcamphor (**35**), gives only the aldehyde **36**; no cyclic acetal could be detected in the crude photolysate.[4,19,26] It is noteworthy that it is the Δ^2 aldehyde **36** that is formed and not its Δ^3 isomer. Other bicyclo[2.2.1]heptan-2-ones whose irradiation in alcoholic solution does not lead

---

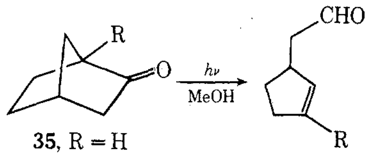
(22) J. K. Crandall and R. J. Seidewand, *J. Org. Chem.*, **35**, 697 (1970).

(23) Depending upon the reaction conditions, aldehydic products from photolyses in methanolic solution may be converted partially or wholly to their dimethyl acetals; in the present Account only the original aldehydic products are indicated.

(24) Cf. A. Sonoda, I. Moritani, J. Miki, and T. Tsuji, *Tetrahedron Lett.*, 3187 (1969); A. Sonoda, I. Moritani, J. Miki, T. Tsuji, and S. Nishida, *Bull. Chem. Soc. Jpn.*, **45**, 1777 (1972).

(25) W. G. Dauben, L. Schutte, G. W. Schaffer, and R. B. Gagosian, *J. Am. Chem. Soc.*, **95**, 468 (1973).

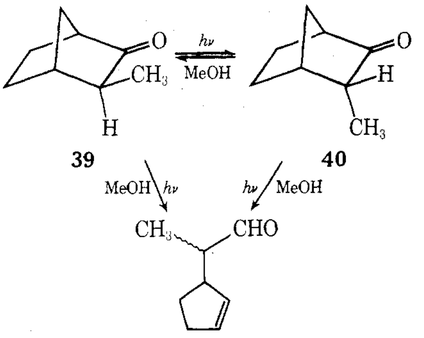
(26) J. A. Meinwald and R. A. Chapman, *J. Am. Chem. Soc.*, **90**, 3218 (1968).



35, R = H
37, R = CH_3

36, R = H
38, R = CH_3

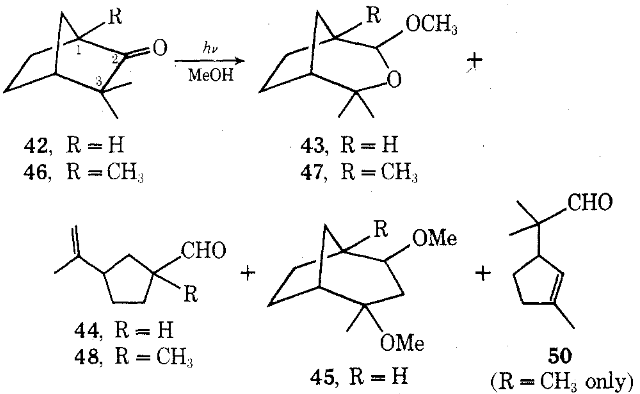
to ring expansion include 1-methyl-2-norbornanone (**37**), which gives the aldehyde **38**, and the exo and endo epimers of 3-methyl-2-norbornanone, **39** and **40**, which undergo photoepimerization and conversion to the diastereomeric Δ^2 aldehyde mixture **41**.[19]



39 **40**

41

The occurrence of ring expansion has been observed for bicyclo[2.2.1]heptan-2-ones with two types of substitution pattern, i.e., 3,3-dialkyl and 7,7-dialkyl. Irradiation of camphenilone (**42**) gives the acetal **43**, together with the aldehyde **44** and the ether **45**; the latter is considered to be a secondary product formed from **44**.[27] Fenchone (**46**) gives the analogous products **47**–**49** together with the aldehyde **50**.[27,28]



42, R = H
46, R = CH_3

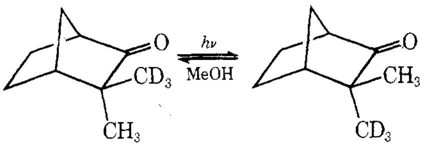
43, R = H
47, R = CH_3

44, R = H
48, R = CH_3

45, R = H
49, R = CH_3

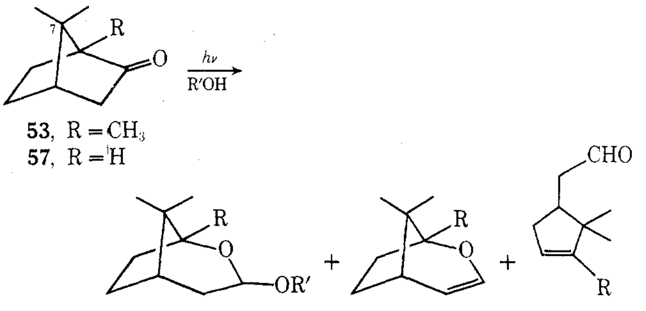
50
(R = CH_3 only)

The lack of regiospecificity in the α cleavage of **46** is in accord with expectation, since each α-carbon atom has the same degree of substitution; it may be noted that although aldehydic products were formed via cleavage of either the 1,2 or 2,3 bond, ring expansion was associated with 2,3-bond cleavage only. The occurrence of degenerate photoepimerization was established in the case of camphenilone by demonstration of the conversion of the trideuteriocamphenilone **51** to its epimer **52**.[19]



51 **52**

Agosta and Herron[29] have investigated the photolysis of camphor (**53**) in ethanol and have isolated the acetal **54**, the vinyl ether **55**, and the aldehyde **56**. Irradiation of **53** in heptane also gave **55**. Irradiation of apocamphor (**57**) in methanol[19] has shown that this 7,7-dialkylnorbornanone also gives a ring expansion product (**58**) together with the aldehyde **59** analogous to **56**.



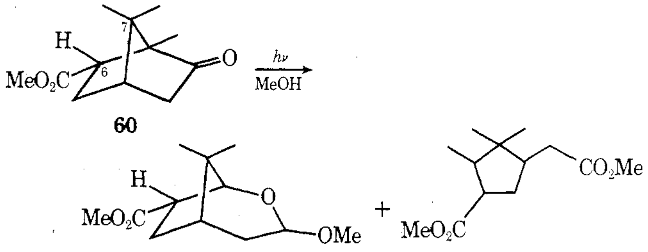
53, R = CH_3
57, R = H

54, R = CH_3; R′ = Et
58, R = H; R′ = CH_3

55
(R = CH_3 only)

56, R = CH_3
59, R = H

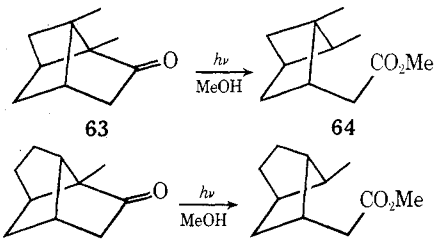
Yates and Tam[20] have recently investigated the photolysis of the keto ester **60** as an example of a 7,7-disubstituted 2-norbornanone in which the absence of a C-6 endo hydrogen atom excludes formation of an aldehyde of type **56**. The major product was the acetal **61** accompanied by a small amount of the ketene-derived product **62**.



60

61 **62**

This result is in striking contrast to the observation by Meinwald and Erman and coworkers[30] that irradiation of carvonecamphor (**63**), whose structural features also inhibit formation of an aldehyde of type **56**, gives the ketene-drived product **64** as the major product. Irradiation of the tricyclic ketone **65** has also been found to give the ketene-derived product **66** and no ring-expansion product.[20]



63 **64**

65 **66**

Interestingly, the closely related tricyclic ketone **67** undergoes nonregiospecific cleavage to give the ring-

---

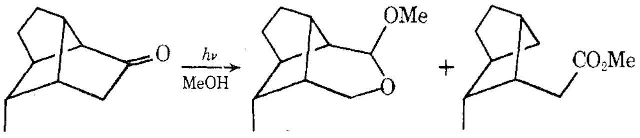
(27) P. Yates and R. Hagens, *Tetrahedron Lett.*, 3623 (1969).

(28) Cf. P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 4621 (1967).

(29) W. C. Agosta and D. K. Herron, *J. Am. Chem. Soc.*, **90**, 7025 (1968).

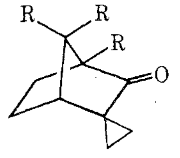
(30) J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, **87**, 5218 (1965); T. Gibson and W. F. Erman, *J. Org. Chem.*, **31**, 3028 (1966); J. Meinwald, R. A. Schneider, and A. F. Thomas, *J. Am. Chem. Soc.*, **89**, 70 (1967).

expanded acetal **68** as the major product, together with a small amount of the ketene-derived ester **69**, analogous to **64** and **66**, as the only product arising from α cleavage at the more highly substituted α-carbon atom.[20] This can be attributed to the circumstance that the secondary radical formed by the latter cleavage is at the C-7 position of a norbornyl system.[31] In the case of **65** (and **63**), the destabilization due to this factor is more than offset by the tertiary nature of the radical.

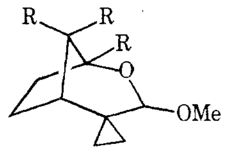


67 **68** **69**

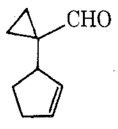
We have examined[20] the photochemistry of two bicyclo[2.2.1]heptan-2-one derivatives, **70** and **73**, that incorporate a cyclopropyl ring adjacent to the carbonyl group—a structural feature that, as previously discussed, favors ring expansion in simple cyclopentanones. Irradiation of the spiro ketone **70** in methanol gave the ring-expansion product **71** as a minor product, together with the aldehyde **72** as the major product; this result may be compared with the case of norcamphor (**35**), where cleavage of the analogous α bond occurs, but only aldehyde and no ring-expansion product is formed. Irradiation of **73** gave acetal **74** as the major product; this result may be compared with the case of camphor (**53**), where ring-expansion products represent the minor part of the photolysate, and formation of aldehyde predominates.



70, R = H
73, R = CH$_3$

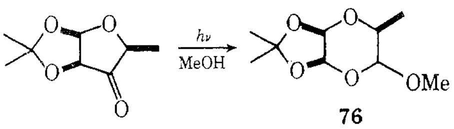


71, R = H
74, R = CH$_3$

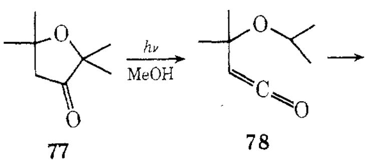


72

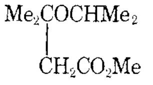
The first example of the photochemical ring expansion of a 3-oxacyclopentanone to an acetal has been reported very recently. Collins and coworkers[32] have found that irradiation of the furanosidulose **75** in methanol gives the dioxane **76**. This is in interesting contrast to the case of the related compound **77**, which gives no acetal but only the esters **79–81** that are considered to be derived from the ketene **78**.[33]



75 **76**



77 **78**

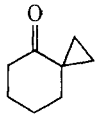


$$\underset{\displaystyle CH_2CO_2Me}{Me_2\overset{|}{C}OCHMe_2} + Me_2C{=}CHCO_2R$$

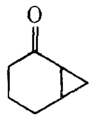
79

80, R = Me
81, R = CHMe$_2$

No six-membered or larger *carbocyclic* ketone has been observed to undergo ring expansion to an acetal. Furthermore, incorporation of a cyclopropyl group at the α position as in **82** and **83**, which led to the occurrence of ring expansion in the case of cyclopentanone (cf. **28** and **32**), fails to lead to ring expansion in the case of cyclohexanone.[10,22]



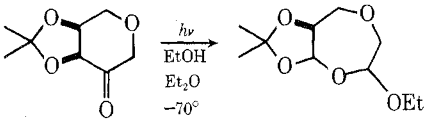
82



83

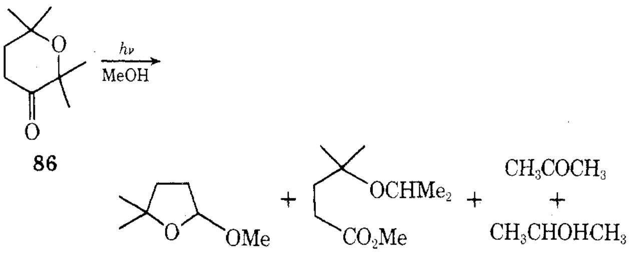
Brook and coworkers[34] have observed ring expansion in the case of α-silacyclohexanones. These results have been reviewed in a recent Account,[34b] and, since the presence of the silicon atom introduces factors not germane to the carbocyclic cases, they are not discussed further here.

Very recently Collins and coworkers[32] have reported that another type of six-membered cyclic ketone undergoes photochemical ring expansion to an acetal. Irradiation of the 3-oxacyclohexanone **84** at −70° in diethyl ether–ethanol gave the dioxepane **85** as the major product.



84 **85**

Wasacz and Joullié[35] earlier examined the photochemistry of the related 3-oxacyclohexanone **86** in methanol and observed the formation of the *ring-contracted* acetal **87** together with the ketene-derived ester **88**, acetone, and isopropyl alcohol.



86 **87** **88**

Mechanistic Aspects

Multiplicity of the Reactive Excited State. It is now well established that in general α cleavage occurs via both the n,π* singlet and triplet excited states.[36-38] However, the information available on the excited states involved in the photochemical ring expansion of cyclic ketones is meager.

---

(31) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(32) P. M. Collins, N. N. Oparaeche, and B. R. Whitton, *J. Chem. Soc., Chem. Commun.*, 292 (1974).

(33) G. Hagens, J. P. Wasacz, M. Joullié, and P. Yates, *J. Org. Chem.*, **35**, 3682 (1970).

(34) (a) A. G. Brook, R. Pearce, and J. B. Pierce, *Can. J. Chem.*, **49**, 1622 (1971); J. M. Duff and A. G. Brook, *ibid.*, **51**, 2869 (1973); (b) A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974); (c) the only known cases of the formation of oxacarbene-derived products upon irradiation of acyclic ketones have involved α-sila ketones: A. G. Brook and J. M. Duff, *J. Am. Chem. Soc.*, **89**, 454 (1967).

(35) J. P. Wasacz and M. M. Joullié, *Tetrahedron Lett.*, 2501 (1970).

(36) J. M. Beard and R. H. Eastman, *Tetrahedron Lett.*, 3029 (1970).

(37) N. C. Yang and R. H.-K. Chen, *J. Am. Chem. Soc.*, **93**, 530 (1971).

(38) D. S. Weiss, N. J. Turro, and J. C. Dalton, *Mol. Photochem.*, **2**, 91 (1970).

In the case of cyclobutanones in solution, where ring expansion is a general reaction, there is mounting evidence that the reaction occurs via the n,π* singlet excited state:

(i) The formation of the photolysis products (cyclic acetals, decarbonylation and cycloelimination products) is not quenched by high concentration of 1,3-dienes that are known triplet quenchers.[14,39]

(ii) Several attempts to sensitize the photoreactions of cyclobutanones in solution by triplet sensitizers have been unsuccessful.[11,40,41] Turro and Morton[11] have found that the triplet sensitization with *m*-xylene (E_T = 82–83 kcal/mol) of a substituted cyclobutanone increased the ratio of the decarbonylation product to the ring-expansion product by a factor of 4, providing indirect evidence for singlet involvement in the ring-expansion reaction.

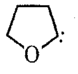
(iii) Lee and coworkers[42,43] have provided strong spectroscopic evidence supporting the photoreactivity of the singlet state of cyclobutanone.

In the case of simple cyclopentanones, where ring expansion occurs only rarely, the accumulated evidence suggests that in general the n,π* singlet state largely undergoes intersystem crossing to the triplet state, which is the main reactive precursor for photochemical transformations.[44,45] Indeed, the formation of the ring-expansion product **29** on photolysis of spiro[2.4]heptan-4-one (**28**) in methanol is quenched by 3.0 *M* 1,3-pentadiene,[11] supporting the view that the triplet excited state of the ketone ($\tau_T \simeq 2 \times 10^{-9}$ sec) is the reactive precursor of the ring-expansion product.

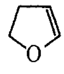
Little is known concerning the reactive excited state responsible for ring expansion in the case of bicyclo[2.2.1]heptanones. In general, the photochemical reactions of these systems are not quenchable by 1,3-dienes, indicating that they proceed via a singlet precursor and/or a very short-lived triplet state. Since singlet lifetimes of several bicyclic ketones are no shorter than those of simple cyclopentanones, Turro and coworkers[46] have concluded that α cleavage must arise, at least in part, from the triplet state.

Cyclic Oxacarbene as Intermediate. The original proposal[1,5] of the intermediacy of cyclic oxacarbenes as intermediates in the photochemical ring expansion of cyclic ketones has now gained general acceptance. The formation of ring-expanded acetals, lactones, and spirocyclopropyl derivatives in the presence of alcohol, oxygen, and alkenes, respectively, can all be accommodated in terms of this postulate. Furthermore, Quinkert and coworkers[47] have observed transient ultraviolet absorption ($\lambda_{max} \sim 360$ nm) on irradiation of cyclobutanone derivatives in glasses at −186° that they consider arises from the corresponding oxacarbenes.

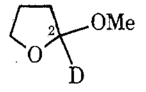
In the case of cyclobutanone (**12**), Turro and Southam[9] have obtained evidence that the acetal **13** is derived from the oxacarbene **89** rather than the vinyl ether **90** by carrying out the irradiation in CH_3OD, when they observed exclusive deuterium incorporation at C-2 as in **91**.



89

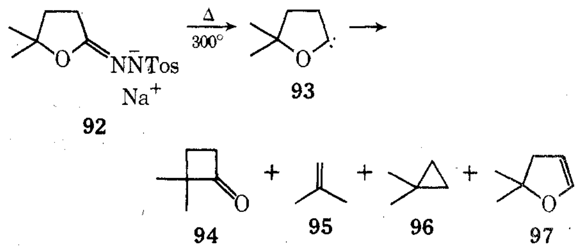


90



91

Agosta et al.[48] generated cyclic oxacarbenes by the thermal decomposition of lactone tosylhydrazone sodium salts and examined their decomposition products. Pyrolysis of **92** gave the products **94–97**, which are considered to arise from the cyclic oxacarbene **93**. The formation of **94** indicates that the photochemical transformation of **94** to **93** may be reversed thermally, which could account for the difficulty experienced in trapping the oxacarbene with alkenes and for the inefficiency of the photochemical reaction.



Both a process involving the intermediate formation of an alkyl acyl biradical and a concerted process have been proposed to account for the photochemical formation of oxacarbenes from ketones.[1,6,11,13,14]

A concerted process provides the simplest interpretation of the retention of configuration in the ring expansion of cyclobutanones with chiral α-carbon atoms.[12-14] Quinkert and coworkers[6a,13] consider that, although the earlier stereochemical observations are inconclusive because of the possibility of through-bond coupling in 1,4 biradicals,[49] their demonstration of retention of configuration in the ring expansion of the 3-methylenecyclobutanones **16** and **17** provides compelling evidence for concerted oxacarbene formation in the case of cyclobutanones. However, Wagner[50] has pointed out that in a biradical intermediate a rotational barrier would have to be surmounted before the alkyl radical could partake of allylic resonance; this barrier would be enhanced by through-bond coupling. Thus the possibility remains that such an intermediate could close to an oxacarbene faster than it rotates, resulting in retention of configuration.

The enhanced occurrence of ring expansion relative to cycloelimination on substitution of alkyl groups at the α-carbon atoms of cyclobutanones can be interpreted in terms of concerted formation of the oxacarbene as resulting from increased nucleophilicity of the α-carbon atoms. It can also be interpreted

---

(39) R. F. Klemm, *Can. J. Chem.*, 48, 3320 (1970).

(40) P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, 88, 1242 (1966).

(41) N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, 2, 39 (1970).

(42) E. K. C. Lee, J. C. Hemminger, and C. F. Rubutt, *J. Am. Chem. Soc.*, 93, 1867 (1971).

(43) J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, 54, 1405 (1971).

(44) A. T. Blades, *Can. J. Chem.*, 48, 2269 (1970).

(45) H. M. Frey and I. C. Vinall, *J. Chem. Soc. A*, 3010 (1970).

(46) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Am. Chem. Soc.*, 92, 2564 (1970).

(47) G. Quinkert, K. H. Kaiser, and W.-D. Stohrer, *Angew. Chem., Int. Ed. Engl.*, 13, 198 (1974).

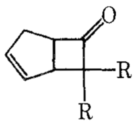
(48) A. B. Smith III, A. M. Foster, and W. C. Agosta, *J. Am. Chem. Soc.*, 94, 5100 (1972); A. M. Foster and W. C. Agosta, *ibid.*, 94, 5777 (1972); 95, 608 (1973).

(49) R. Hoffmann, *Acc. Chem. Res.*, 4, 1 (1971).

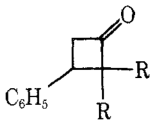
(50) P. J. Wagner, private communication; cf. L. M. Stephenson and T. A. Gibson, *J. Am. Chem. Soc.*, 94, 4599 (1972).

in terms of a biradical intermediate as resulting from increased stabilization of the alkyl radical; this could also account for the decrease in total photochemical efficiency. Exclusive formation of ring-expansion products from cyclobutanones has only been observed when these possess an α-ethylenic bond or α-spirocyclopropyl ring. Turro and Morton[11] have made the reasonable proposal that this is due to stabilization of the oxacarbene with respect to the intermediate biradical: a similar stabilization effect could be invoked in terms of concerted formation of the oxacarbene.

It has been suggested[11] that the failure of the cyclobutanones **98** and **99** to form ring-expansion products upon irradiation in methanol, in contrast to their dimethyl analogs **9** and **100**, which form ring-expanded acetals as major products, is best interpreted in terms of the intermediacy of a biradical in oxacarbene formation. This view is based on the expectation that the electron-withdrawing Cl or CF_3 substituents would inhibit nucleophilic attack by the carbon radical on the acyl oxygen atom. However, the electron-withdrawing nature of these substituents could also be invoked to interpret the inhibition of oxacarbene formation by a concerted process.



98, R = Cl
9, R = CH_3

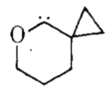


99, R = CF_3
100, R = CH_3

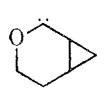
Thus, the question of the concertedness of oxacarbene formation from cyclobutanones is incompletely resolved. It is clear that cyclobutanones can undergo cleavage to biradicals, and indeed Dowd and coworkers have reported the trapping of such a species,[51] but it remains to be rigorously established whether these arise from oxacarbenes formed in a primary concerted process or are themselves primary products that are intermediates in the formation of oxacarbenes.

Quinkert and his coworkers[6a,52] have proposed a theoretical interpretation of the circumstance that cyclobutanones generally undergo ring expansion to oxacarbenes while larger ring cycloalkanones do not, based on their view that oxacarbene formation from cyclobutanones is concerted. They conclude from a consideration of correlation diagrams that in the case of the larger ring cycloalkanones concerted oxacarbene formation cannot compete with α cleavage to a biradical, whereas in the case of cyclobutanones concerted oxacarbene formation is favored as a result of through-bond coupling. They have also carried out calculations for a simple extended Hückel model for the cyclobutanone–oxacarbene isomerization that they consider supports this view.[6a,52]

In the case of five-membered cyclic ketones, the fact that the bicyclic ketones **28** and **32** give ring-expansion as well as cleavage products,[10,22,25] while monocyclic cyclopentanones do not, can be accounted for in terms of stabilization of the oxacarbenes **101** and **102**. Turro and Morton[11] have shown that the quantum yield for formation of the ring-expansion product **29** from **28** is comparable to that for the formation of the enal **30**, which itself is only somewhat smaller than the quantum yield for the formation of enal from cyclopentanone.

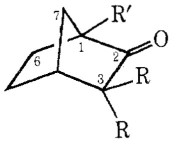


101

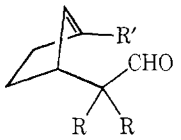


102

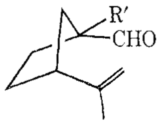
No stabilizing effect appears to account for the observation that five-membered cyclic ketones in the bicyclo[2.2.1]heptan-2-one series undergo ring expansion only when they are 3,3 or 7,7 disubstituted. Here, the original proposal[4] that oxacarbene-derived products are formed when structural features render competing reactions unfavorable remains as the best interpretation. For five-membered cyclic ketones in solution, the most important such reaction is usually enal formation, since ketene formation, decarbonylation, and reduction are unfavorable. Norcamphor (**35**) gives only the unsaturated aldehyde **36** on irradiation in methanol.[4] Camphenilone (**42**) gives both the unsaturated aldehyde **44** and the oxacarbene-derived product.[27] This is attributed to increase in the difficulty of formation of the unsaturated aldehyde, both because it involves abstraction of a methyl rather than a methylene hydrogen atom and because the transition state for hydrogen abstraction is seven rather than five membered.



35, R = R′ = H
42, R = CH_3; R′ = H
46, R = R′ = CH_3

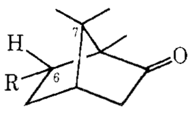


36, R = R′ = H
50, R = R′ = CH_3

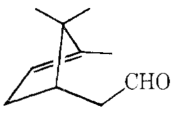


44, R′ = H
48, R′ = CH_3

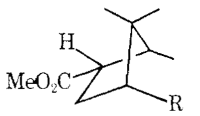
Fenchone (**46**) gives the unsaturated aldehyde **48** together with oxacarbene-derived product by cleavage of the 2,3 bond, but only the aldehyde **50** by cleavage of the 1,2 bond.[27] In the case of camphor (**53**), the unsaturated aldehyde **56** is formed as the major product, but is accompanied by oxacarbene-derived products.[29] This is interpreted in the following terms: it is known in the case of norcamphor (**35**) that hydrogen abstraction occurs exclusively from C-7 to give **36** rather than from C-6 to give the Δ^3 isomer; in camphor (**53**) the less favorable abstraction of hydrogen from C-6 is involved in aldehyde formation because of the presence of a 7-syn substituent and thus oxacarbene formation is able to compete.



53, R = H
60, R = CO_2Me



56



62, R = CH_2CO_2Me
103, R = CH=C=O

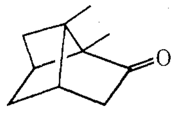
These interpretations are corroborated by the observation that irradiation of a methanolic solution of **60**, in which hydrogen abstraction from the 6-endo position is also prevented by substitution, gives oxa-

---

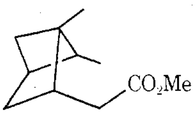
(51) P. Dowd, A. Gold, and K. Suchdev, *J. Am. Chem. Soc.*, **92**, 5724 (1970).

(52) W.-D. Stohrer, G. Wiech, and G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **13**, 199, 200 (1974).

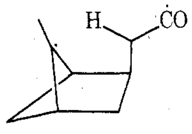
carbene-derived product as the only major product.[20,53] Significantly, it is accompanied by the diester 62 as a minor product; this must be derived from the ketene 103. The formation of such a ketene-derived product was not detected in the irradiation of 35, 42, 46, or 53 in methanol. As mentioned previously carvonecamphor 63 gives the ketene-derived product 64 on irradiation in methanol as the major product and no oxacarbene-derived product;[30] this can be interpreted in terms of greatly increased facility for hydrogen abstraction leading to ketene formation due to the presence of the additional ring (cf. 104). A similar interpretation can be made in the case of 65.



63

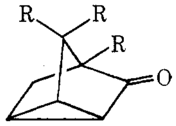


64

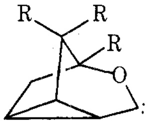


104

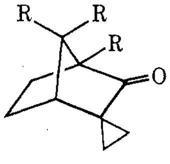
The formation of oxacarbene-derived products as the major products from irradiation of the tricyclic ketones 1 and 5[1,3] may well represent the combined operation of the two factors discussed above, i.e., the presence of the cyclopropyl ring facilitates formation of an oxacarbene, 7, and also retards aldehyde formation by making the required hydrogen abstraction less favorable than in the case of norcamphor. Related considerations apply to the case of the ketone 73 where again the oxacarbene-derived product is the major product; here, as in the case of camphor, the 7-*syn*-methyl substituent reduces the ease of aldehyde formation, while the cyclopropyl ring enhances the ease of oxacarbene formation; indeed, here as for 1 and 5, no aldehyde formation is involved. This may be compared with the case of ketone 70, where aldehyde formation is the major pathway since the 7-syn position is unsubstituted, but oxacarbene-derived product is formed as a minor product, unlike the case of norcamphor, due to facilitation by the presence of the cyclopropyl ring.



1, $R = CH_3$
5, $R = H$

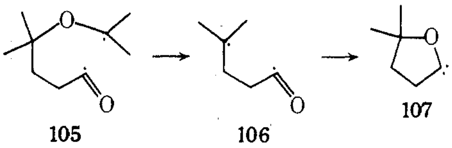


7



70, $R = H$
73, $R = CH_3$

The recent observations by Collins and coworkers[32] that the five- and six-membered 3-oxacycloalkanones 75 and 84 undergo oxacarbene formation are of considerable interest; however, studies of related systems will be required to define the structural features of 75 and 84 that lead to ring expansion in these cases but not in the cases of the oxacycloalkanones 77 and 86. The formation of the *ring-contracted* acetal 87 in the latter case is best interpreted in terms of loss of acetone from the biradical 105 to give the biradical 106, which closes to the oxacarbene 107.[35] This demonstrates that although oxacarbenes may be formed in some cases by concerted photoisomerization of cyclic ketones, a stepwise pathway proceeding via a biradical intermediate is certainly available.



We conclude this discussion by briefly considering oxacarbene formation in relation to the photochemical reactions of cyclic ketones in general. Although the question as to whether all of the photochemical products from cyclic ketones are formed via an intermediate acyl alkyl biradical or via concerted pathways is incompletely resolved, it is now clear that such biradicals are intermediates in many of these reactions. Support for this interpretation comes from isomerization studies of cyclohexanones[37,54,55] and cyclopentanones[37,56] and the trapping of the biradical generated in the low-temperature photolysis of cyclobutanone.[51] The observation of chemically induced dynamic nuclear polarization (CIDNP) has provided evidence in some cases for the intermediacy of short-lived biradicals and for the nature of the excited state involved. Proton CIDNP emission has been observed by Closs and Doubleday[57] during the photolysis of several cyclic ketones, and Kaptein and coworkers[58] have reported ^{13}C CIDNP for a number of cyclic ketones. Cyclohexanone, fenchone (46), and camphor (53) exhibited emission compatible with α cleavage; however, cyclopentanone and cyclobutanone did not give CIDNP signals.

The present state of our knowledge of the reaction pathways that may be traversed during the photolysis of cyclic ketones in solution is summarized in Scheme I.[59] The singlet and triplet $n \rightarrow \pi^*$ excited states, 109 and 110, respectively, of the cyclic ketone 108 give rise to a transition state of type 111. In the case of cyclobutanones ($n = 1$) this is singlet in nature, but can be either singlet or triplet when $n > 1$;[60] further, for cyclobutanones the orbital interactions in 111 may differ from those in the other cases.[6a,52] In general, the biradical intermediate 112 is formed via 111 and gives rise to products 113 (by decarbonylation and closure)[61] and 114 and 115[62] (by hydrogen transfer), or reverts to 108; in the case of

---

[53] We have recently shown that, in accordance with our interpretation, the quantum yield for the formation of 61 is very low ($\Phi = 0.03$): J. C. Tam and P. Yates, unpublished results.

[54] C. C. Badcock, M. J. Perona, G. O. Pritchard, and B. Rickborn, *J. Am. Chem. Soc.*, **91**, 543 (1969); J. A. Barltrop and J. D. Coyle, *Chem. Commun.*, 1081 (1969); J. D. Coyle, *J. Chem. Soc. B*, 1736 (1971).

[55] W. C. Agosta and W. L. Schreiber, *J. Am. Chem. Soc.*, **93**, 3947 (1971).

[56] H. M. Frey, *Chem. Ind. (London)*, 947 (1966).

[57] G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.*, **94**, 9248 (1972).

[58] R. Kaptein, R. Freeman, and H. D. W. Hill, *Chem. Phys. Lett.*, **26**, 104 (1974).

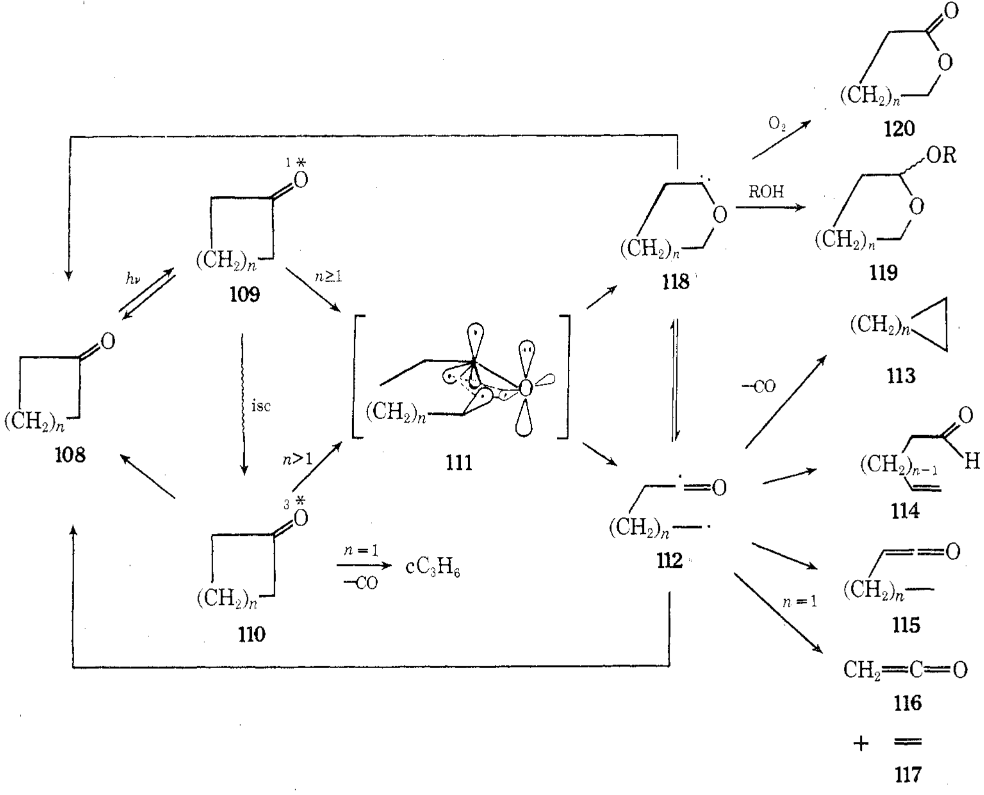
[59] Turro and Morton[11] have formulated a related scheme for cyclobutanone photochemistry which, however, differs in some aspects from that proposed here.

[60] In the latter case spin inversion may occur during or after the formation of the proximate product; cf. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970, p 100.

[61] When $n > 1$, decarbonylation normally occurs in solution only when loss of carbon monoxide from 112 leads to a highly stabilized biradical. When $n = 1$, 113 is a commonly observed product and may also arise directly from 110.

[62] In alcoholic solution products 115 and 116 are converted to the corresponding carboxylic esters.

Scheme I



cyclobutanones cleavage to 116^{62} and 117 can also occur. A further reaction pathway is open to 112, viz., closure to the oxacarbene 118, which gives rise to products 119 and 120 in the presence of alcohols and oxygen, respectively, or reverts to 108. The conversion of 112 to 118 is an inefficient process in the cases where $n > 1$, and occurs only when structural features inhibit the competing processes or stabilize the oxacarbene. In the case of cyclobutanones ($n = 1$), however, formation of 118 is normally a major reaction pathway, perhaps because it is formed directly from 111, while 112 arises in a secondary reaction by cleavage of 118.

P.Y. is happy to acknowledge the contributions of his coworkers, Lindsay Kilmurry, Graham Hagens, Alex Fallis, Wing Yeung, and Janet Tam, and the support of the National Research Council of Canada and of the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to Professor P. J. Wagner, Michigan State University, for his detailed and cogent comments.