(19) To our knowledge, the *g* factor of the acetophenone anion has not been measured, but it may safely be estimated as 2.0035 from $g((C_6H_5)_2CO^-\cdot)$ = 2.003 59[20a] and $g((CH_3)_2CO^-\cdot)$ = 2.003 35.[20b]

(20) (a) M. S. Blois, Jr., H. W. Brown, and J. E. Maling, *Arch. Sci.,Colloq.*, **13**, 243–255 (1960); (b) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **75**, 1186–1201 (1971).

(21) (a) F. A. Neugebauer, private communication; (b) F. A. Neugebauer, S. Baumberger, and W. R. Groh, *Chem. Ber.*, **108**, 2406–2415 (1975).

(22) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.

(23) Wagner has shown that biphenyl quenches the triplet state of butyrophenone ($E_T \simeq$ 3.15 eV) with a rate about 2.5 times less than the diffusion limit, and that biphenyl is a rather inefficient quencher for benzophenone photoreduction. See P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820–2825 (1967).

(24) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834–839 (1969).

(25) For $^1K^* \rightarrow {}^3K^*$, $k_{isc} \simeq 10^{10}\ s^{-1}$ from ref 6, p 198.

(26) For quenching of excited singlet ketone by amine, $k \simeq 10^{10}\ M^{-1}\ s^{-1}[A:^0] = 10^9\ s^{-1}$. For related systems, see N. J. Turro and R. S. Engel, *J. Am. Chem. Soc.*, **91**, 7113–7121 (1969).

(27) For quenching of triplet ketone by amine, $k \simeq 4 \times 10^9\ M^{-1}\ s^{-1}[A:^0] = 4 \times 10^8\ s^{-1}$. For related systems, see (a) R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, **50**, 4050–4052 (1972); (b) S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, 837–840 (1970).

(28) For $^1A^* \rightarrow {}^3A^*$, $k_{isc} < 4 \times 10^8\ s^{-1}$. For related systems see (a) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed., Academic Press, New York, 1971; (b) E. J. Land, J. T. Richards, and J. K. Thomas, *J. Phys. Chem.*, **76**, 3805 (1972).

(29) Quenching of excited singlet amine by ketone to give the ion pair is assumed to be near the diffusion limit: $k \simeq 10^{10}\ M^{-1}\ s^{-1}[A:^0] = 10^9\ s^{-1}$. See D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259–271 (1970).

(30) Quenching of excited singlet amine by ketone via excitation transfer is probably faster than the diffusion limit: $k > 10^{10}\ M^{-1}\ s^{-1}[A:^0] = 10^9\ s^{-1}$.

(31) For triplet quenching of ketone by 0.5 M biphenyl, $k \simeq 2 \times 10^9\ M^{-1}\ s^{-1}[B] = 10^9\ s^{-1}$; see ref 23.

(32) K. Schulten, H. Staerk, A. Weller, H. J. Werner, and B. Nickel, *Z. Phys. Chem. (Frankfurt am Main)*, **101**, 371–390 (1976).

(33) H. Schomburg, H. Staerk, and A. Weller, *Chem. Phys. Lett.*, **22**, 1–4 (1973).

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# Cyclopropylcarbinyl Radicals in the Photochemistry of β,γ-Cyclopropyl Ketones


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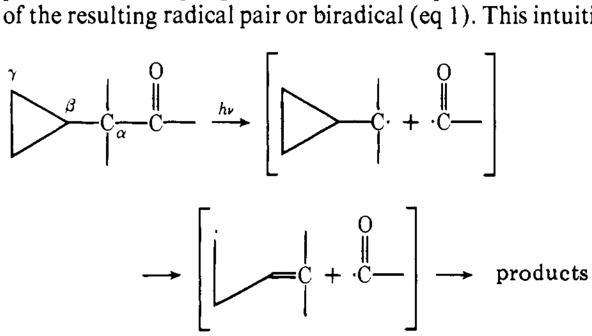
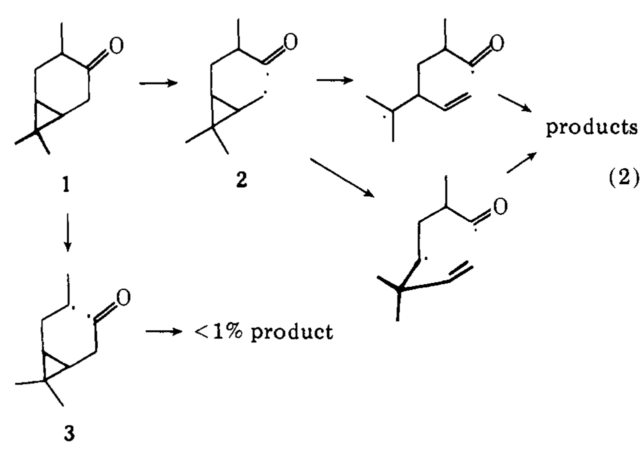
**Abstract:** Photolysis of tricyclic ketones **8b–d**, **9b**, and **10** leads to the products collected in Table I. These results, along with earlier findings with related ketones **6** and **7**, are interpreted as strong evidence for the stepwise mechanism of eq 1, in which opening of the three-membered ring occurs by way of α-cleavage, rearrangement of the initial cyclopropylcarbinyl radical to a homoallyl radical under stereoelectronic control, and then product formation.


One of the principal modes of photochemical reaction of β,γ-cyclopropyl ketones can be explained as an α-cleavage, rearrangement of the cyclopropylcarbinyl radical to a homoallyl radical, and then product formation through disproportionation, coupling, or some more complex transformation of the resulting radical pair or biradical (eq 1). This intuitively



(1)

reasonable, stepwise mechanism, first advanced over a decade ago,[1] satisfactorily accounts for a variety of rearrangements,[2,3] although there is at least one observation suggesting that some refinement of it may be necessary. This is the report[3] that photolysis of both *cis*- and *trans*-4-caranone (**1**) leads selectively to products explainable by way of eq 1, as particularized in eq 2. There is no concomitant epimerization of the methyl group, and less than 1% of product attributable to α-cleavage toward the methyl group (as **3**) is found. This result contrasts with the behavior of typical 2-alkylcyclohexanones, which



(2)

undergo α-cleavage predominantly or solely on the more substituted side; the products from 2-methylcyclohexanone (**4**), for example, arise only from biradical **5**.[4] Thus, if the photochemistry of the 4-caranones (**1**) follows eq 1, it is necessary to specify that the β,γ-cyclopropane ring controls the site of α-cleavage. As originally suggested,[3] the cyclopropane ring appears to weaken the appropriate bond α to the carbonyl group by conjugative or inductive effects. Although the authors did not carry the argument so far, at the extreme this observation might mean that no discrete cyclopropylcarbinyl intermediate is involved and that α-cleavage and fragmentation

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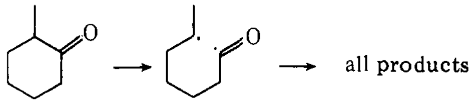
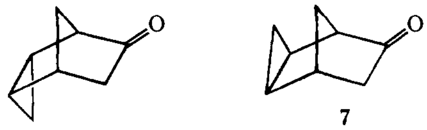
are concerted. To our knowledge there is no other evidence directly concerning this possible alternative to eq 1. However, there is evidence that, in the gas phase at least, rupture of the three-membered ring of cyclopropylacetone occurs without prior or concomitant $\alpha$-cleavage.[1]

If photochemical reactions of $\beta,\gamma$-cyclopropyl ketones do involve a discrete cyclopropylcarbinyl radical intermediate, its rearrangement should be under stereoelectronic control, with preferential cleavage of the $\beta,\gamma$-cyclopropane bond that can better overlap the orbital on C($\alpha$) containing the odd electron.[5,6] The studies noted above,[1-3] however, dealt only with ketones that would lead to cyclopropylcarbinyl radicals in which rotation about the original C($\alpha$)-C($\beta$) bond is unconstrained, so that the question of stereoelectronic control could not be answered. As we discuss below, a previous brief study demonstrated that the photochemistry of tricyclic ketones **6** and **7** is in fact consistent with such stereoelectronic



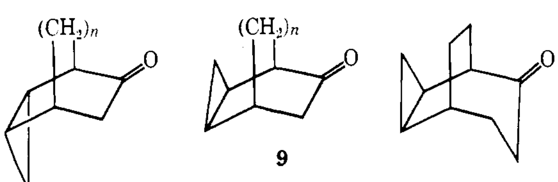

**4** **5**



**6** **7**

control.[7] We have now studied the photochemistry of several additional tricyclic $\beta,\gamma$-cyclopropyl ketones related to **6** and **7**. This series of compounds has the advantage that, if discrete cyclopropylcarbinyl radicals are involved, the site of stereoelectronically controlled cleavage can be predicted and is expected to change along the series.

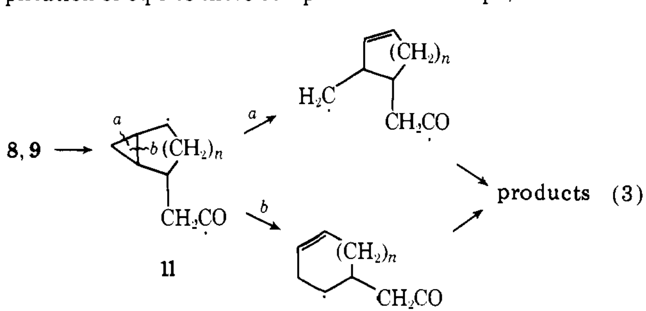
The entire set of compounds comprises seven tricyclic ketones: **8a–d**, in which the bridge of methylene groups ostensibly



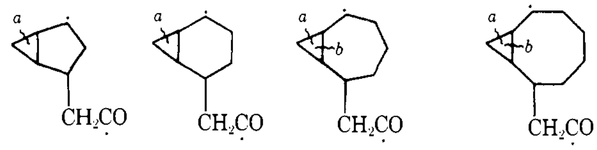
**8** **9** **10**

a, $n$ = 1 c, $n$ = 3
b, $n$ = 2 d, $n$ = 4

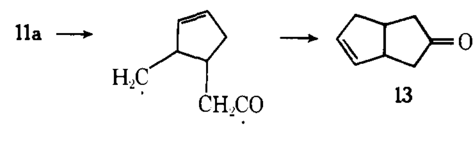
uninvolved in reaction is progressively increased from one to four members; **9a,b**, in which the cyclopropane stereochemistry of **8a,b** is inverted; and **10**, in which the carbonyl group of **8c** has been formally transposed to the three-carbon bridge. Application of eq 1 to these compounds leads to eq 3, and we note




that the site of cyclopropylcarbinyl rupture ($a$ or $b$) in biradical **11** should be largely a function of the value of $n$. Both from previous work with related radicals[6] and from examination of molecular models, one can conclude that, when $n$ is 1 or 2, the orbital containing the odd electron can efficiently overlap only with external bond $a$. However, when $n$ is 3, the flexibility of **11** is materially increased, and conformations permitting orbital overlap of the radical center with either bond $a$ or bond $b$ are reasonable. This will also be true for larger values of $n$, of course, but study of space-filling models suggests that, when $n$ is 4, the molecular motions necessary to achieve these favorable conformations may be hindered by transannular interactions of the hydrogen atoms in the eight-membered ring. These predictions are summarized in structures **11a–d**. Several



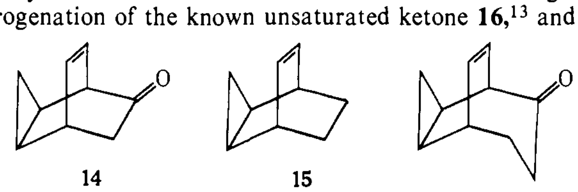
**11a** **11b** **11c** **11d** (hindered rotation?)




**12** **13**

points are noteworthy: (1) The conformational changes that favor facile cleavage at $a$ and/or $b$ can take place only in the bicyclic biradicals **11** and cannot occur in the tricyclic starting ketones **8–10**. Thus if $\alpha$-cleavage is not the first step in these reactions, no simple relationship between $n$ and the site of opening of the cyclopropane is obvious. (2) The stereochemistry of the acyl side chain relative to the three-membered ring should be irrelevant, so that isomers from series **8** and **9** should fragment similarly. (3) Lengthening the acyl side chain should be irrelevant, so that **10** should open like **9b**. (4) Ketones **6** and **7** are **8a** and **9a**, respectively, and their photochemistry follows these predictions. The only pertinent products from their photolysis are the bicyclooctenones *cis*- and *trans*-**13**, respectively, and these are regarded as arising through cleavage $a$ in **11a** and subsequent coupling of homoallyl biradical **12**.[7] Guided by these considerations we turned to examination of the photochemistry of the remaining ketones with a particular interest in any difference between the behavior of **8b** and **8c**.

Ketones **8b** and **9b** are well-known and were prepared from **14**.[8] Hydrogenation gave **9b**, as previously reported,[9] while Wolff-Kishner reduction[10] furnished hydrocarbon **15**, which has been prepared in other ways in the past;[9,11] hydroboration[9] and subsequent oxidation[9,12] then gave **8b**. Properties of the products and intermediates were in agreement with those already on record.[8,9,11,12] Ketone **10** was available through hydrogenation of the known unsaturated ketone **16**,[13] and we

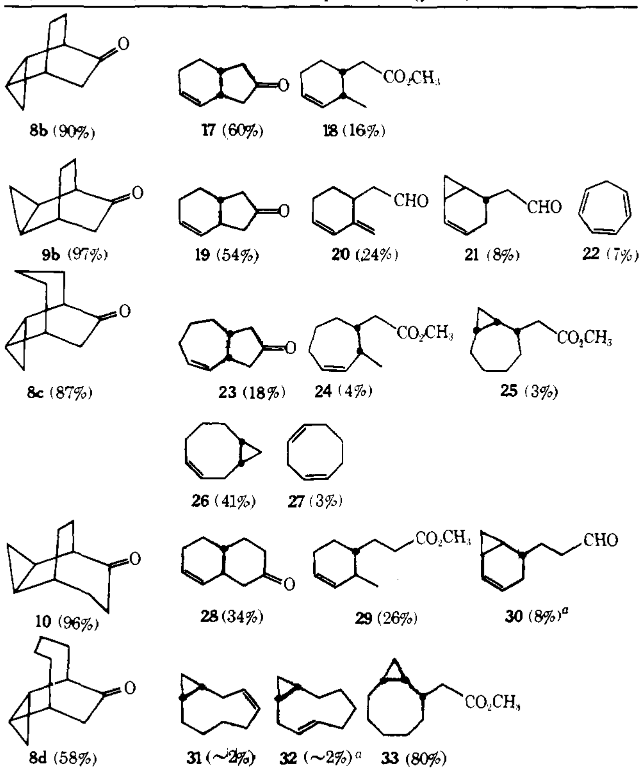


**14** **15** **16**

have described elsewhere the preparation of **8c**[13] and **8d**.[14]

Solutions of **8b–d**, **9b**, and **10** (0.025 M) in benzene containing 3.0% methanol (v/v, 0.74 M) were irradiated through Pyrex ($\lambda$ >2800 Å) using a 450-W medium-pressure mercury lamp. Under these conditions ketene products are trapped as the related photochemically unreactive methyl esters, and all isolated esters are presumed to have arisen in this fashion. Products and unreacted starting ketones were isolated by preparative vapor phase chromatography (VPC). The results are presented in Table I. Yields are based on converted starting material and generally were determined by calibrated VPC

**Table I.** Products of Photolysis of Ketones **8b–d, 9b,** and **10**

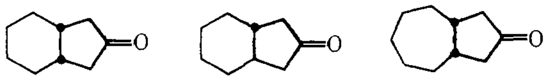


| substrate ketone (conversion) | products (yield) |
|---|---|
| **8b** (90%) | **17** (60%), **18** (16%) |
| **9b** (97%) | **19** (54%), **20** (24%), **21** (8%), **22** (7%) |
| **8c** (87%) | **23** (18%), **24** (4%), **25** (3%), **26** (41%), **27** (3%) |
| **10** (96%) | **28** (34%), **29** (26%), **30** (8%)[a] |
| **8d** (58%) | **31** (~2%), **32** (~2%)[a], **33** (80%) |

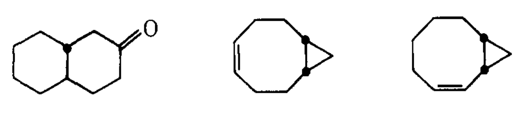
[a] Characterization incomplete; see text.

measurements; they varied somewhat from run to run, and those given are typical.

With the two exceptions noted, the products listed were completely characterized. For compounds not discussed further here, structural assignments rest on spectroscopic data given in the Experimental Section. The structures of **17** and **19** were substantiated by hydrogenation to yield *cis*- and *trans*-2-hydrindanone (**34** and **35**), respectively, which had IR and



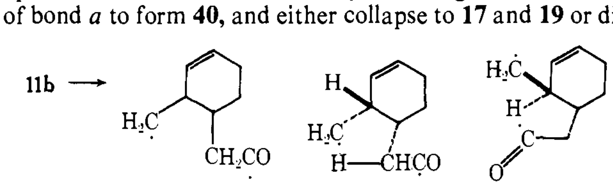
**34** **35** **36**



**37** **38** **39**

NMR spectra that agreed with published values.[15] Similarly, reduction of **23** furnished **36**, which was identified by comparison of melting points of the derived semicarbazone and 2,4-dinitrophenylhydrazone with those reported,[16] and reduction of **28** gave *trans*-2-decalone (**37**), the properties of which matched those of an authentic sample. Cycloheptatriene (**22**) was identical with the commercially available material. Hydrocarbon **26** was indistinguishable from samples prepared from either **38**[17] or **39**[18] by base-catalyzed equilibration,[18] and *cis,cis*-1,4-cyclooctadiene (**27**) was identical with an authentic sample prepared as described by Moon and Ganz.[19] The bicyclodecene **31** appears to be previously unknown but was identical with the product of Simmons-Smith monocyclopropanation[20] of *cis,cis*-1,4-cyclononadiene.[21,22] The structural assignment for the corresponding trans olefin **32** is tentative and is based only on the similarity in IR spectra and VPC retention times of **31** and **32** and the fact that formation of this product is reasonable (see below). The assignment for **30** is fully supported by IR and NMR spectra, but the small amount available, along with persistent impurities, prevented our obtaining an analytically pure sample. The incomplete characterization of **30** and **32** in no way affects the analysis of our results given below.

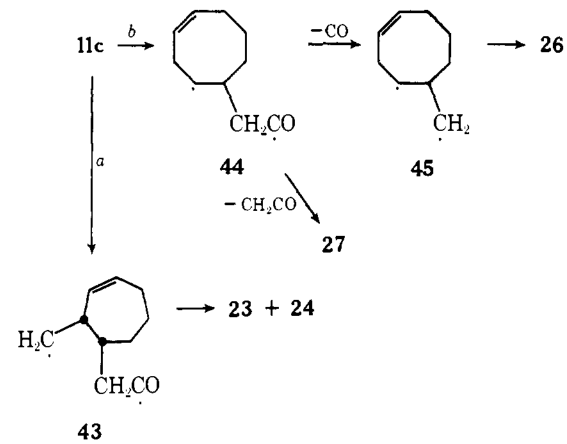
Considering first the isomeric ketones **8b** and **9b**, we note that products **17–20**, in which the cyclopropane ring has opened, can all be accounted for by α-cleavage to **11b,** scission of bond *a* to form **40**, and either collapse to **17** and **19** or dis-



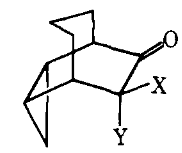
**40** **41** **42**

proportionation to **18** and **20**. The latter process involves a different 1,4 hydrogen shift in each case, a result indicating that steric and electronic factors favor the cis transition states **41** (from **8b**) and **42** (from **9b**). The aldehyde **21** is explained as the product of competitive hydrogen transfer in **11b** without opening of the three-membered ring. Since a separate experiment showed that irradiation of **21** efficiently yields cycloheptatriene (**22**), the small amount of **22** formed on photolysis of **9b** is believed to arise in this way. The pertinent reactions of **8b** and **9b** thus involve only cleavage of bond *a*, in agreement with stereoelectronic control in opening of **11b.**

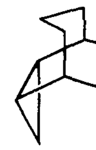
From our earlier discussion the key compound in this study should be **8c**, and it is obvious from Table I that the behavior of this substrate differs from that of its lower homologues. Ketone **23** and ester **24** are analogous to **17** and **18** and can be accounted for by collapse or disproportionation of biradical **43**. However, the isolation of two products with eight-membered rings strongly implies concomitant cleavage of **11c** at bond *b* to furnish the isomeric species **44**. Straightforward



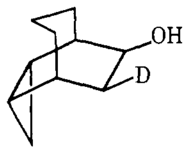

fragmentation of this 1,4 biradical could then yield diene **27**, while decarbonylation and ring closure could lead to **26**. From molecular models it is clear that generation of the observed cis disubstituted double bond of **27** and cis disubstituted cyclopropane of **26** should be energetically preferred in these reactions of **44**. Since hydrocarbon **26** is the dominant product from **8c**, its derivation by a pathway requiring scission of bond *b* is particularly significant. However, the mechanism suggested for its formation is unusual (but not unique[2a]) in requiring the uneconomical opening of one cyclopropane ring followed by the closure of another. Also, any mechanism leading to **26** involves a decarbonylation that is remarkably efficient for a photochemical reaction in solution at ~30 °C.[2a] For these reasons we investigated the origin of **26** through preparation and photolysis of deuterated ketones **46–48**. It is convenient to discuss this work before considering the remaining entries in Table I.



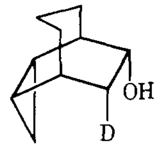
**46,** X = Y = D
**47,** X = D; Y = H
**48,** X = H; Y = D



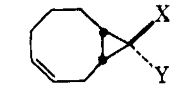
**49**



**50**



**51**



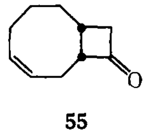
**52,** X = Y = D
**53,** X = D; Y = H
**54,** X = H; Y = D

Treatment of **8c** with sodium carbonate in hot ethanol-*O-d* yielded the dideuterated ketone **46**. The two monodeuterated isomers were available from the related olefin **49**.[13] Deuterioboration[22] gave a mixture of the epimeric alcohols **50** and **51**, which could be separated by preparative VPC of their trimethylsilyl ethers and identified by comparison with their known[13] undeuterated analogues. The stereochemistry of the deuterium substituents was confirmed through lanthanide-shifted NMR spectra of the deuterated and undeuterated species. Oxidation of **50** and **51** with ruthenium tetroxide[24] in carbon tetrachloride solution then gave **47** and **48**.

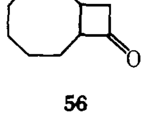
Photolysis of ketone **46** furnished a deuterated hydrocarbon that could be assigned structure **52** from its NMR spectrum. This result substantiates the general features of the mechanism suggested above, which requires that the new cyclopropane methylene group of **26** (or **52**) arise from the $\alpha$-methylene group of **8c** (or **46**). Thus scission of bond *b* in this transformation is assured.

We were interested in the photolysis of **47** and **48** because of a recent suggestion made by Weiss, Haslanger, and Lawton. On the basis of studies in another system, in which a 1,6 acyl alkyl biradical undergoes stereospecific decarbonylation with carbon–carbon bond formation, these investigators postulated that in conformationally favorable cases such decarbonylation of the acyl radical may be facilitated through backside assistance by the alkyl radical.[25] Assistance of this sort in decarbonylation of **44** could account for the efficiency of this reaction and would presumably lead to generation of **26** with inversion at the methylene carbon atom. However, photolysis of **47** and **48** gave in each case a nearly 1:1 mixture, as indicated by NMR measurements, of the deuterated hydrocarbons **53** and **54**, indicating a virtually complete loss of stereochemistry at this center. Thus there is no stereochemical evidence for assisted decarbonylation of **8c**, and stepwise reaction by way of **45** cannot be dismissed.

An alternative route to **26** and **27** entails collapse of **44** to the cyclobutanone **55**, followed by secondary photolysis. This



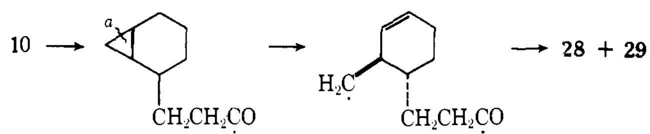
**55**



**56**

would offer a convenient explanation for the efficient decarbonylation, since cyclobutanones undergo exceptionally easy loss of carbon monoxide in solution.[26] We consider this pathway unlikely, however, for several reasons. (1) We found no evidence for **55** in the early stage of reaction of **8c**. (2) The decarbonylation of cyclobutanones is known to be a stereospecific reaction,[26] but our findings with **47** and **48** indicate a loss of stereochemistry in formation of **26**. (3) The photochemistry of the closely related *cis*- and *trans*-bicyclodecanones **56** is on record.[27] Not only does each ketone give cyclopropane and olefin with predominant retention of stereochemistry, but much more olefin than cyclopropane is formed from *cis*-**56**, both in benzene (70:30) and in methanol (88:12). In contrast, from photolysis of **8c** in benzene–methanol the ratio of olefin **27** to cyclopropane **26** is 7:93.

Thus a convincing rationalization for the decarbonylation of **8c** awaits further investigation, but we may conclude for present purposes that this reaction does involve cleavage at bond *b*. Judged by the products, opening at *b* is twice as important as opening at *a* in **8c**. We considered the possibility that this change on passing from **8b** and **9b** to **8c** was attributable simply to the increased molecular flexibility of the tricyclo[3.3.2.0$^{2,4}$]decane carbon skeleton of **8c** relative to that of the lower homologues. This possibility led us to investigation of the photochemistry of **10**, a ketone that has the same carbon skeleton as **8c**. As we pointed out above, $\alpha$-cleavage in **10** would furnish a species (see **57**) which should behave like **11b**. In fact




**57** **58**

the photochemistry of **10** parallels that of **8b** and **9b**, and both **28** and **29** are products of the opening of bond *a*. It is interesting to note that, although **9b** and **10** have the same stereochemistry, 1,5 hydrogen transfer in **58** leads to ketene (ester) and therefore occurs in the direction opposite to the 1,4 transfer in **9b** (see **42**).

Finally, we prepared and photolyzed **8d** in the hope of finding reactivity similar to that of **8c**. This effort met with only limited success. The hydrocarbon products **31** and **32** are indeed analogous to their lower homologue **26**, and thus their presence presumably does signal opening of bond *b* in **11d**. However, the striking result with **8d** is that opening of the cyclopropane ring is such a minor process. Under our standard conditions photolysis of **8d** is considerably slower than that of the lower members of the series, and the major product **33** is a compound in which the original three-membered ring remains intact. Essentially this same distribution of products resulted from photolysis of **8d** in refluxing benzene–methanol or on irradiation through quartz with either benzene–methanol or methanol as solvent. We ascribe this divergent behavior of **8d** to hindered rotation in **11d** due to nonbonded transannular interactions that should lead to preferential collapse of the biradical back to starting ketone. In models these appear to interfere severely with the motions necessary to attain any of the conformations favoring opening of *a* or *b* with generation of either a *cis*- or a *trans*-homoallyl radical. As a consequence there is reduced fragmentation of the three-membered ring, and simple disproportionation becomes the predominant isomerization of **11d**.

In summary the photochemistry of tricyclic ketones **6**, **7**, **8b–d**, **9b**, and **10** is in accord with the involvement of discrete cyclopropylcarbinyl radicals that open under stereoelectronic control. This single assumption provides a straightforward explanation for the relatively simple behavior of **6**, **7**, **8b**, **9b**, and **10**, a basis for the otherwise unexpectedly complex photochemistry of **8c**, and a rationale for the failure of **8d** to undergo significant cleavage of the cyclopropane ring at all. These results then provide strong support for the stepwise mechanism of eq 1.

## Experimental Section

**Materials and Equipment.** These have been previously described.[13] In the present work, the following VPC columns were used: A, 29 g of 20% DEGS, 9.7 ft; B, 16 g of 20% Carbowax 20M, 5 ft. Columns were constructed of standard aluminum tubing having $^3/_{16}$-in. i.d., and Chromosorb P, mesh 60/80, was used as the solid support. An ultraviolet (UV) spectrum was recorded on a Cary Model 14 PM spectrophotometer. Infrared (IR) spectra were obtained on a Perkin-Elmer Model 621 (PE-621), or on a Perkin-Elmer Model 237B grating infrared spectrophotometer. Exceptions to the above are noted.

**General Procedure for Photolysis and VPC Analysis of the Photolysates.** Photolyses were carried out in benzene (distilled, J. T. Baker) solution containing 3.0% (by volume) methanol through a double Pyrex filter (λ >2800 Å) using a 450-W Hanovia lamp. Details of the procedure are described elsewhere.[28] Yields for the products from **8b,c** and **9b** were ascertained by the internal standard technique. For those from **10** VPC calibration curves were constructed, and yields from **8d** were determined by collecting and weighing VPC fractions. All yields are based on converted starting material. Exceptions to these procedures are noted.

***endo*-Tricyclo[3.3.2.0$^{2,4}$]nonan-6-one (8b).** Ketone **14**[8] (4.86 g, 36.2 mmol) was treated with 97% hydrazine (21.4 g) and KOH (28.5 g) in diethylene glycol (86 mL) according to a modified Wolff-Kishner procedure[10] to give 4.1 g (34 mmol) of *endo*-tricyclo[3.2.2.0$^{2,4}$]non-6-ene (**15**). Crude **15** was hydroborated with disiamylborane (34 mmol) in THF following a standard procedure[23] to obtain 3.2 g of *endo*-tricyclo[3.2.2.0$^{2,4}$]nonan-*exo*-6-ol. A sample purified by VPC on column B gave mp 166–168 °C (sealed tube) (lit.[9] 165–168 °C). Oxidation[29] and purification by VPC on column A gave 2.93 g of **8b** as a white solid (59% based on **14**). Analytical samples of **8b, 14,** and **15** had the same physical and spectroscopic properties as those reported.[8,9,11,12]

***exo*-Tricyclo[3.3.2.0$^{2,4}$]decan-6-one (10).** A mixture of *exo*-tricyclo[3.3.2.0$^{2,4}$]dec-9-en-6-one (**16**,[13] 476 mg, 3.21 mmol) and 5% Pd/C (77 mg) in methanol (20 mL) was hydrogenated at atmospheric pressure. Purification by VPC on column B gave 397 mg (82%) of a white solid: mp 116–117 °C (sealed tube): IR (PE-621) 3389 (w), 3079 (w), 3012 (m), 2943 (s), 2926 (s), 2885 (m), 2864 (m), 1704 (s), 1476 (m), 1454 (m), 1427 (m), 1285 (w), 1177 (m), 1160 (m), 1105 (w), 1026 (m), 1014 (w) cm$^{-1}$; NMR (60 MHz) δ 0.36–1.28 (m, 4 H), 1.28–2.06 with major absorption at 1.56 (m, 6 H), 2.06–2.79 (m, 4 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.19; H, 9.55.

***cis*-(*Z*)-Bicyclo[7.1.0]dec-3-ene (31).** *cis,cis*-1,4-Cyclononadiene (62 mg, 0.50 mmol)[21] was cyclopropanated for 18 h with diiodomethane (405 mg, 3 equiv) and zinc-copper couple (198 mg, 6 equiv) in the presence of a catalytic amount of iodine in ether (10 mL).[9,13] Preparative VPC on column A (75 °C, 78 mL/min) gave starting diene (22 min, 16 mg, 74% conversion) and a colorless oil identified as **31** (36 min, 18 mg, 35% based on converted diene): IR 3050 (w), 3000 (m), 2985 (m), 2955 (m), 2930 (s), 2860 (m), 1470 (m), 1435 (w), 1270 (w), 1015 (w), 970 (w), 840 (w), 715 (w), 690 (w) cm$^{-1}$; NMR (60 MHz) δ −0.22 (m, 1 H), 0.20–2.80 (m, 13 H), 4.93–5.87 (m, 2 H).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.24; H, 11.77.

A biscyclopropanated product was also isolated and tentatively assigned as 1α,3β,5β,10α-tricyclo[8.1.0.0$^{3,5}$]undecane (57 min, 6.4 mg, 11% based on converted diene): IR 3055 (m), 2985 (s), 2950 (m), 2930 (s), 2850 (m), 1470 (m), 1440 (w), 1310 (w), 1020 (m), 990 (w), 840 (m) cm$^{-1}$; NMR (60 MHz) δ −0.38 (m, 2 H), 0.083–1.22 with peak maximum of 0.68 (m, 9 H), 1.22–2.45 with peak maximum at 1.63 (m, 7 H).

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.92; H, 12.06.

**Deuterated Ketone 46.** A solution of **8c** (207 mg, 1.38 mmol), anhydrous sodium carbonate (1.46 g, 13.8 mmol), and ethanol-*O-d* was heated at reflux under nitrogen for 43 h. After workup, the crude product was purified by VPC on column B to give 127 mg (60%) of **46.** The NMR spectrum (220 MHz) indicated 79 ± 3% of two deuterium atoms at C(10).

***exo*-Tricyclo[3.3.2.0$^{2,4}$]decan-*anti*-9-ol-*anti*-10-*d* and *exo*-Tricyclo[3.3.2.0$^{2,4}$]decan-*syn*-9-ol-*syn*-10-*d* (50 and 51).** Deuterioboration of **49** (478 mg, 3.56 mmol)[13] was accomplished with $B_2D_6$ as previously described[13] for hydroboration of this olefin to give a quantitative yield of a white solid identified as a mixture of **50** (80%) and **51** (20%) (after separation via their trimethylsilyl ethers[13]) by comparison of the NMR and IR spectra of each with those of the protio analogues.[13] The stereochemistry of deuterium in each alcohol was confirmed by comparison of their $Eu(fod)_3$[30] shifted NMR spectra (60 MHz) with those of the undeuterated alcohols.

***exo*-Tricyclo[3.3.2.0$^{2,4}$]decan-9-one-*anti*-10-*d* and -*syn*-10-*d* (47 and 48).** Oxidation of **50** and **51** with ruthenium tetroxide in $CCl_4$ solution[24] (10 min) followed by VPC purification on column B gave these desired ketones **47** and **48,** respectively.

**Photolysis of *endo*-Tricyclo[3.2.2.0$^{2,4}$]nonan-6-one (8b).** Irradiation of **8b** (197 mg, 1.45 mmol, 0.0290 M, 50.0 mL solution) for 8.00 h followed by VPC analysis on column A (120 °C, 69 mL/min) and using *o*-methylacetophenone (100 min) as internal area standard indicated some starting material (159 min, 90% conversion) and two products (80%) identified as **17** and **18.**

Methyl *cis*-2-methylcyclohex-3-en-1-acetate (**18,** 65 min, 17%): IR (PE-621) 3021 (m), 2960 (s), 2929 (s), 2876 (m), 2842 (m), 1738 (s), 1648 (w), 1435 (s), 1276 (s), 1254 (m), 1199 (m), 1172 (s), 1147 (s), 701 (w), 672 (w), 666 (w) cm$^{-1}$; NMR (60 MHz) δ 0.81 (d, *J* = 6.5 Hz, 3 H), 0.95–2.35 with major absorptions at 1.42, 2.07 (m, 8 H), 3.43 (s, 3 H), 5.24 (m, 2 H). Irradiation at δ 2.00 caused collapse of d into br s.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.22; H, 9.49.

*cis*-Bicyclo[4.3.0]non-2-en-8-one (**17,** 149 min, 63%): IR (PE-621) 3470 (w), 3024 (m), 2925 (s), 2860 (m), 2843 (m), 1742 (s), 1650 (w), 1406 (m), 1161 (m), 1146 (m), 700 (m), 666 (w), 647 (w) cm$^{-1}$; NMR (60 MHz) δ 0.81–2.88 (m, 10 H), 5.37 (m, 2 H).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.25; H, 8.89.

Hydrogenation of **17** (31 mg, 0.23 mmol) was carried out as described below for **19.** VPC purification gave 19 mg (61%) of a colorless liquid the infrared and NMR spectra of which were identical with those of *cis*-bicyclo[4.3.0]nonan-8-one (**34**).[15]

**Photolysis of *endo*-Tricyclo[3.3.2.0$^{2,4}$]decan-9-one (8c).** Ketone **8c** (191 mg, 1.27 mmol, 0.0254 M, 50.0 mL solution)[13] was irradiated for 24.0 h. VPC analysis on column A (initial column temperature 65 °C, raised to 135 °C after 51 min, 69 mL/min) using *p*-xylene (34 min) and valerophenone (167 min) as internal area standards indicated some starting **8c** (184 min, 88% conversion) and seven additional fractions (76%). Infrared and NMR spectroscopy indicated that two of these fractions with retention times of 112 (2.8%) and 119 (3.4%) min were mixtures of two or more products each. The remaining five fractions were identified as **23–27.**

1,4-Cyclooctadiene (**27,** 23 min, 3.2%): This was identical in all respects with an authentic sample prepared by the method of Moon and Ganz.[19]

*cis*-(*Z*)-Bicyclo[6.1.0]non-3-ene (**26,** 43 min, 40%): This was identical in all respects with an authentic sample prepared by equilibration of **38**[17] or by equilibration of **39** with potassium *tert*-butoxide in $Me_2SO$.[18]

Anal. Calcd for $C_9H_{14}$: C, 88.45; H, 11.55. Found: C, 88.31; H, 11.38.

Methyl *cis*-2-methylcyclohept-3-en-1-acetate (**24,** 105 min, 4.7%): IR (PE-621) 3018 (m), 2954 (m), 2929 (s), 2858 (m), 1740 (s), 1648 (w), 1450 (m), 1438 (m), 1259 (m), 1195 (m), 1159 (m), 718 (w), 678 (w) cm$^{-1}$; NMR (60 MHz) δ 1.02 (d, *J* = 7 Hz, 3 H), 1.15–2.88 with major absorptions at 1.63, 2.17 (m, 10 H), 3.60 (s, 3 H), 5.02–5.98 (m, 2 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.70; H, 10.00.

Methyl *cis-endo*-bicyclo[5.1.0]octan-2-acetate (**25,** 132 min, 3.0%): IR (PE-621) 3073 (w), 2994 (m), 2919 (s), 2850 (m), 1740 (s), 1467 (m), 1450 (m), 1435 (m), 1353 (m), 1288 (m), 1273 (m), 1255 (m), 1243 (m), 1213 (m), 1192 (m), 1178 (m), 1148 (m), 1024 (m) cm$^{-1}$; NMR (60 MHz, $CHCl_3$ as internal reference) δ 0–2.62 with major absorptions at 0.35, 0.98, 1.60, 2.35 (m, 15 H), 3.68 (s, 3 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.40; H, 10.00.

*cis*-Bicyclo[5.3.0]dec-2-en-9-one (**23,** 196 min, 19%): IR (PE-621) 3473 (w), 3014 (m), 2928 (s), 2869 (m), 1748 (s), 1450 (m), 1410 (m), 1154 (m), 716 (w), 688 (m) cm$^{-1}$; NMR (60 MHz) δ 1.01–2.75 with major absorptions at 1.71, 2.15 (m, 11 H), 3.08 (m, 1 H), 5.48 (m, 2 H). Irradiation at δ 3.08 simplified m at δ 5.48.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.75; H, 9.34.

Hydrogenation of **23** (85 mg, 0.57 mmol) as for **19** afforded 47 mg (55%) of a colorless liquid identified as **36:** semicarbazone, mp 197.5–198.5 °C dec (lit.[16] 198–199 °C); 2,4-dinitrophenylhydrazone, mp 122–123 °C (lit.[16] 125–126 °C); IR (PE-621) 3465 (w), 2920 (s), 2854 (s), 1742 (s), 1460 (m), 1454 (m), 1442 (m), 1404 (m), 1265 (w), 1240 (w), 1212 (w), 1163 (m) $cm^{-1}$.

**Photolysis of Ketone 46.** The dideuterated ketone **46** prepared above was irradiated (94 mg, 0.62 mmol, 0.025 M) as described for **8c**. The major product was isolated as before and identified as **52**. The NMR spectrum (220 MHz, $CHCl_3$ as internal standard) showed the following differences from that of **26**: $\delta$ −0.084, 0.1 H rather than 1.0 H; 0.60, 1.2 H rather than 2.0 H.

**Photolysis of Ketones 47 and 48.** The monodeuterated ketone **47** (65 mg, 0.43 mmol, 0.017 M) was irradiated as described for **8c**. The major product was identified as a mixture of **53** and **54**. The NMR spectrum (220 MHz, $CHCl_3$ as internal standard) showed the following differences from that of **26**: $\delta$ −0.084, 0.59 H rather than 1.0 H; 0.60, 1.4 H rather than 2.0 H. Similar results were obtained with **48**.

**Photolysis of *exo*-Tricyclo[4.3.2.0^7,9^]undecan-10-one (8d).** Ketone **8d** (86 mg, 0.52 mmol, 0.021 M, 25.0 mL solution) was irradiated for 41.0 h. Preparative VPC of the concentrated photolysate on column A (initial column temperature 70 °C, raised to 150 °C after 46 min, 78 mL/min) afforded starting **8d** (129 min, 36 mg, 58% conversion) and three products (50 mg, 84% based on unrecovered **8d**) which were identified as **31–33**.

*trans*-Bicyclo[7.1.0]dec-3-ene (**32**, 35 min, ~1 mg, ~2%): IR 3050 (w), 3005 (m), 2970 (m), 2920 (s), 2845 (m), 1455 (m), 1440 (m), 1100 (m), 1090 (m), 1070 (m), 1020 (w), 900 (w), 690 (m) $cm^{-1}$. This identification is tentative; see text.

*cis*-(*Z*)-Bicyclo[7.1.0]dec-3-ene (**31**, 43 min, ~1 mg, ~2%): This was identical in all respects with an authentic sample prepared as described above.

Methyl *cis*-bicyclo[6.1.0]nonan-2-acetate **33**, 91 min, 48 mg, 80%): IR 3050 (w), 2980 (m), 2915 (s), 2855 (m), 2840 (m), 1740 (s), 1470 (m), 1450 (m), 1440 (m), 1430 (m), 1350 (w), 1280 (m), 1255 (m), 1245 (m), 1185 (m), 1155 (s), 1130 (m), 1020 (m), 985 (w) $cm^{-1}$; NMR (60 MHz) $\delta$ −0.22 (m, 1 H), 0.23–2.80 with maxima at 1.57, 2.28 (m, 16 H), 3.62 (s, 3 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.37; H, 10.21.

Photolysis of **8d** under the following modified conditions gave essentially the same distribution of products as above: (1) Ketone **8d** (27.2 mg) in 10.0 mL of benzene–3% methanol at reflux for 21.1 h. (2) Ketone **8d** (11.4 mg) in 10 mL of benzene–3% methanol through quartz for 17.4 h (100% conversion). (3) Ketone **8d** (22.9 mg) in 12.0 mL of methanol through quartz for 5.0 h.

**Photolysis of *exo*-Tricyclo[3.2.2.0^2,4^]nonan-6-one (9b).** Ketone **9b** (197 mg, 1.45 mmol, 0.0290 M, 50.0 mL solution) was irradiated for 5.00 h. VPC analysis on column A (initial column temperature 65 °C, raised to 120 °C after 40 min, and raised again to 150 °C after 156 min, 72 mL/min), using *p*-xylene (33 min) and *o*-methylacetophenone (133 min) as internal area standards, indicated some starting **9b** (179 min, 96% conversion) and four products (95%) which were identified as **19–22**.

Cycloheptatriene (**22**, 22 min, 6.7%) was identical in all respects with an authentic sample of cycloheptatriene (Aldrich Chemical Co.).

2-Methylenecyclohex-3-en-1-acetaldehyde (**20**, 113 min, 23%): UV (absolute EtOH) $\lambda_{max}$ ($\epsilon$) 231 nm (27 300); IR (PE-621) 3080 (w), 3030 (m), 2927 (s), 2862 (m), 2840 (m), 2716 (m), 1726 (s), 1639 (m), 1600 (m), 1451 (m), 1435 (m), 887 (s), 587 (m) $cm^{-1}$; NMR (60 MHz) $\delta$ 1.0–3.1 with major absorptions at 1.62, 2.01, 2.39, 2.74 (m, 7 H), 4.56 (m, 2 H), 5.20–5.96 (m, 2 H), 9.27 (t, $J$ = 2 Hz, 1 H).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.17; H, 8.81.

*endo*-Bicyclo[4.1.0]hept-4-en-2-acetaldehyde (**21**, 120 min, 9.6%): IR (PE-621) 3076 (w), 3037 (m), 3005 (m), 2925 (m), 2917 (m), 2897 (m), 2880 (m), 2859 (m), 2818 (m), 2716 (m), 1725 (s), 1639 (w), 1455 (m), 1401 (m), 1024 (m), 697 (m) $cm^{-1}$; NMR (60 MHz) $\delta$ 0.50–1.33 (m, 4 H), 1.33–2.83 with major absorptions at 1.78, 2.28 (m, 5 H), 4.97 (m, 1 H), 5.68 (m, 1 H), 9.30 (t, $J$ = 1.5 Hz, 1 H).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.42; H, 8.90.

Irradiation of **21** (19.7 mg, 0.145 mmol, 0.0145 M, 10.0 mL solution) for 16.1 h followed by VPC analysis indicated **21** (42%) and cycloheptatriene (**22**, 58%).

*trans*-Bicyclo[4.3.0]non-2-en-8-one (**19**, 144 min, 56%): IR (PE-621) 3475 (w), 3025 (m), 2964 (m), 2923 (m), 2895 (m), 2864 (m), 2840 (m), 1748 (s), 1635 (w), 1412 (m), 1183 (m), 1179 (m), 1128 (m), 1118 (m), 680 (m) $cm^{-1}$; NMR (60 MHz) $\delta$ 1.92 (m, 10 H), 5.37 (m, 2 H).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.06; H, 8.96.

Hydrogenation of **19** (73 mg, 0.54 mmol) with 5% Pd/C in methanol at ~1 atm followed by VPC isolation gave 44 mg (59%) of a colorless liquid which had identical infrared and NMR spectra with those of *trans*-bicyclo[4.3.0]nonan-8-one (**35**).[15]

**Photolysis of *exo*-Tricyclo[3.3.2.0^2,4^]decan-6-one (10).** Ketone **10** (97.2 mg, 0.647 mmol, 0.0259 M, 25.0 mL solution) was irradiated for 8.00 h. VPC analysis of the photolysate was carried out on column A (140 °C, 109 mL/min) and yields were determined from calibrated chromatograms. The longest retention time fraction was identified as starting **10** (71 min, 96% conversion) with the other three fractions (68%) identified as **28–30**.

Methyl *trans*-2-methylcyclohex-3-ene-1-propanoate (**29**, 22 min, 26%): IR (PE-621) 3060 (w), 3019 (s), 2952 (s), 2927 (s), 2874 (s), 2841 (s), 1739 (s), 1647 (w), 1459 (s), 1451 (s), 1434 (s), 1418 (m), 1370 (m), 1315 (m), 1300 (m), 1257 (s), 1198 (s), 1170 (s), 1083 (w), 1016 (m), 880 (w), 705 (m), 684 (s) $cm^{-1}$; NMR (60 MHz) $\delta$ 0.83–2.50 with d, $J$ = 7 Hz, at 1.03 (m, 13 H), 3.62 (s, 3 H), 5.47 (m, 2 H). Irradiation at $\delta$ 1.97 caused collapse of d at $\delta$ 1.03 into br s.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.45; H, 9.95.

*exo*-Bicyclo[4.1.0]hept-4-en-2-propanal (**30**, 33 min, 7.9%): IR (PE-621) 3073 (w), 3033 (m), 3006 (m), 2929 (s), 2893 (m), 2858 (m), 2816 (m), 2714 (m), 1790 (w), 1727 (s), 1637 (w), 1451 (m), 1409 (w), 1388 (w), 1169 (w), 1020 (m), 970 (w), 949 (w), 724 (w), 692 (m) $cm^{-1}$; NMR (60 MHz) $\delta$ 0.42–2.80 with major absorptions at 0.65, 1.07, 1.87 and with dt, $J$ = 1, 7 Hz, at 2.42 (m, 11 H), 5.22 (m, 1 H), 5.96 (m, 1 H), 9.74 (t, $J$ = 1 Hz, 1 H).[31]

*trans*-Bicyclo[4.4.0]dec-2-en-9-one (**28**, 45 min, 34%): IR (PE-621) 3055 (w), 3024 (m), 2923 (s), 2863 (s), 2842 (m), 1789 (w), 1716 (s), 1676 (w), 1644 (w), 1455 (m), 1447 (w), 1434 (m), 1428 (m), 1419 (m), 1336 (m), 1315 (m), 1253 (m), 1228 (m), 1213 (m), 1166 (m), 1157 (w), 694 (m), 664 (w), 650 (m) $cm^{-1}$; NMR (60 MHz) $\delta$ 0.95–2.68 with peak maxima at 1.23, 1.48, 1.65, 1.92, 2.12, 2.22, 2.35, 2.42 (m, 12 H), 5.48 (m, 2 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.94; H, 9.50.

Hydrogenation of **28** (76 mg, 0.51 mmol) as described above for **19** gave 59 mg (77%) of a colorless liquid identified as *trans*-2-decalone (**37**) from comparison of its infrared and NMR spectra with those of an authentic commercial sample.

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(31) As noted in the text, no analytically pure sample of this product was obtained. Several samples gave incorrect results for elemental analysis.

# Competitive Condensation and Proton-Transfer Reactions. Temperature and Pressure Effects and the Detailed Mechanism

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**Abstract:** At high pressures ($P \gtrsim 1$ Torr) carbonium ions ($R^+$) and amines (A) undergo proton-transfer reactions yielding $AH^+$ in competition with the formation of condensation products $RA^+$. For example, $t$-$C_4H_9^+$ reacts with $NH_3$ to give $NH_4^+$ in competition with the formation of $t$-$C_4H_9NH_3^+$; $i$-$C_3H_7^+$ reacts with $C_2H_5NH_2$ to give $C_2H_5NH_3^+$ in competition with $i$-$C_3H_7(C_2H_5)NH_2^+$, etc. The product distribution ratio $I_{RA^+}/I_{AH^+}$ increases linearly with third body pressure at low pressures, but levels off to small finite values at high pressures. The product distribution ratio does not vary significantly with temperature between 200 and 500 K in any of five reactions whose temperature dependence was measured. Displacement-exchange reactions such as $i$-$C_3H_7^+ + C_2H_5NH_2 \rightarrow i$-$C_3H_7NH_3^+ + C_2H_6$ do not take place even when those reactions would be more exothermic than the proton-transfer reactions. The pressure effects and the absence of exothermic displacement reactions suggest that the major channel for proton transfer does not proceed through the excited condensation-product-like $\sigma$-bonded complexes $(RA^{+*})_{tight}$. Rather, the data is consistent with a two-stage mechanism (see Scheme II) in which $(RA^{+*})_{tight}$ and $AH^+$ are formed from a common precursor. It is proposed that the collision between $R^+$ and A forms first a loose, electrostatically bonded complex $(R^+{\cdot}A)^*_{loose}$ in which $R^+$ and A undergo multiple internal collisions, some of which may produce $AH^+$ or $RA^{+*}$ depending on the geometry of the intracomplex collision. It is further proposed that a similar two-stage mechanism can account for some unexpected pressure and temperature effects in other ion–molecule reactions.

The theoretical treatment of bimolecular and higher order reactions in general, and ion–molecule reactions in particular, should be greatly facilitated if the reactions proceed through intermediates which possess well-defined structures and whose internal energy is distributed statistically among the internal degrees of freedom. The decomposition rates of such intermediates to products or to reactants may then be calculated using unimolecular decomposition theory.[1] However, in order properly to evaluate the role of the intermediate in the overall reaction, the detailed mechanism of the reaction must be known. The present work deals with the detailed mechanism of competitive condensation and proton-transfer reactions between carbonium ions and alkylamines as model ion–molecule processes.

Several authors have applied unimolecular theory to the decomposition of intermediates in ion–molecule reactions. For example, Buttrill[2] applied statistical unimolecular theory to calculate product distributions in the decomposition of the $C_4H_8^{+*}$ and $C_4H_6^{+*}$ intermediates in the reaction of $C_2H_4^+$ with $C_2H_4$ and $C_2H_2$. Several workers used statistical unimolecular theory to interpret temperature and pressure effects in clustering reactions of protonated amines.[3–5] Olmstead and Brauman[6] used RRKM theory to calculate reaction efficiencies of nucleophilic displacement reactions involving negative ions. Su and Bowers[7] also considered that such an approach may be applicable to the decomposition of the reaction intermediate in proton transfer from $t$-$C_4H_9^+$ to ammonia. In these treatments it was generally assumed that a specifically bonded complex with randomized internal energy is formed in every capture collision of the reactants.

The present work deals with reactions between carbonium ions ($R^+$) and amines (A). At high pressures ($P \gtrsim 1$ Torr) these reactants yield condensation products $RA^+$, in competition with the major product $AH^+$ which results from proton transfer. It is safe to assume that the condensation product $RA^+$ is preceded by a $\sigma$-bonded excited species $RA^{+*}$ whose structure is identical with that of $RA^+$. This intermediate could then be treated by statistical unimolecular theory. The objective of the present study is to use competition kinetics to examine whether proton transfer also proceeds through this

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