3.02 (t), 4.6 (broad d). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48. Found: C, 70.11; H, 6.64.

The compound with X = p-CH₃ had mp 86.5–87.5°, nmr δ 3.05 (t), 4.6 (d). *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.75; H, 6.79. Found: C, 70.39; H, 6.08.

The compound with X = p-Cl had mp 108.5–109°, nmr δ 2.94 (t), 4.43 (d). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.72; H, 5.62. Found: C, 63.94; H, 5.50.

The compound with X = m-Cl had mp 87.5–88.5°, nmr δ 3.00 (t), 4.5 (broad s). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.72; H, 5.62. Found: C, 63.44; H, 5.81.

endo-3-(X-Phenyl)-endo-2-norbornanol Tosylates.—The compound with X = H had mp 113–114° (reported 111–112°),[13] nmr δ 3.12 (2 d), 5.1 (2 d). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48. Found: C, 70.29; H, 6.65.

The compound with X = p-CH₃ had mp 109–109.5°, nmr δ 3.03 (2 d), 5.0 (2 d). *Anal.* Calcd for $C_{21}H_{24}O_3S$: C, 70.77; H, 6.79. Found: C, 71.13; H, 7.00.

The compound with X = p-Cl had mp 123°, nmr δ 3.18 (2 d), 5.02 (2 d). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.7; H, 5.62. Found: C, 63.6; H, 5.68.

The compound with X = m-Cl had mp 123–125°, nmr δ 3.04 (2 d), 5.06 (2 d). *Anal.* Calcd for $C_{20}H_{21}O_3SCl$: C, 63.7; H, 5.62; S, 8.50. Found: C, 63.6; H, 5.60; S, 8.40.

exo-3-(X-Phenyl)-endo-2-norbornanol Tosylate.—The compound with X = H had mp 99–100° (reported 96–97°),[13] nmr δ 2.52 [q(?)], 4.82 (t). *Anal.* Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48. Found: C, 69.6; H, 6.23.

exo-3-Phenyl-exo-2-norbornyl tosylate was prepared from the alcohol supplied by Professor D. C. Kleinfelter, University of Tennessee,[10,13] mp 101–102° (reported[13] 102–103°).

Kinetic Procedures.—Kinetic analyses were performed as described previously.[1] Olefin product yields were calculated from the measured extinction coefficients: 2-phenylnorbornene, ε 14,800 at λmax 262.5 mμ (lit.[19] ε 10,715 at λmax 262.5); 2-p-methylphenylnorbornene, ε 15,600 at λmax 264.5 mμ (lit.[19] ε 12,023 at 264.0); 2-p-chlorophenylnorbornene, ε 18,800 at λmax 267.5 mμ (lit.[19] ε 15,490 at 267.0); 2-m-chlorophenylnorbornene, ε 14,100 at λmax 265.0 mμ.

Registry No.—A (Z = H), 23430-74-2; A (Z = p-CH₃), 23430-75-3; A (Z = p-Cl, 23430-76-4; A (Z = m-Cl), 23430-77-5; B (Z = H), 10472-58-9; B (Z = p-CH₃), 23430-79-7; B (Z = p-Cl, 23430-80-0; B (Z = m-Cl), 23430-81-1; C, 23430-82-2; D, 10472-63-6; 2-p-methylphenylnorbornene, 23430-54-8; 2-m-chlorophenylnorbornene, 23465-01-2; 2-p-chlorophenylnorbornene, 23430-55-9; endo-3-p-methylphenyl-exo-2-norbornanol, 23430-84-4; endo-3-m-chlorophenyl-exo-2-norbornanol, 23430-85-5; endo-3-p-chlorophenyl-exo-2-norbornanol, 23430-86-6; 3-(p-methylphenyl)-2-norbornanone, 23465-02-3; 3-(p-chlorophenyl)-2-norbornanone, 23430-56-0; 3-(m-chlorophenyl)-2-norbornanone, 23430-57-1; endo-(3-p-methylphenyl)-endo-2-norbornanol, 23430-87-7.

Reexamination of Type II Elimination Reactions in the Photolysis of Aliphatic Carboxylic Acids and Amides

COLIN H. NICHOLLS AND PETER A. LEERMAKERS[1]

Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457

Early and sparse accounts of the type II process in simple aliphatic carboxylic acids and amides have been scrutinized experimentally and conceptually. Little of a photochemical nature is known about these important classes of compounds, owing primarily to experimental problems. We have found the early work on these systems to be incomplete and possibly misleading, and thus present the results of our own study of products, quantum yields, and spectroscopy of the above compounds. The type II process does take place, from a high-lying probably n,π* state, in butyric and valeric acid. In the case of the amides, in contrast to a previous report, irradiation at 254 nm causes virtually no reaction of unsubstituted propionamide, butyramide, and valeramide. However, the N,N-dimethyl derivatives do decompose, via the type I process, relatively efficiently via an unspecified electronic state.

The type II photochemical elimination reaction has often been demonstrated to occur readily during the photolysis of such carbonyl compounds as aldehydes, ketones, keto acids, and certain esters; however, evidence for this reaction occurring with aliphatic carboxylic acids and amides is less conclusive. Indeed, very little about the latter processes is known, owing both to experimental difficulty and poor understanding of the relevant spectroscopic states.

Booth and Norrish[2] examined the gaseous products from the photolysis of the aliphatic amides propionamide (C₃), butyramide (C₄), valeramide (C₅), and hexanomide (C₆) dissolved in dioxane or hexane. They obtained some unsaturated hydrocarbon gas, which was established as ethylene (insoluble in concentrated sulfuric acid but soluble in fuming sulfuric acid) for the C₃ and C₄ amides, and inferred as propylene

and butylene for the C₅ and C₆ amides, respectively. Despite the fact that more "ethylene" was obtained from propionamide than from butyramide and that none of the unsaturated gases was identified, the authors suggested that evidence for type II elimination existed. On the other hand Volman[3] found no photodecomposition of aliphatic amides in water at 25°. At 92° he found that the quantum yields for the formation of ammonia from acetamide, propionamide, and butyramide were 0.16, 0.023, and 0.029, respectively. He examined only the gaseous products of the photodegradation, but records no evidence for the formation of ethylene from any of the amides.

The gaseous products from the photolysis of butyric acid dissolved in isooctane or water were determined by Borrell and Norrish.[4] They found that ethylene was a
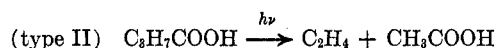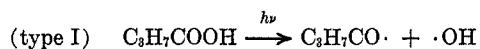
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(1) Alfred P. Sloan Fellow, 1967–1970.

(2) G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952).

(3) D. H. Volman, *J. Amer. Chem. Soc.*, **63**, 2000 (1941).

(4) P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **262**, 19 (1961).

major product from *n*-butyric acid but not from iso-butyric acid, and that, whereas the production of other gaseous products was temperature dependent, suggesting a radical mechanism (type I reaction), the amount of ethylene formed was independent of temperature. By analogy with similar results obtained with ketones and esters they concluded that the ethylene resulted from the type II elimination reaction. Their proposed reactions were

$$(\text{type I}) \quad C_3H_7COOH \xrightarrow{h\nu} C_3H_7CO\cdot + \cdot OH$$

$$(\text{type II}) \quad C_3H_7COOH \xrightarrow{h\nu} C_2H_4 + CH_3COOH$$

In the above investigation no attempt was made to isolate and estimate the acetic acid, the other product in the type II reaction.

The purpose of the present investigation was to re-examine the photolysis of aliphatic acids and amides paying particular attention to the nongaseous products formed. As a secondary (and unfulfilled) hope, some understanding of the natures of the excited states was also sought.

Results and Discussion

Photolysis of Acids.—Irradiation at 253.7 nm of propionic, butyric, and valeric acids dissolved in dioxane or acetonitrile produced significant loss of starting material. One of the major products, apart from gaseous products, from butyric and valeric acids was acetic acid; no trace of acetic acid was detected in the product mixture from propionic acid.

Irradiation was carried out in a Rayonnet irradiator containing sixteen mercury resonance lamps. Accurate quantum yield determinations in this system presents a number of difficulties: the large output of the lamps rapidly exhausts the conventional actinometer solutions, no convenient filter systems are available, and cylindrical sample tubes are employed. Furthermore, irradiation at 253.7 nm is into the edges of the absorption bands of the acids where the extinction coefficients are quite small (<0.3), and, to use concentrations at which loss of starting material can be accurately determined, actinometer solutions with absorbances less than 1.0 are required. Some of these difficulties have been overcome (a) by using as the actinometer chloracetic acid which has an absorption curve at 253.7 nm similar in shape to the substances under investigation, (b) by ensuring that the initial absorbance at 253.7 nm (as determined on a nonscanning Carey 16 spectrophotometer) of all solutions, including the actinometer solutions, were identical (0.56 for 1-cm cells), (c) by restricting irradiation times to ensure no more than 10% loss of starting material, and (d) by bringing the temperature of all solutions to that of the irradiator (48°), which had been run for at least 1 hr to reach a stable temperature. For irradiations longer than 2 hr it was found necessary to replace the actinometer solutions every 2 hr. The value of 0.52 for the quantum yield for chloride ion formation at 48° was obtained from the work of Smith, Leighton, and Leighton.[5]

(5) R. N. Smith, P. A. Leighton, and W. G. Leighton, *J. Amer. Chem. Soc.*, **61**, 2299 (1939).

Utilizing this method of actinometry, the quantum yields for the disappearance of acid (Φ loss) and formation of acetic acid (Φ acid) in dioxane as solvent were determined; the values are given in Table I. The

TABLE I

PHOTOLYSIS OF ACIDS IN DIOXANE IRRADIATED AT 48°
WITH 253.7 nm

Acid	Concentration,[a] *M*	Φ loss[b]	Φ acid[c]
Propionic	2.8	0.19	0.00
Butyric	1.75	0.16	0.05
Valeric	1.75	0.16	0.08

[a] Concentration required to give an absorbance of 0.56 in 1-cm cell at 253.7 nm. [b] Quantum yield for acid loss. [c] Quantum yield for acetic acid formation.

values for acetic acid formation include a small correction factor for the degradation of the acetic acid formed; this was determined by irradiating a solution of propionic acid (from which it had previously been shown no acetic acid formed) containing 5% acetic acid. Very little acetic acid photolysis occurs since it has a much lower extinction coefficient at 253.7 nm compared with the other acids and having such a low concentration, it absorbs very little of the energy available. Similar results to those shown in Table I were obtained with acetonitrile as solvent, but the quantum yields were less accurate owing to discoloration of the solvent after several hours irradiation.

The isolation of acetic acid from butyric and valeric acids is evidence that type II elimination does take place during photolysis of these acids. The results of Borrell and Norrish,[4] based only on evolved gases, have now been much more firmly substantiated. The higher value of Φ acid for valeric acid compared with butyric acid is to be expected since it has been shown[6] that secondary hydrogens are more readily extracted from the γ carbon than are primary hydrogens.

Excitation of Acids by Energy Transfer.—Since the absorbance at 253.7 nm of aliphatic acids in solution is so low (<0.3), the possibility of sensitizing the photolysis by intra- and intermolecular energy transfer from benzene, which absorbs relatively strongly at this wavelength, was investigated. 4-Phenylbutyric and 5-phenylvaleric acids dissolved in cyclohexane were irradiated and examined for the formation of acetic acid styrene, acetic acid, and allyl benzene, respectively. Loss of starting material was also monitored. These materials showed small loss of starting material, but apparently intramolecular energy transfer failed (as also indicated by emission measurements, *vide infra*) since no acetic acid or other expected degradation products of the starting materials were detected. Cursory spectral observation indicated that photolysis is restricted to the benzene ring. Intermolecular energy transfer was also ineffective. Irradiation of butyric and valeric acids in benzene solution yielded no loss of starting material, even after 24 hr of continuous irradiation. However, the benzene solutions became quite yellow, as did the pure solvent control sample, indicating considerable photodegradation of benzene with formation of polymeric material. From these results it is apparent, therefore, that photolysis of carboxylic acids cannot be sensitized by energy transfer from the benzene ring.

(6) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965).

Apparently the triplet energy of the carboxyl group is higher than that of benzene.

Phosphorescence Spectra.—An examination of the phosphorescence spectra, at 77°K, of a series of phenyl derivatives of acids dissolved in EPA gave spectra which were simply those of perturbed benzene phosphorescence, the perturbation decreasing as the carbon chain length increased. Spectra very similar to that obtained from propyl benzene were recorded for 4-phenylbutyric and 5-phenylvaleric acids.

Other Products.—It was noted that irrespective of the reagent being photolyzed in spectroquality cyclohexane, the same major product was isolated by vapor phase chromatography after photolysis for 15–24 hr periods; this product was ultimately identified as bicyclohexyl. Subsequently, it was found that irradiation of the pure Spectrograde solvent also produced bicyclohexyl but in small yields compared with that obtained with the more highly absorbing solutions. This product is undoubtedly formed by the extraction of hydrogen from the cyclohexane.

In most of these investigations using prolonged irradiation with a bank of 253.7-nm lamps, the stability of the solvents has presented difficulties. Degradation products from the solvents have altered the absorbance of the solutions and have complicated the vapor phase chromatographic analyses of the photolysis products. Of the solvents used, benzene degrades quite rapidly, acetonitrile and cyclohexane to a limited extent, whereas dioxane appeared relatively stable.

Photolysis of Amides.—Even after prolonged irradiation (in excess of 24 hr) at 253.7 mn, no loss of amide nor the presence of any photochemical degradation product could be detected in solutions of acetamide, propionamide, butyramide, and valeramide dissolved in dioxane or acetonitrile. This result is in conflict with the report of Norrish[2] in the days prior gas chromatography. It is apparent, therefore, that these amides are quite resistant to photolysis at 48° in these solvents, in accordance with Volman's work[3] which showed that amides were resistant to photolysis in water at 25° but some photodecomposition occurred at temperatures in excess of 50°.

When solutions of the N,N-dimethyl derivatives of acetamide, propionamide, and butyramide were photolyzed in cyclohexane (0.04–0.05 M) and dioxane (0.16–0.20 M) significant loss of amide was detected. The quantum yields recorded are given in Table II.

TABLE II

PHOTOLYSIS OF N,N-DIMETHYLAMIDES IRRADIATED WITH
253.7 nm AT 48°

| | Φ loss, reagent | |
	Cyclohexane	Dioxane
N,N-Dimethylacetamide	0.12	0.10
N,N-Dimethylpropionamide	0.16	0.12
N,N-Dimethylbutyramide	0.15	0.12

Examination by gas chromatography of the solutions after photolysis indicated a complex mixture of products, all in very low concentrations. A careful examination of the products from the photolysis of N,N-dimethylbutyramide revealed no trace of N,N-dimethylacetamide, certainly one of the products ex-

pected if the type II elimination had occurred. To eliminate the possibility that some N,N-dimethylacetamide had been produced, but was itself immediately photolyzed, equal amounts of N,N-dimethylacetamide (equivalent to 5% conversion of the butyramide by the type II process) were added to solutions, of equal absorbance, of the N,N-dimethyl derivatives of propionamide and butyramide. There was a just perceptible, but equal, loss of the acetamide derivative in each case, indicating that no N,N-dimethylacetamide had been produced from the butyramide by the type II elimination reaction.

The absence of evidence for type II elimination indicates that the photolysis of N,N-dimethylamides proceeds by a type I reaction with breakdown of the C–N bond as follows

$$RCON(CH_3)_2 \xrightarrow{h\nu} R - \dot{C}O + \cdot N(CH_3)_2$$
$$R\cdot + CO$$
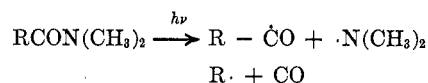
with the alkyl and dimethylamine radicals interacting in a variety of ways. The complexity of the photolysis product mixture indicated that some of the likely photolysis products such as tetramethyl hydrazine and dimethyl propylamine (which we detected in the photolysis of N,N-dimethylbutyramide) underwent subsequent photolysis. Reasons for the greater stability to photochemical degradation of the unsubstituted amides relative to the N,N-dimethyl derivatives are not apparent at present.

It is surprising to find that whereas aliphatic acids undergo type II photochemical elimination, the corresponding amides or N,N-disubstituted amides do not. One possible explanation may be that amide absorption is due to a "charge-transfer" transition, as proposed by Neilsen and Schellman,[7] whereas acids have no such transition (leading to a corresponding excited state) but rather are excited n → π*. However, much more information than is presently available about the excited states of the carboxyl and amide groups will be required before a satisfactory explanation for this apparent anomaly can be reached.

Experimental Section

Chemicals.—All materials were commercially available. The acids, N,N-dimethylamides and chloracetic acid were purified by distillation, the amides by recrystallization from acetone-hexane and the phenyl derivatives of the acids from hexane. The solvents, dioxane, acetonitrile, benzene, and cyclohexane, were Matheson Coleman and Bell Spectrograde, used without further purification.

Spectra.—Absorption spectra were recorded on a Perkin-Elmer 202 spectrophotometer. Absorbances at 253.7 nm were measured on a Carey 16 spectrophotometer. Emission spectra were taken with an Aminco-Bowman spectrofluorometer.

Irradiation.—Samples (5 ml) were degassed and sealed in 15-mm quartz tubes and supported on a revolving tube holder inside a Rayonnet irradiator containing 16 253.7-nm Westinghouse Sterilamp G 8T5 tubes.

Actinometry.—After the lamps had been running for 1 hr to allow the irradiator to reach temperature equilibrium, the actinometer solution, 5 ml of 0.5 M chloracetic acid (absorbance 0.56 at 253.7 nm), in a 15-mm quartz tube was inserted, together with the preheated degassed samples, into the rotating tube holder. For irradiations longer than 2 hr the actinometer tubes

(7) E. B. Neilsen and J. A. Schellman, *J. Phys. Chem.*, **71**, 3914 (1967).

STERIC EFFECTS IN INTRAMOLECULAR REARRANGEMENTS

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were replaced each 2 hr. The chloride ion formed was estimated by volumetric titration with mercuric nitrate.[8]

Analysis of Products.—All nongaseous products were detected by gas chromatography, using a $1/4$-in. column packed with 5% FFAP on Chromosorb W, and compared with authentic samples.

Registry No.—Propionic acid, 79-09-4; butyric acid, 107-92-6; valeric acid, 109-52-4; N,N-dimethyl-

(8) "Standard Methods for the Examination of Water and Waterwaste," 12th ed, American Public Health Association, New York, N. Y., 1965, p 87.

acetamide, 127-19-5; N,N-dimethylpropionamide, 758-96-3; N,N-dimethyllbutyramide, 760-79-2.

Acknowledgments.—The authors are indebted to Mr. Bruce Cochrane for technical assistance, and to the U. S. Army Research Office (Durham), the National Science Foundation, and the Petroluem Research Fund of the American Chemical Society for financial assistance.

Steric Effects in Intramolecular Rearrangements Involving a [3.2.1]-Bicyclic Mechanism[1]

MELVIN S. NEWMAN, SURESH S. GUPTE, AND S. K. SANKARRAPPA

Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210

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Pyrolyses of 1-ethoxyvinyl 2-benzoylbenzoate (5), 1-ethoxyvinyl 6-methyl-2-benzoylbenzoate (6), 1-ethoxyvinyl 3-methyl-2-benzoylbenzoate (7), and 1-ethoxyvinyl 3,6-dimethyl-2-benzoylbenzoate (8) have been studied. Qualitative studies show that the methyl group in the 6 position facilitates the rearrangement to lactone ester whereas a methyl group in the 3 position hinders the rearrangement. An explanation for the facts is presented.

The idea that bicyclic mechanisms might be involved in organic reactions arose from the facts that the rate of alkaline hydrolysis of methyl 6-methyl-2-benzoylbenzoate (1) is greater than that of methyl 2-benzoylbenzoate[2] (2) and the rate of acid-catalyzed esterification of 6-methyl-2-benzoylbenzoic acid (3) is greater than that of 2-benzoylbenzoic acid[3] (4). These facts were explained by assuming that attack of the reagent in question took place mainly at the ketonic group rather than at the carbonyl group of the carboxyl function.
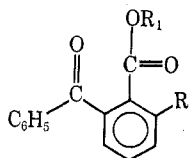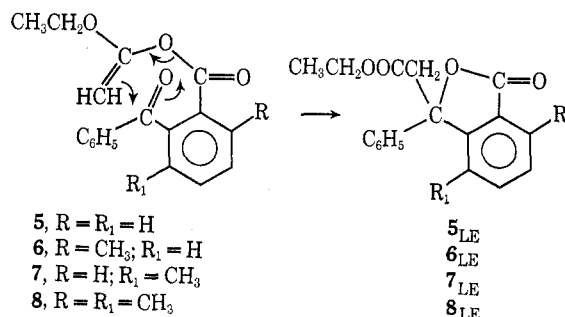

1, R = CH₃; R₁ = CH₃
2, R = H; R₁ = CH₃
3, R = CH₃; R₁ = H
4, R = H; R₁ = H

By synthesizing compounds which had functions at R_1 which could lead to intramolecular cyclization, reactions were found to occur on pyrolysis in which groups ended up preferentially on the ketonic carbonyl carbon rather than the carboxylic carbon. The mechanisms by which these reactions occur have been termed bicyclic mechanisms.[4]

In previous work, no study of steric effects on the rate of reactions proceeding by bicyclic mechanisms was made. In this paper the relative rate of thermal rearrangement of ethoxyvinyl 2-benzoylbenzoate (5), ethoxyvinyl 6-methyl-2-benzoylbenzoate (6), and ethoxyvinyl 3,6-dimethyl-2-benzoylbenzoate (8) to the corresponding lactone esters 5_{LE}, 6_{LE}, and 8_{LE} have

5, R = R₁ = H
6, R = CH₃; R₁ = H
7, R = H; R₁ = CH₃
8, R = R₁ = CH₃

5_LE
6_LE
7_LE
8_LE

been determined qualitatively. As the rate of rearrangement of 6 was greater than that for 5, 7, and 8, the steric assistance noted in alkaline hydrolysis[2] and acidic esterification[3] is also of importance in the intramolecular [3.2.1]-bicyclic rearrangement. However, the presence of a methyl group in the 3 position in compounds 7 and 8 retards the bicyclic path strongly. In the case of 7 rearrangement to 7_{LE} did not occur. Instead, at the temperature of 200–220° needed for pyrolysis, only the normal-pseudo anhydride of 3-methyl-2-benzoylbenzoic acid was formed. Since pyrolysis of 8 gives mainly 8_{LE}, another example of the favorable effect of a methyl group in the 6 position is provided as it overcomes the unfavorable effect of the methyl group at the 3 position.

The favorable effect of the 6-methyl group in the rearrangements of 6 and 8 relative to 5 and 7, respectively, is probably due to two factors: (a) the steric effect of the 6-methyl group which keeps the carboxyl function from coplanarity with the ring (raising the energy of the ground state for the rearrangement) and (b) the relief of strain in the product (lowering the energy of the transition state). The adverse effect of the 3-methyl group probably acts mainly by increasing

(1) This research was supported in part by Grant 5552 of The National Science Foundation and by Grant DA-ARO-D-31-124-G846 from the U. S. Army Research Office, Durham, N. C.

(2) M. S. Newman and S. Hishida, *J. Amer. Chem. Soc.*, **84**, 3582 (1962).

(3) M. S. Newman and C. Courduvelis, *J. Org. Chem.*, **30**, 1795 (1965).

(4) A bicyclic mechanism is defined as an intramolecular cyclic mechanism in which the atoms involved in change of bonding are not in a continuous chain. In cyclic mechanisms the atoms involved form a continuous chain. For examples of [3.2.1]-, [3.3.1]-, and [4.2.2]-bicyclic mechanisms, see the following articles and references therein: (a) M. S. Newman and C. Courduvelis, *J. Amer. Chem. Soc.*, **88**, 781 (1966); (b) M. S. Newman, S. Mladenovic, and L. K. Lala, *ibid.*, **90**, 747 (1968).