185-nm Photolysis and Pyrolysis of the Spirocyclopropane-Substituted Azoalkanes of 2,3-Diazatricyclo[4.3.0.0^{4,9}]non-2-ene and Their Denitrogenated Hydrocarbon Products, the Tricyclo[3.2.0.0^{2,7}]heptanes

Waldemar Adam* and Gerald Zang

Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, Federal Republic of Germany

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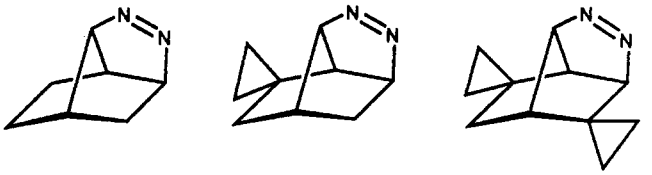
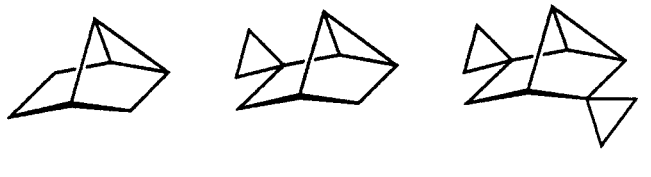
The 185-nm photolysis and pyrolysis of the spirocyclopropane derivatives of the azoalkanes 2,3-diazatricyclo[4.3.0.0^{4,9}]non-2-ene (**1a**), 4′,5′-diazaspiro(cyclopropane-1,8′-tricyclo[4.3.0.0^{3,7}]non-4′-ene) (**1b**), and 4′,5′-diazadispiro(cyclopropane-1,2′-tricyclo[4.3.0.0^{3,7}]non-4′-ene-8′,1″-cyclopropane) (**1c**) and their denitrogenated hydrocarbon derivatives tricyclo[3.2.0.0^{2,7}]heptane (**2a**), spiro(cyclopropane-1,3′-tricyclo[3.2.0.0^{2,7}]heptane) (**2b**), and dispiro(cyclopropane-1,3′-tricyclo[3.2.0.0^{2,7}]heptane-6′,1″-cyclopropane) (**2c**) were investigated. It was shown that the 185-nm photochemical behavior of these substrates does not depend on the degree of spirocyclopropane substitution. As common products in the 185-nm photolysis of the azoalkanes **1a–c** were obtained the tricycloalkanes **2a–c** (major products), the norbornenes **3a–c**, the vinylcyclopentenes **5a–c** (minor products), and the *exo*-methylenecyclohexenes **6a–c** (traces). In the case of the parent azoalkane **1a** additionally bicyclo[3.2.0]hept-2-ene (**4**) and bicyclo[4.1.0]hept-2-ene (**7a**) were detected. The major products in the photolysis of the tricycloheptanes **2a–c** were the vinylcyclopentenes **5a–c**, but also the norbornenes **3a–c** and the methylenecyclohexenes **6a–c** were formed in considerable amounts. Although the norbornenes **3a–c** and the bicyclo[3.2.0]heptene **4a** are logical Wagner–Meerwein rearrangement products, attempts to trap the suspected radical-cationic and zwitterionic intermediates with CF_3CH_2OH failed. Efforts to generate the authentic radical-cationic species by means of photosensitized electron transfer (PET) by using sensitizers such as cyanoarenes, quinones, and pyrylium salts were unproductive. Vibrationally excited bicyclo[2.2.1]hepta-2,7-diyls, generated by the pyrolyses of **2a–c**, are not precursors to the norbornenes **3a–c** because, instead of such rearrangement products, cyclobutane cleavage of the bicyclo[2.1.0]pentane moiety takes place to afford the isomeric vinylcyclopentenes **5′a–c**. Carbene intermediates, produced either from the 1,3-diyl-type species through fragmentation or from the photodenitrogenation of diazoalkanes, which are generated by retro-cleavage of n,π^* excited azoalkanes **1a–c**, in turn obtained through internal conversion of higher excited states such as $^1\pi,\pi^*$, ^{1}n,σ^*, and R_y, are proposed as the most likely precursors to either the vinylcyclopentenes **5a–c** or methylenecyclohexenes **6a–c**, respectively. In violation of Kasha's rule, photochemistry directly from the higher excited states of the azoalkanes **1a–c** competes with internal conversion to the lowest excited state, namely the n,π^* state, as it was shown by the formation of norbornenes **3a–c**.

The 350-nm photochemistry and the thermal behavior of mono- and polycyclic azoalkanes have been the subject of numerous investigations.[1] Nevertheless, up to now no unequivocal assignments have been made that concern the nature of the excited states reached in the 185-nm photolysis of azoalkanes.[2] The first detailed mechanistic comparison of the thermolysis, 350-nm photolysis, sensitized photolysis, and 185-nm irradiation of azoalkanes was made by us some years ago.[3] On the basis of a Salem diagram, a mechanistic scheme was presented in which zwitterions were postulated as probable precursors for the rearrangement products in the 185-nm photolysis. These rearrangement products were not at all or only to a small extent found in the direct 350-nm photolysis or thermolysis.

In this paper, the previous observations were explored experimentally in further detail by investigating the 185-nm photolysis and thermolysis of the azoalkane 2,3-diazatricyclo[4.3.0.0^{4,9}]non-2-ene (**1a**) and its denitrogenated hydrocarbon tricyclo[3.2.0.0^{2,7}]heptane (**2a**), as well as their spirocyclopropane derivatives **1b,c** and **2b,c**. In the case of the azo compounds **1a–c**, the thermolysis and the 350-nm photochemistry have already been reported.[4] For this





reason, azoalkanes **1a–c** are particularly suited substrates for a detailed comparison of the previously investigated modes of denitrogenation with that of the 185-nm photolyses. Since the spirocyclopropane-substituted derivatives **1b,c** and **2b,c** are bichromophoric systems, we posed the question whether a more varied and interesting product spectrum than for the parent systems **1a** and **2a** would be obtained.

Of special interest was to compare the thermolysis with the 185-nm photolysis of the tricycloalkanes **2a–c**. In particular, we questioned whether the primary step in the photochemical reactions was homolytic cleavage of the

(1) (a) Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982. (b) Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973**, *6*, 275. (c) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (d) Adam, W.; De Lucchi, O. *Angew. Chem.* **1980**, *92*, 815.

(2) (a) Adam, W.; Mazenod, F. *J. Am. Chem. Soc.* **1980**, *102*, 7131. (b) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1975; Vols. I and II. (c) Adam, W.; Oppenländer, T. *Angew. Chem.* **1986**, *98*, 659. (d) Meier, H.; Zeller, K.-P. *Angew. Chem.* **1977**, *89*, 876.

(3) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303.

(4) (a) Adam, W.; Carballeira, N.; De Lucchi, O. *J. Am. Chem. Soc.* **1981**, *103*, 6406. (b) Adam, W.; Carballeira, N.; Gillaspey, W. D. *Tetrahedron Lett.* **1983**, *24*, 5473. (c) Adam, W.; Dörr, M.; Hill, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *J. Org. Chem.* **1985**, *50*, 587.

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Table I. Product Studies in the Photolyses of Azoalkanes 1a–c

entry	1a–c[b]	conditions	conversion (%)	mass balance (%)	product distribution[a] (%) 2a–c	3a–c	4a–c	5a–c	6a–c	7a–c
1	1a	185 nm, *n*-pentane	100 (51)[c]	27	73 (77)	8 (3)	<1 (<1)	5 (3)	4 (1)	3 (2)
	Φ, 0.57[d]				0.43[d]	0.076[d]				
2	1a	350 nm, benzene[e]	100	100	93				7	
3	1a	>400 nm, TPT[f]	100	90–100	6	93			1	
4	1b	185 nm, *n*-pentane	100	20	77	7		4	4	
	Φ, 0.62[d]				0.27[d]	0.049[d]				
5	1b	350 nm, benzene[g]	95		99				1	
6	1c	185 nm, *n*-pentane	100	26	88	5		3	2	
	Φ, 0.52[d]				0.51[d]	0.050[d]				
7	1c	350 nm, benzene[g]	75		97				3	

[a] By capillary GC; the deficit from 100% consists of unidentified volatile products (error ca. 2%). [b] a (R + R = R′ + R′ = H), b (R + R = $-(CH_2)_2-$, R′ + R′ = H), and c (R + R = R′ + R′ = $-(CH_2)_2-$). [c] The values in parentheses were determined in a photolysis experiment using CF_3CH_2OH as solvent. [d] Determined by *cis/trans*-cyclooctene actinometry[22] (error ca. 10%). [e] Reference 4a,b. [f] Reference 6; TPT = triphenylpyrylium tetrafluoroborate. [g] Reference 4c.

most strained carbon–carbon bond or whether heterolytic bond cleavage occurred. A further mechanistic query concerned possible trapping of radical-cation-like Rydberg states or zwitterions formed in the 185-nm photolysis of these substrates by a hydroxylic solvent such as CF_3CH_2OH. Fluorinated alcohols are to our best knowledge the only easily available substances that are transparent enough at 185 nm and still sufficiently nucleophilic for trapping cationic intermediates under in situ photolysis conditions.[5]

To assess the chemical behavior of the radical cations derived from the azoalkanes 1 and their corresponding tricycloalkanes 2, it was of interest to generate these species by photosensitized electron transfer (PET) with electron acceptors (EA) such as chloranil and 9,10-dicyanoanthracene. Valuable mechanistic information was expected to be gained by comparing the PET results with those of the 185-nm photolyses. It was expected that removal of an electron from tricycloalkane **2a** would produce its intermediary radical cation $\mathbf{2a}^{\bullet+}$, which subsequently would presumably rearrange within the solvent cage. The resulting product radical cation would reacquire an electron to give the neutral rearrangement product (eq 1).

$$\mathbf{2a} + EA \longrightarrow \left[\mathbf{2a}^{\bullet+}\ EA^{\bullet-}\right]_{\text{solvent cage}} \xrightarrow{\text{in-cage rearrangement}} \left[\text{product}^{\bullet+}\ EA^{\bullet-}\right]_{\text{solvent cage}} \longrightarrow \text{product} + EA \quad (1)$$

Thus, similar product distributions in the PET process and the 185-nm photolysis would provide evidence for a radical-cation-like intermediate in the 185-nm photolysis. Since the PET chemistry was already reported for the azoalkane **1a**,[6] it merely was necessary to investigate it for the corresponding tricycloalkane **2a**. Efforts were also to be expended to observe the radical cation of tricycloalkane **2a** in the PET reaction by time-resolved laser flash photolysis and/or by photo-CIDNP experiments. Presently, we report the results of our investigations.

Results

Starting Materials. The preparation of the azoalkanes **1a–c** and the tricycloalkanes **2a–c** was carried out following literature procedures.[4] The strained hydrocarbons **2b,c** were obtained by direct 350-nm photolysis of **1b,c** and **2a** by benzophenone-sensitized photolysis of the parent compound **1a**.

UV Spectra and Control Photolyses at 254 nm. No regularity in the intensity and patterns of absorption was revealed by the UV spectra of the azoalkanes 1 and hydrocarbons 2. Thus, an increasing degree of spirocyclopropane substitution does not lead to an increasing lgε value or to appearance of fine structure in the 185–215-nm region (*n*-pentane as solvent). The $lg\epsilon_{187}$ values of the azoalkanes vary from 3.39 for **1a** to 4.17 for **1b**; also, the values for the tricycloalkanes **2a–c** fall in this region.

Control photolyses showed that the longer wavelength emissions ($\lambda \geq 254$ nm) of the 185-nm lamps caused negligible formation of photoproducts in the case of the tricycloalkanes **2a–c**. For the azoalkanes **1a–c**, however, lamp output above 300 nm led to denitrogenation and had to be corrected for in the quantitative photolysis experiments.

185-nm Photolyses of the Azoalkanes 1a–c. The results of these experiments are summarized in Table I. The yields of isolated products varied from 20 to 27%. These low yields are due to two main reasons: (a) subsequent photoreactions of the primary products limit the amount of substance that can be accumulated, and (b) due to the high volatility of the hydrocarbon photoproducts, considerable losses in the workup must be reckoned with. The mass balance, determined by capillary GC, varied from 67 to 91% for 16-min irradiation of ca. 0.02 M solutions of **1a–c** in *n*-pentane at 21 °C. Under these conditions losses due to volatility could be minimized.

The results (Table I) clearly demonstrate that spirocyclopropane substitution does not complicate the product studies in the photochemistry of azoalkanes **1a–c** in regard to cyclopropane ring-opening, except the cyclopentene

(5) Zang, G., Thesis, Universität Würzburg, 1990, p. 72.
(6) Dörr, M., Thesis, Universität Würzburg, 1986.

Table II. Product Studies in the 185-nm Photolysis and Pyrolysis of Tricycloalkanes 2a–c

					product distribution[a] (%)				
entry	2a–c[b]	conditions	conversion (%)	mass balance (%)	3a–c	5a–c	5'a–c	6a–c	7a–c
1	2a	185 nm, *n*-pentane	30 (71)[c]	50 (7)	10 (13)	44 (56)[d]		14 (11)	16 (20)
	Φ, 0.30[e]				0.019[e]				
2	2a	540 °C, 15 Torr	82	29			100[d]		
3	2b	185 nm, *n*-pentane	42	39	12	44		12	
	Φ, 0.32[e]				0.014[e]				
4	2b	540 °C, 15 Torr	57	28			100		
5	2c	185 nm, *n*-pentane	38	39	20	37		5	
	Φ, 0.21[e]				0.017[e]				
6	2c	540 °C, 17 Torr	100	32[f]					

[a] By capillary GC; the deficit from 100% consists of unidentified volatile products (error ca. 2%). [b] a (R + R = R' + R' = H), b (R + R = $-(CH_2)_2-$, R' + R' = H), and c (R + R = R' + R' + $-(CH_2)_2-$). [c] The values in parentheses were determined in a photolysis experiment with CF_3CH_2OH as solvent. [d] For the parent system, product **5a** is identical with **5'a**; for mechanistic clearity this mode of presentation was selected. [e] Determined by *cis/trans*-cyclooctene actinometry (error ca. 10%).[22] [f] More than seven dozen products were detected; at 480 °C (17 Torr) 95% **2c** was recovered.

product **5c**. Thus, for all three examples one finds a similar product distribution pattern. Also, the quantum yields showed that there is no influence by the spirocyclopropane rings in that no significant increase in the reactivity was observed on account of these additional chromophores.

In the case of azoalkane **1a**, a trapping experiment with CF_3CH_2OH showed that indeed some further products could be detected by capillary GC, compared with the photolyses in *n*-pentane as solvent. Also, the yield of norbornene (**3a**) was lowered relative to that of 3-vinylcyclopentene (**5a**), which indicates that competing reactions must have intervened. Unfortunately, insufficient product was formed for isolation by preparative GC and thus a rigorous structure determination was precluded.

The cyclopentene products **5b,c** have not been described so far in the literature. To confirm the structure assignment of **5b**, the ^1H NMR spectrum was simulated with the help of the LAOCOONIII program.[7] The very good agreement of the measured and calculated spectrum substantiated the suggested structure. In all other cases, the authentic material itself or at least its ^1H NMR spectrum was available for identification.

The characterized photoproducts are all primary products, which was established by plotting the ratio of the GC area of the particular product and the sum of the GC areas of all products, i.e., $A(P)/\sum A(P)$ versus the irradiation time *t* (cf. Experimental Section, Gas Chromatographic Analyses; one exception could be the cyclopentenes **5a–c**, cf. Discussion). The fact that within the experimental error horizontal lines were obtained for such product plots indicated that no significant secondary photolysis, either decomposition or interconversion, took place in the course of the irradiation period.

A coinjection experiment of independently synthesized 3-allylcyclobutene to the photolysate of azoalkane **1a** and tricycloalkane **2a** showed that this compound is not a photolysis product. This observation is important for our later mechanistic discussion (cf. Scheme II).

185-nm Photolyses and Pyrolyses of the Tricycloalkanes 2a–c. A summary of the results is given in Table II. As one can immediately observe, the product pattern is qualitatively the same as for the azoalkanes **1a–c**, which facilitated the analysis of the products. At conversions of 30–42%, mass balances between 39 and 50% were determined by capillary GC. In comparison to the azoalkanes **1a–c**, these mass balances are notably worse. This is also the case for the quantum yields, which are significantly lower (Φ = 0.21 to 0.32) for the tricycloalkanes than for the azo compounds.

Degradation of the olefinic products **3** and **5–7** by secondary photolysis competes with the primary photoreaction of the tricycloalkanes **2a–c** because the olefins strongly absorb at 185 nm. For example, for norbornene (**3a**) the quantum yield is Φ = 0.18, as already reported by Inoue and Srinivasan,[8] while we determined herein for spironorbornene **3b** Φ = 0.18 and for **3c** Φ = 0.11. We dispensed with the identification of these secondary and possibly even tertiary products because of insufficient material even in preparative-scale runs.

In regard to the possibility that the products **3–7** in the photolysis of the azoalkanes **1a–c** arose only from secondary photolysis of the tricycloalkanes **2a–c**, the already mentioned $A(P)/\sum A(P)$ versus time plots speak against this query. On the other hand, a more convincing argument against this possibility is the fact that the cyclopentenes **5a–c** are by far the major products in the photolyses of **2a–c**. If these were only derived from the secondary photolysis sequence $1 \rightarrow 2 \rightarrow 5$, then **5a–c** should have been the dominant side product in the 185-nm photolysis of the azoalkanes **1a–c**, but instead the norbornenes **3a–c** predominate.

Concerning the dependence of the photochemical behavior of the tricycloalkanes **2a–c** on spirocyclopropane substitution, the product data in Table II reveal that there is no significant influence. Also, the change from *n*-pentane to CF_3CH_2OH for tricycloalkane **2a** did not cause much change in the relative yields of the photoproducts. Nevertheless, the low mass balance, which derives from the poor solubility of tricycloalkane **2a** in CF_3CH_2OH, renders such product studies problematic.

In the pyrolysis, the tricycloalkanes **2a–c** behaved quite differently than in the photolysis. Although the pyrolysis of **2a** at 540 °C (15 Torr) gave the vinylcyclopentene **5a** as the only volatile product, which is also the major product in the photolysis, the spirocyclopropane derivative

(7) Bothner-By, A. A.; Castellano, S. In *Computer Programs for Chemistry*, 1st ed.; De Tar, D. F., Ed.; Benjamin: New York, 1968; Vol. 1.

(8) (a) Inoue, Y.; Mukai, T.; Hakushi, T. *Chem. Lett.* **1982**, 1045. (b) Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 4602.

2b afforded as major product 4-vinylspiro[2.4]hept-5-ene (5'b), i.e., the regioisomer of 6-vinylspiro[2.4]hept-4-ene (5b). When the dispirocyclopropane derivative 2c was subjected to the same pyrolysis conditions as the tricycloalkanes 2a,b, a complex product pattern was observed with more than seven dozen products being detected by capillary GC. Lowering the temperature to 510 °C (17 Torr) still generated close to three dozen products, but at 480 °C (17 Torr) tricycloalkane 2c was stable toward pyrolysis.

In view of this complexity in the pyrolysis of the hydrocarbon 2c, a temperature study was performed on the parent system 2a. Pyrolysis at 680 °C (15 Torr) yielded benzene (13%) and toluene (19%) as major product, with only negligible amounts of other volatile compounds. A control experiment showed that norbornene (3a), which already is transformed into cyclopentadiene and ethene at 400 °C (15 Torr), was not even formed in traces because coinjection of cyclopentadiene to the pyrolysate of 2a indicated the absence of the latter. The formation of benzene and toluene from 2a via 5a is not specific, since also the hydrocarbons 6a or 7a gave benzene and toluene in comparable ratio.

Attempted Generation of the Radical Cation of Tricycloalkane 2a. To generate the radical cation of tricycloalkane 2a, photosensitization experiments with the electron acceptors 9,10-dicyanoanthracene, triphenylpyrylium tetrafluoroborate, chloranil, and 1-cyanonaphthalene were carried out. A nonpolar solvent was desirable, particularly *n*-pentane, because then the PET reaction could be more directly compared with the 185-nm photolysis. Furthermore, it is also known[9] that nonpolar solvents minimize escape of the ion pairs from the solvent cage, which should optimize the chances for observing the desired in-cage rearrangement of the radical cation $2a^{\bullet+}$.

We first repeated successfully Gassman's[10] experiment with tricyclo[4.1.0.0^{2,7}]heptane (Moore's hydrocarbon). He had generated the radical cation of Moore's hydrocarbon with 9,10-dicyanoanthracene as photosensitizing electron-transfer agent and had observed the formation of the dimer product *trans*-dicyclohexen-3-ylethene. Unfortunately, our PET efforts with 9,10-dicyanoanthracene failed for tricycloalkane 2a because 2a was inert under these conditions. With triphenylpyrylium tetrafluoroborate 2a was consumed, but the volatile hydrocarbon products reacted further after the light source was switched off. Small amounts of acid were generated in the course of the photolysis of the pyrylium tetrafluoroborate, which presumably catalyzed the decomposition of the photolysis products derived from the tricycloalkane 2a and thus precluded definitive conclusions whether a photosensitized reaction took place.

Partial success was achieved with chloranil and 1-cyanonaphthalene as photosensitizers. Electronically excited chloranil is a strong oxidant, but only soluble in a polar solvent such as CH_3CN.[11] Indeed, tricycloalkane 2a was readily consumed in the PET reaction with chloranil, but no cage rearrangement product such as norbornene was found.

That electron transfer occurred was established by detection of the radical anion of chloranil (λ_{max} = 435 nm, $\tau_{1/2}$ = 10 μs) during time-resolved laser flash photolysis when a ca. 10^{-3} M solution of chloranil in CH_3CN was irradiated in the presence of the equimolar amount of tricycloalkane 2a under an argon gas atmosphere. Unfortunately, the radical cation $2a^{\bullet+}$ could not be detected in this experiment. Presumably, it is either too short-lived ($\tau < 1$ μs; the observation of shorter lived species is prevented by the T → T absorption of chloranil) and/or it possesses no significant absorption above 380 nm (the strong absorption of chloranil prevents detection below 380 nm).[12]

An attempt to observe photo-CIDNP with chloranil and tricycloalkane 2a gave only weak, undefined signals. No CIDNP effects were exhibited by using the electron acceptors 9,10-dicyanoanthracene, 9-cyanophenanthrene, and 1-cyanonaphthalene in the photolysis with tricycloalkane 2a.[13]

With 1-cyanonaphthalene, a weak photooxidant that is soluble in *n*-pentane, only poor conversion took place during photolysis with tricycloalkane 2a. The amount of impure, volatile hydrocarbon products that could be isolated was too small for a rigorous structure determination. The ^{1}H NMR spectrum of this crude product mixture indicated cyclopropyl but not olefinic protons.

Discussion

The UV spectra of the azoalkanes 1 and tricycloalkanes 2 give no information on the electronic transitions that could be attributed to the spirocyclopropane rings. Similar observations were made by Srinivasan et al.[14]

The 185-nm photochemistry of the azoalkanes 1a–c and tricycloalkanes 2a–c derives undoubtedly from the azo group and the annelated cyclopropane ring. Photoproducts resulting from ring opening of the spirocyclopropane moiety were not found in any of the cases investigated here. Most likely, the low quantum yields with which the spirocyclopropane chromophores react are responsible. Quite similarly, Srinivasan et al.[15] observed in the photolysis of the 2-spirocyclopropane-substituted norbornane a quantum yield for decomposition of merely $\Phi = 0.18$. This apparently cannot compete effectively with the values for the azo group ($\Phi \approx 0.5$–0.6) and the annelated cyclopropane rings ($\Phi \approx 0.3$).

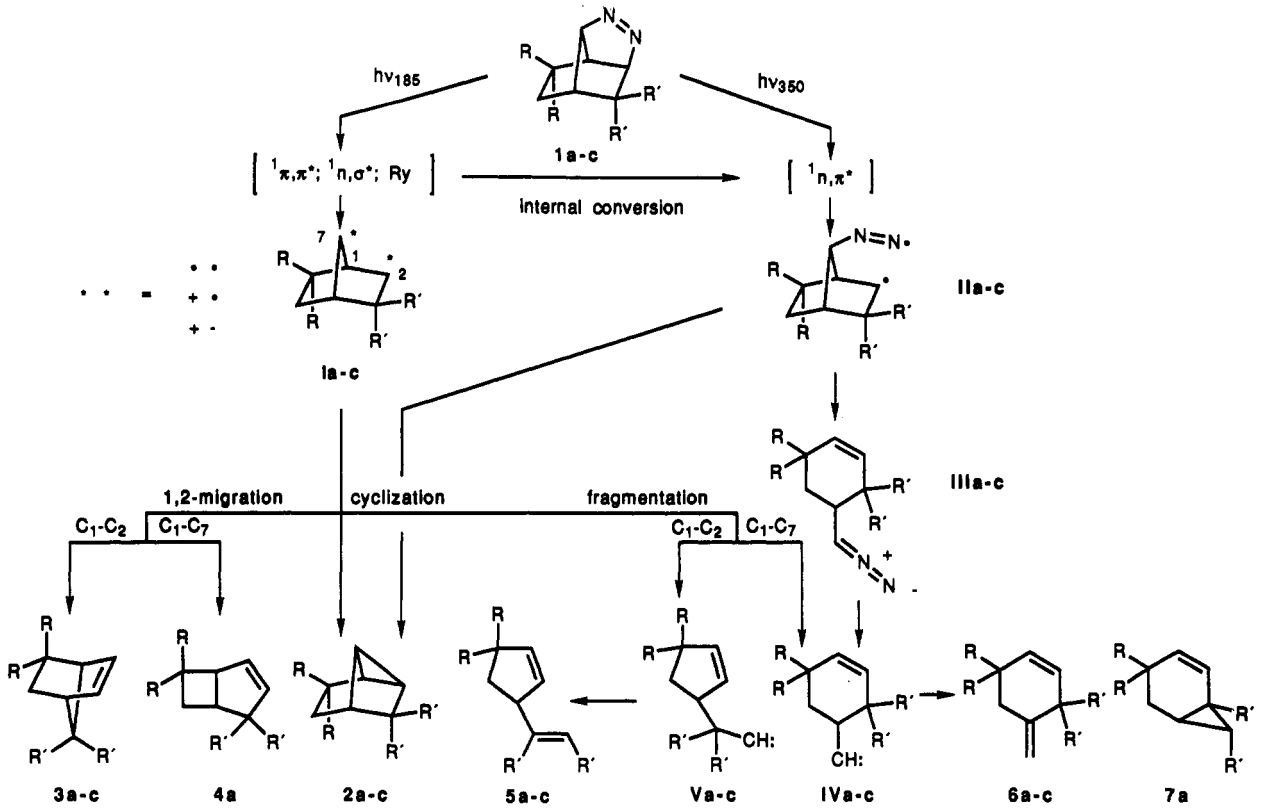
In addition to the 350-nm photolysis of azoalkane 1a,[4b] at 185 nm the hydrocarbons 3–5a are found. The mechanism in Scheme I suggests that in contrast to the direct 350-nm photolysis, presumably higher excited states such as $^1\pi,\pi^*$, ^{1}n,σ^*, and Ry are reached in the 185-nm irradiation. Since these higher energy states are separated from the ^{1}n,π^* state by a large energy gap of ca. 70 kcal/mol,[2d] photochemistry of such higher states may compete with internal conversion, a photophysical behavior regarded as violation of Kasha's rule.[16]

We postulate, therefore, that denitrogenation of the higher excited states leads to the intermediates Ia–c, which may possess substantial diradical character (* * = · ·, cf. Scheme I), or exist in the radical cationic (* * = • +) and/or zwitterionic (* * = +–) forms. Cyclization of the diradical-type intermediates Ia–c into the tricycloalkanes 2a–c is the expected main pathway.

Vibrationally excited singlet intermediates Ia–c appear not to be involved, because the pyrolysis of the tricyclo-

(9) Santamaria, J. In *Photoinduced Electron Transfer Part B*; Fox, M. A.; Chanon, M., Ed.; Elsevier: Amsterdam, 1988; p 483.
(10) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977.
(11) Chanon, M.; Eberson, L. In *Photoinduced Electron Transfer Part A*; Fox, M. A.; Chanon, M., Ed.; Elsevier: Amsterdam, 1988; pp 469, 470.
(12) We thank Dr. H. Görner of the Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, D-4330 Mülheim a.d. Ruhr 1 for carrying out this experiment for us.
(13) We thank Prof. Dr. K. Hildenbrand and Dr. M. Braun at the above address for their help with this experiment.
(14) Srinivasan, R.; Ors, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 3411.
(15) Srinivasan, R.; Baum, T.; Ors, J. A. *Tetrahedron Lett.* **1981**, *22*, 4795.
(16) Turro, N. J. *Modern Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, 1978; p 103.

Scheme I. Mechanism for the 185- and 350-nm Photolyses of Azoalkanes 1a–c[a]



[a] The isolated products are designated by Arabic numerals, the proposed intermediates by Roman numerals, and the degree of spirocyclopropanation by a (R + R = R′ + R′ = H), b (R + R = $-(CH_2)_2-$, R′ + R′ = H), and c (R + R = R′ + R′ = $-(CH_2)_2-$).

alkanes **2a–c** afforded exclusively the cyclopentenes **5′a–c** or their secondary products, which are not observed in the 185-nm photolysis of azoalkanes **1a–c**. Alternatively, the intermediates Ia–c may fragment into the cyclopentenes **5a–c** via carbenes Va–c and cyclohexenes **6a–c** and **7a** via the carbenes IVa–c. Such high-energy pathways are plausible in vacuum-UV photolysis, and precedents have been documented.[17,18a,b] Carbenes IVa–c could as well arise from photodenitrogenation of the diazoalkanes IIIa–c, produced by retrocleavage of the $^1n,\pi^*$ excited state of the azoalkanes **1a–c** via the diazenyl diradicals IIa–c that are formed by internal conversion from their higher excited states $^1\pi,\pi^*$, $^1n,\sigma^*$, and Ry (cf. Scheme I). The latter process has been established in the direct laser photolysis (334–364 nm) of the azoalkanes **1a–c**.[4b,c]

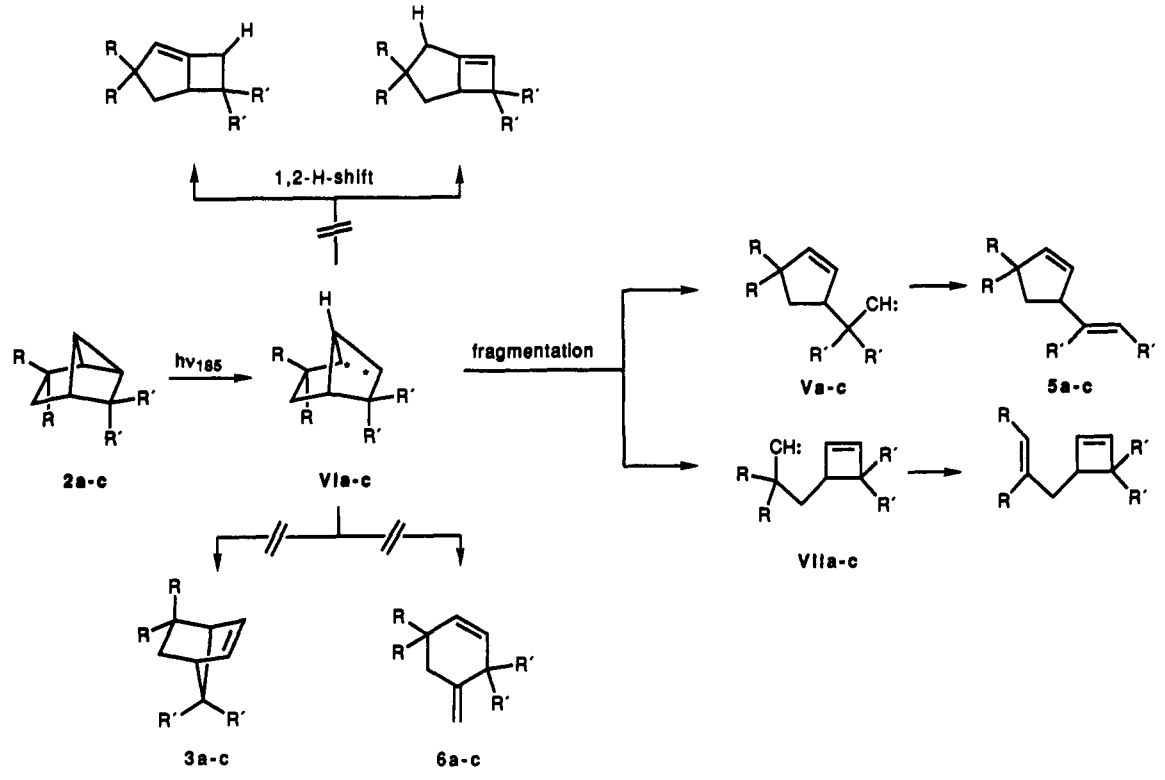
On the basis of the present data it is difficult to decide to which extent the Ia–c → IVa–c → **6a–c** + **7a** pathway competes with the sequence IIa–c → IIIa–c → IVa–c → **6a–c** + **7a** (cf. Scheme I), in view of the fact that the diazoalkanes IIIa–c are photolabile at 185 nm and efficiently denitrogenate. However, the production of the vinylcyclopentenes **5a–c** by way of a diazoalkane, generated in a similar way through internal conversion from the higher excited states $^1\pi,\pi^*$, $^1n,\sigma^*$, and Ry to give the lowest excited state $^1n,\pi^*$ (Scheme I), is improbable because in the direct 350-nm photolysis ($^1n,\pi^*$ excitation) such products were not observed. In view of the high propensity of formation of the vinylcyclopentenes **5a–c** in the 185-nm photolysis of the tricycloalkanes **2a–c**, the observed linear plot of $A(P)/\sum A(P)$ versus t for these products might be an unreliable criterion against subsequent product photolysis, so that **5a–c** could also be formed as secondary products from **2a–c** in the 185-nm photolysis of **1a–c** (**1a–c** and/or **2a–c** → Ia–c → Va–c → **5a–c**). Nevertheless, the absence of vinylcyclopentenes **5a–c** in the direct 350-nm photolysis of the azoalkanes **1a–c** is a puzzling fact. Even if one regards the generation of **5a–c** in the 185-nm photolysis of **1a–c** only as a secondary process arising from the tricycloalkanes **2a–c**, the formation of a ground-state diradical Ia–c as intermediate is necessary. Since such a ground-state diradical Ia–c is considered as precursor of the tricycloalkanes **2a–c** in the 350-nm photolysis of the azoalkanes **1a–c**,[4c] the formation of at least traces of the vinylcyclopentenes **5a–c** is indispensable. Formulating for the 350-nm photolysis of **1a–c** a direct pathway from the diazenyl diradicals IIa–c to **2a–c**, thereby avoiding the diradicals Ia–c (Scheme I), is speculation that merits further investigation.

The norbornenes **3a–c** and the bicyclo[3.2.0]heptene (**4a**) are expected Wagner–Meerwein rearrangement products of radical-cationic and/or zwitterionic forms of the intermediates Ia–c (cf. Scheme I). Previous PET work on azoalkane **1a**[6] established that norbornene (**3a**) is the major product of the corresponding intermediary radical cation; however, it is puzzling that no bicyclo[3.2.0]heptene (**4a**) is formed in the latter process. It is unfortunate that attempts to trap the radical cation of intermediate Ia by CF_3CH_2OH in the 185-nm photolysis of azoalkane **1a** failed. Nevertheless, the fact that in the PET process and in the 185-nm photolyses the norbornene products **3a–c** are observed in significant amounts (cf. Table I) makes radical-cationic species plausible intermediates in the 185-nm photochemistry of the azoalkanes **1a–c**.

In view of the fact that the tricycloalkanes **2a–c** are the predominant products in the 185-nm photochemistry of **1a–c** (Table I), their 185-nm photochemistry was investigated. As the results in Table II display, the dominating

(17) Steinmetz, M. G. In *Organic Photochemistry*; Padwa, A.; Ed.; Marcel Dekker: New York/Basel, 1987; Vol. 8, p 67.
(18) (a) Babad, H.; Flemon, W.; Wood III, J. B. *J. Org. Chem.* **1967**, *32*, 2871. (b) Kirmse, W.; Pook, K. H. *Angew. Chem.* **1966**, *78*, 604.

Scheme II. Alternative Mechanism for the 185-nm Photolysis of Tricycloalkanes 2a–c

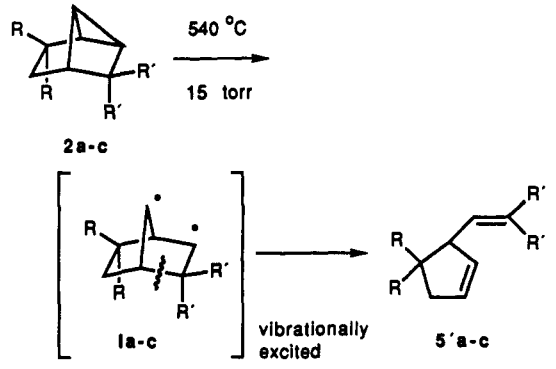


products are the vinylcyclopentenes **5a–c** and not the expected norbornenes **3a–c**, which are significant products in the 185-nm photolysis of the azoalkanes **1a–c** besides the tricycloalkanes **2a–c** (cf. Table I). Either different proportions of the diradical, radical-cationic, and zwitterionic forms of the intermediates Ia–c (Scheme I) intervene in these two processes or an alternative mechanism (Scheme II) operates.

The key distinguishing feature of Scheme II compared to Scheme I is that lateral instead of central cyclopropane bond breaking of the bicyclo[2.1.0]pentane moiety in **2a–c** takes place to afford the intermediates VIa–c (Scheme II) rather than Ia–c (Scheme I). It is difficult to envisage rational pathways of converting VIa–c into the norbornenes **3a–c** and the cyclohexenes **6a–c**; however, additional rearrangement of VIa–c into the 3-allylcyclobutenes via carbenes VIIa–c would support the idea of a pathway **2a–c** → VIa–c → Va–c → **5a–c**. For this reason, it was essential to establish rigorously whether the 3-allylcyclobutenes were formed in the 185-nm photolysis of the tricycloalkanes **2a–c**. For this purpose, the parent 3-allylcyclobutene was prepared and a coinjection experiment showed that not even traces of it could be detected in the 185-nm photolysis of tricycloalkane **2a**. Therefore, the alternative mechanism (Scheme II) is possible but not probable for the 185-nm photochemistry of the tricycloalkanes **2a–c**. Another argument against this mechanism is the fact that the two possible bicyclo[3.2.0]heptenes should have been formed from hydrogen 1,2-shift in the intermediates VIa–c (Scheme II).[19] Despite the fact that a control experiment showed that the bicyclo[3.2.0]hept-1-ene survives the 185-nm photolysis conditions,[3] such products were not observed in the 185-nm photolysis of **2a**. Consequently, the diradical forms (ground state and electronically excited) of the intermediates Ia–c appear to be more plausible precursors to the products **3** and **5** to **7** (Scheme I) also in the 185-nm photolysis of the tricycloalkanes **2a–c**.

(19) Adam, W.; Oppenländer, T. *Tetrahedron Lett.* **1982**, *23*, 5391.

As already stated in connection with the 185-nm photolysis of the azoalkanes **1a–c**, the chemistry of the vibrationally excited diradicals Ia–c was assessed by generating them independently through pyrolysis of the tricycloalkanes **2a–c**. It was found that diradical Ib suffered formal [2+2] cycloreversion to afford the isomeric vinylcyclopentene **5′b** (eq 2). This pyrolytic transformation



(2)

could only be confirmed for the tricycloalkane **2b** because for **2a** the vinylcyclopentenes **5a** and **5′a** are identical and for **2c** the pyrolysate was too complex to detect **5′c**. This is easily understood because the isomeric **5′c** constitutes a methylenecyclopropane, and it is well-established for such labile compounds that they react thermally already at ~170 °C (0.5 Torr) to give complex product mixtures.[20a,b] Thus, we conclude from these experiments that in the photolyses of tricycloalkanes **2a–c** vibrationally excited diradicals Ia–c do not serve as precursors for the vinylcyclopentenes **5a–c** and the other products.

Radical-cationic and zwitterionic forms of the intermediates Ia–c appear to play a role in the photolyses of the tricycloalkanes **2a–c**, since norbornene products **3a–c**,

(20) (a) Crawford, R. J.; Tokunaga, H.; Schrijver, L. M. H. C.; Godard, J. C. *Can. J. Chem.* **1978**, *56*, 998. (b) Le Fevre, G. N.; Crawford, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 1019.

especially pronounced by the relatively high yield of **3c** in the photolysis of **2c**, were observed; but these polar forms of Ia–c are hardly precursors to the vinylcyclopentenes **5a–c** because, if this were so, the yields of **5a–c** should be appreciably larger in the 185-nm photolysis of azoalkanes **1a–c**. In this respect, our attempted trapping experiments of such polar species with CF_3CH_2OH in the 185-nm photolysis of tricycloalkane **2a** revealed no new products. Nevertheless, like Kropp,[21] who used methanol and 238-nm radiation, we also detected trapping products with CF_3CH_2OH in the 238-nm photolysis of 2,3-dimethyl-2-butene.[5] Efforts to generate the radical cations of the tricycloalkane **2a** by photosensitized electron transfer with various sensitizers (cf. Results) were inconclusive. Thus, except for the rearrangement products **3a–c**, we cannot provide at this stage additional mechanistic evidence for the radical-cationic or zwitterionic forms of the intermediates Ia–c in the 185-nm photochemistry of the tricycloalkanes **2a–c**.

We are left with considering the ground-state diradical forms of the intermediates Ia–c as precursors to the vinylcyclopentenes **5a–c**, the cyclohexenes **6a–c**, and **7a** in the 185-nm photolysis of the tricycloalkanes **2a–c**. This implies that a rational pathway is the sequence **2a–c** → Ia–c (diradical form) → Va–c/IVa–c → **5a–c**/**6a–c** and **7a** in Scheme I for the 185-nm photochemistry of these tricycloalkanes. Furthermore, we postulate that different proportions of the diradical, radical-cationic, and zwitterionic forms of the intermediates Ia–c (Scheme I) serve to differentiate mechanistically the photochemical behavior of the azoalkanes **1a–c** and the tricycloalkanes **2a–c** in the vacuum-UV region.

Experimental Section

General Aspects. All photolyses were conducted in degassed, purified *n*-pentane.[22] The 5-mL scale 185-nm photolyses were carried out with a sigmoidal mercury low-pressure capillary lamp No. 4 (Grāntzel Co., Karlsruhe) under a N_2 atmosphere in a closed Suprasil quartz cuvette. For the preparative 185-nm photolyses, the unfiltered light of a low-pressure mercury arc (HNS 10W/U_{OZ}, Osram Co.) was used by performing the irradiations under a nitrogen gas atmosphere in an immersion well vessel.

Quantitative Results. The quantitative results were acquired by electronic integration of capillary GC peaks. The response factor *f* for quantitative measurements was determined by applying eq 3, the percent conversion was calculated according to eq 4, for the relative yields eq 5 was used, and the mass balance was determined by means of eq 6

$$[A(S)/A(IS)]f = [C(S)/C(IS)] \quad (3)$$

$$\% \text{ conversion} = [1 - [A_t(S)/A_t(IS)]/[A_0(S)/A_0(IS)]]100 \quad (4)$$

$$\text{rel yield } (\%) = [A(P)/\sum A(P)]100 \quad (5)$$

$$\% \text{ MB} = [\sum A_t(P)/A_t(IS)]/[A_0(S)/A_0(IS) - A_t(S)/A_t(IS)]100 \quad (6)$$

where $A(S)$ is the peak area of the substrate; $A(IS)$, the peak area of the internal standard; $C(S)$, the concentration of the substrate; $C(IS)$, the concentration of the internal standard; A_t, the peak area at a time t; A_0, the peak area before the reaction; $A(P)$ the peak area of a product; and $\sum A(P)$ the sum of the product peak areas. The gas chromatographically determined yields are within an error of ca. 2% and quantum yields within ca. 10%. The purity of the new compounds was judged to be >90% by capillary GC.

Characterization of the Photoproducts. For preparative purposes, a solution of the azoalkanes **1a–c** in *n*-pentane was flushed with dry nitrogen gas for 15 min to deaerate and irradiated under vigorous magnetic stirring until total consumption of the starting material occurred. The reaction course was monitored by capillary gas chromatography. After completion of the photolysis, the yellow solution was filtered over Al_2O_3 (neutral, activity I), the main part of the solvent removed by distillation (35–36 °C (760 Torr)) on a 30-cm Vigreux column, and the residue submitted to preparative gas chromatography for isolation and purification of the individual products. The products were characterized by ^1H NMR, mass spectrometry, and coinjection of the authentic compounds, when available, on several capillary GC columns.

In the case of the tricyclic hydrocarbons **2a–c**, photolyses on a 5-mL scale were sufficient, since in all experiments the same product patterns as for the azoalkanes **1a–c** were obtained, which facilitated the identification of the products by coinjection of the authentic compounds on several capillary GC columns.

254-nm Control Experiments. Samples (5.00 mL, ca. 0.01 M) of the azoalkanes **1a–c** in *n*-pentane were irradiated with the capillary lamp No. 4 by using a Vycor M 235 cut-off filter or in a Rayonet photochemical reactor (254-nm lamps) at 21 °C for 30–120 min. Before and after the photolysis the samples were examined by capillary GC to determine substrate consumption.

Quantum Yields. The determination of quantum yields of substrate conversion and product formation was achieved by calibrating the capillary lamp with the cyclooctene actinometer.[22]

Preparation of Authentic Materials. 3-Vinylcyclopentene (5a) was prepared as described earlier and further purified by preparative GC (1.5 m, 10% SE 30 on Chromosorb WHP column; N_2 flow of 2.0 kp/cm^2; oven, injector, and detector temperatures of 75 °C for 6 min, raised at 39 °C/min to 170 °C, and kept there for 4 min, 150, 150 °C; t_R = 3.5 min).[23]

4-Methylenecyclohexene (6a) was prepared as earlier reported.[24a–d]

Bicyclo[4.1.0]hept-2-ene (7a) was synthesized by $SnCl_2 \cdot 2H_2O$-mediated rearrangement of tricyclo[4.1.0.0^{2,7}]heptane as reported[25,26a–c] and purified by preparative GC (1.5 m, 10% SE 30 on Chromosorb WHP column; N_2 flow of 1.6 kp/cm^2; oven, injector, and detector temperatures of 100, 160, and 160 °C; t_R = 11.0 min).

3-Allylcyclobutene. (a) 4-Hydroxyhepta-1,6-diene was prepared as described.[27]

(b) 4-Chlorohepta-1,6-diene was prepared by chlorination of the previous 4-hydroxyhepta-1,6-diene as earlier reported.[28]

(c) 1,3,6-Heptatriene was obtained by HCl elimination from the previous 4-chlorohepta-1,6-diene[28] and purified by preparative GC (1.5 m, 10% SE 30 on Chromosorb WHP column; N_2 flow of 1.3 kp/cm^2; oven, injector, and detector temperatures of 70, 120, and 150 °C; t_R = 4.25 min).

(d) 3-Allylcyclobutene. A sample of 94.0 mg (1.00 mmol) 1,3,6-heptatriene (t_R = 7.15 min) in 100 mL of *n*-pentane was irradiated at 254 nm in a Rayonet photochemical reactor (N_2 as inert gas) and the reaction progress monitored by capillary GC (50 m, OV 101 column; N_2 flow of 0.5 kp/cm^2; oven, injector, and detector temperatures of 70, 130, and 150 °C). An intermediate, presumably *cis*-1,3,6-heptatriene (t_R = 7.22 min) was detected, which was converted to 3-allylcyclobutene as major final product (t_R = 6.80 min). After 10 h of irradiation, nearly all of the starting material was consumed. The *n*-pentane was removed by distillation at 36 °C on a 30-cm Vigreux column and the residue submitted to duplicate preparative GC to afford 10.0 mg (11%) 3-allylcyclobutene as colorless liquid (1.5 m, 10% SE 30 on Chromosorb WHP column; N_2 flow of 1.5 kp/cm^2; oven, injector, and detector temperatures of 70, 150, and 150 °C; t_R = 11.5 min): GC–FTIR 3082, 3055, 2989, 2922, 2857, 1649, 1455, 1300, 993, 914, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.11 (d, $J_{4,4'}$ = 13.4 Hz,

(21) Kropp, P. J.; Reardon, E. J., Jr.; Gaibel, Z. L. F.; Williard, K. F.; Hattaway, J. H., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 7058.
(22) Adam, W.; Oppenländer, T. *Photochem. Photobiol.* **1984**, *39*, 719.
(23) Hill, E. A.; Theissen, R. J.; Cannon, C. E.; Miller, R.; Guthrie, R. B.; Chen, A. *J. Org. Chem.* **1976**, *41*, 1191.
(24) (a) Wilcox, C. F., Jr.; Chibber, S. S. *J. Org. Chem.* **1962**, *27*, 2210. (b) Wilcox, C. F., Jr.; Chibber, S. S. *J. Org. Chem.* **1962**, *27*, 2332. (c) Rey, M.; Begrich, R.; Kirmse, W.; Dreiding, A. S. *Helv. Chim. Acta* **1968**, *51*, 1001. (d) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 514.
(25) Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7748.
(26) (a) Dehmlow, E. V. *Angew. Chem.* **1977**, *89*, 521. (b) Doering, W. von E.; Hoffmann, A. K. *J. Am. Chem. Soc.* **1954**, *76*, 6162. (c) Gassman, P. G.; Richmond, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2090.
(27) Marvel, C. S.; Baumgarten, H. E. *J. Polym. Sci.* **1951**, *6*, 127.
(28) Saytzeff, M. *Liebigs Ann. Chem.* **1877**, *185*, 144.

1 H, 4-H), 2.22 (m_c, 2 H, 5-H), 2.65 (ddd, $J_{4',4}$ = 13.4 Hz, $J_{4',3}$ = 4.1 Hz, $J_{4',2}$ = 0.9 Hz, 1 H, 4'-H), 2.88 (m_c, 1 H, 3-H), 4.98 (dddd, $J_{7',8}$ = 10.3 Hz, $J_{7',7}$ = 2.2 Hz, $J_{7',5}$ = 1.1 Hz, 1 H, 7'-H), 5.03 (dddd, $J_{7,8}$ = 17.0 Hz, $J_{7,7'}$ = $J_{7,5}$ = 1.8 Hz, 1 H, 7-H), 5.84 (dddd, $J_{6,7}$ = 17.0 Hz, $J_{6,7'}$ = 10.3 Hz, $J_{6,5}$ = 6.8 Hz, 1 H, 6-H), 6.04–6.06 (m, 1 H, 2-H), 6.10 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 38.6, 36.3 (d, C-4, C-5), 43.1 (d, C-3), 115.0 (t, C-7), 135.3, 137.1, 140.4 (d, C-1, C-2, C-6); GC–MS (70 eV) *m/e* 94 (1, M^+), 93 (11), 91 (13), 80 (5), 79 (100), 78 (8), 77 (40), 67 (8), 66 (27), 65 (10), 63 (5), 54 (5), 53 (76), 52 (6), 51 (12), 50 (6), 41 (18), 39 (41), 38 (6), 27 (28).

185-nm Photolyses. 2,3-Diazatricyclo[4.3.0.0^{4,9}]non-2-ene (1a). A sample of 371 mg (3.04 mmol) azoalkane **1a** in 200 mL of *n*-pentane was irradiated for 120 min with the HNS 10 W/U_{OZ} lamp. The products were isolated in a total yield of 27% by preparative GC (1.5 m, 10% CW 20 M on Volaspher A2 column; N_2 flow of 1.2 kp/cm^2; oven, injector, and detector temperatures of 70, 125, and 150 °C). The relative yields of photoproducts are given in Table I. The retention times in parentheses are capillary GC values (50 m, OV 101 column; N_2 flow of 0.5 kp/cm^2; oven, injector, and detector temperatures of 70, 125, and 150 °C). The following products were identified by ^{1}H NMR, independent synthesis, and/or capillary GC coinjection of authentic material: **3-vinylcyclopentene (5a)**, t_R = 6.0 (8.30) min, ca. 9 mg (ca. 0.10 mmol);[23] **norbornene (3a)**, t_R = 6.0 (8.70) min, ca. 11 mg (ca. 0.12 mmol), ^{1}H NMR;[29] **bicyclo[3.2.0]hept-2-ene (4a)**, t_R = 7.3 (9.46) min, ca. 2 mg (ca. 0.02 mmol), ^{1}H NMR;[30,24d] **4-methylenecyclohexene (6a)**, t_R = 9.3 (9.59) min, ca. 5 mg (ca. 0.05 mmol), ^{1}H NMR;[24d] **tricyclo[3.2.0.0^{2,7}]heptane (2a)**, t_R = 9.3 (10.2) min, ca. 45 mg (ca. 0.48 mmol), ^{1}H NMR;[4a] **bicyclo[4.1.0]hept-2-ene (7a)**, t_R = 13.8 (11.1) min, ca. 1 mg (ca. 0.01 mmol), ^{1}H NMR.[25]

In an attempted trapping experiment, a sample of 205 mg (1.68 mmol) of **1a** in 5 mL of CF_3CH_2OH was irradiated for 5 h with the capillary lamp. Capillary GC analysis as earlier established that the C_7H_{10} hydrocarbons were formed in nearly the same relative yields as in *n*-pentane (cf. Table I). Smaller amounts of at least seven compounds with longer retention times were also detected, but besides recovery of ca. 100 mg **1a**, only traces (<1 mg) of possible trapping products could be obtained by preparative GC, too small for structure elucidation by ^{1}H NMR.

4',5'-Diazaspiro(cyclopropane-1,8'-tricyclo[4.3.0.0^{3,7}]non-4'-ene) (1b). A sample of 237 mg (1.60 mmol) of **1b** in 200 mL of *n*-pentane was irradiated for 105 min with the HNS 10W/U_{OZ} lamp. The products were isolated in 20% yield by preparative GC (1.5 m, 10% CW 20 M on Chromosorb WHP 80/100 column; N_2 flow of 1.3 kp/cm^2; oven, injector, and detector temperatures of 70, 120, and 150 °C). Relative yields of the photoproducts are given in Table I. The retention times in parentheses are capillary GC values (50 m, OV 101 column; N_2 flow of 1.0 kp/cm^2; oven, injector, and detector temperatures of 70 °C for 15 min, raised at 25 °C/min to 130 °C, and kept for 10 min, 150, and 200 °C). The following products were identified by ^{1}H NMR, GC–MS, independent synthesis, and/or capillary GC coinjection of authentic material: **Spiro(bicyclo[2.2.1]hept-5-ene-2,1'-cyclopropane) (3b)**, t_R = 22.0 (7.50) min, ca. 5 mg (ca. 0.04 mmol), ^{1}H NMR;[4c] **7-methylenespiro[2.5]oct-4-ene (6b)**, t_R = 48.0 (9.15) min, ca. 1 mg (ca. 0.01 mmol), ^{1}H NMR;[4c] **spiro(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane (2b)**, t_R = 58.0 (9.33) min, ca. 30 mg (ca. 0.25 mmol), ^{1}H NMR;[4c] **6-vinylspiro[2.4]-hept-4-ene (5b)**, t_R = 26.5 (7.33) min, ca. 2 mg (ca. 0.02 mmol), ^{1}H NMR (($CDCl_3$, 400 MHz) δ 0.57–0.73 (m, 4 H, 1-H, 2-H), 1.70 (dd, $J_{7',7}$ = 12.5 Hz, $J_{7',6}$ = 5.8 Hz, 1 H, 7'-H), 2.09 (dd, $J_{7,7'}$ = 12.5 Hz, $J_{7,6}$ = 8.8 Hz, 1 H, 7-H), 3.51 (m_c, 1 H, 6-H), 4.92 (ddd, $J_{9',8}$ = 10.0 Hz, $J_{9',9}$ = 1.8 Hz, $J_{9',6}$ = 0.8 Hz, 1 H, 9'-H), 5.02 (ddd, $J_{9,8}$ = 17.0 Hz, $J_{9,9'}$ = 1.8 Hz, $J_{9,6}$ = 0.8 Hz, 1 H, 9-H), 5.28 (dd, $J_{4,5}$ = 5.5 Hz, $J_{4,6}$ = 2.0 Hz, 1 H, 4-H), 5.56 (dd, $J_{5,4}$ = 5.5 Hz, $J_{5,6}$ = 2.3 Hz, 1 H, 5-H), 5.84 (ddd, $J_{8,9}$ = 7.0 Hz, $J_{8,9'}$ = 10.0 Hz, $J_{8,6}$ = 7.5 Hz, 1 H, 8-H)), GC–MS ((70 eV) *m/e* 120 (8, M^+), 105 (36), 92 (24), 91 (100), 79 (51), 78 (49), 77 (44), 66 (23), 65 (29), 63 (17), 53 (19), 52 (17), 51 (41), 50 (17), 41 (40)).

4',5'-Diazadispiro(cyclopropane-1,2'-tricyclo[4.3.0.0^{3,7}]-non-4'-ene-8',1''-cyclopropane) (1c). A sample of 417 mg (2.39 mmol) **1c** in 200 mL of *n*-pentane was irradiated for 90 min with the HNS 10W/U_{OZ} lamp. The products were isolated in 26% yield by preparative GC (1.5 m, 10% Apiezon on Chromosorb WHP column; N_2 flow of 1.2 kp/cm^2; oven, injector, and detector temperatures of 110, 125, and 160 °C). Relative yields of the photoproducts are given in Table I. The retention times in brackets are capillary GC values (50 m, OV 101 column; N_2 flow of 1.0 kp/cm^2; oven, injector, and detector temperatures of 80 °C for 15 min, raised at 25 °C/min to 140 °C, and kept there for 15 min, 125, and 150 °C). The following products were identified by ^{1}H NMR, GC–MS, independent synthesis, and/or capillary GC coinjection of authentic material: **dispiro(cyclopropane-1,2'-bicyclo[2.2.1]hept-5'-ene-7',1''-cyclopropane) (3c)**, t_R = 4.5 (12.4) min, ca. 3 mg (ca. 0.02 mmol), ^{1}H NMR;[4c] **dispiro-(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane-6',1''-cyclopropane) (2c)**, t_R = 7.0 (15.4) min, ca. 75 mg (ca. 0.51 mmol), ^{1}H NMR;[4c] **9-methylenedispiro[2.2.2.]dec-4-ene (6c)**, t_R = 8.8 (16.8) min, ca. 6 mg (ca. 0.04 mmol), ^{1}H NMR;[4c] **6-cyclobut-1-enylspiro[2.4]hept-4-ene (5c)**, t_R = 8.8 (17.2) min, ca. 7 mg (ca. 0.05 mmol), ^{1}H NMR (($CDCl_3$, 400 MHz) δ 0.52–0.74 (m, 4 H, 2-H, 3-H), 1.82 (dd, $J_{7',7}$ = 12.9 Hz, $J_{7',6}$ = 5.6 Hz, 1 H, 7'-H), 2.02 (dd, $J_{7,7'}$ = 12.9 Hz, $J_{7,6}$ = 9.0 Hz, 1 H, 7-H), 2.31–2.34 (m, 2 H, 10-H), 2.38–2.48 (m, 2 H, 11-H), 3.45–3.53 (m, 1 H, 6-H), 5.26 (dd, $J_{4,5}$ = 5.6 Hz, $J_{4,6}$ = 2.4 Hz, 1 H, 4-H), 5.61 (dd, $J_{5,4}$ = 5.6 Hz, $J_{5,6}$ = 2.4 Hz, 1 H, 5-H), 5.68 (psq, $J_{9,10}$ = $J_{9,11}$ = 1.1 Hz, 1 H, 9-H)), GC–MS ((70 eV) *m/e* 146 (15, M^+), 131 (19), 117 (34), 115 (17), 93 (15), 92 (24), 91 (100), 79 (30), 78 (28), 77 (80), 65 (63), 63 (39), 53 (80), 52 (33), 51 (89), 50 (33), 41 (90)).

Tricyclo[3.2.0.0^{2,7}]heptane (2a). A sample of 12.9 mg (0.137 mmol) **2a** in 5.00 mL of *n*-pentane was irradiated with the capillary lamp for 70 min (Table II). In an attempted trapping experiment, a sample of 22.5 mg (0.239 mmol) **2a** in 2.50 mL of CF_3CH_2OH was irradiated with the capillary lamp for 75 min (Table II). In view of the low solubility of tricycloheptane **2a** in CF_3CH_2OH, losses of the rather volatile hydrocarbon photoproducts in the course of the irradiation are quite likely, thereby accounting for the low mass balance. No trapping products could be detected by capillary GC analysis of the photolysate.

Spiro(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane) (2b). A sample of 16.0 mg (0.134 mmol) of **2b** in 5.00 mL of *n*-pentane was irradiated with the capillary lamp for 90 min (cf. Table II).

Dispiro(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane-6',1''-cyclopropane) (2c). A sample of 12.6 mg (0.0860 mmol) of **2c** in 5.00 mL of *n*-pentane was irradiated with the capillary lamp for 41 min (Table II).

Pyrolyses. Tricyclo[3.2.0.0^{2,7}]heptane (2a). A sample of 166 mg (1.76 mmol) of **2a** was volatilized at 21 °C (15 Torr) into a 50-cm quartz tube of 13-mm inner diameter kept at 540 °C. The products were collected in a cooling trap at −78 °C. By means of capillary and preparative GC, it was established that 40.0 mg (24%) of 3-vinylcyclopentene (**5a**) and 30.0 mg (18%) of recovered **2a** were formed. Compound **5a** was identified by its ^{1}H NMR and ^{13}C NMR spectra. At 680 °C (15 Torr) were obtained from 155 mg (1.65 mmol) of **2a** 20.0 mg (0.256 mmol) of benzene and 30.0 mg (0.326 mmol) of toluene. Control pyrolyses established that 3-vinylcyclopentene (**5a**), 4-methylenecyclohexene (**6a**), and bicyclo[4.1.0]hept-2-ene (**7a**) gave benzene and toluene in comparable amounts.

Spiro(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane) (2b). A sample of 87.0 mg (0.724 mmol) **2b** was pyrolyzed as earlier at 540 °C (15 Torr) to afford 13.8 mg (16%) of 4-vinylspiro-[2.4]hept-5-ene (**5'b**), 8.40 mg (10%) of a complex volatile fraction, which consisted of at least two dozen components, and 37.8 mg (43%) of tricycloheptane **2b**. Pyrolysis product **5'b** was purified by preparative GC (1.5 m, 10% Carbowax 20M on Volaspher A2 column; N_2 flow of 1.6 kp/cm^2; oven, injector, and detector temperatures of 80, 150, and 150 °C; t_R = 8.0 min). Its structure was assigned on the basis of the following spectral data: IR ($CDCl_3$) 3065, 3000, 2980, 2920, 2890, 2840, 1635, 1610, 1600, 1495, 1442, 1420, 1345, 1255, 1215, 1015, 1000, 960, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.50 (mc, 4 H, 1-H, 2-H), 2.24 (dddd, $J_{7(7'),7'(7)}$ = 16.6 Hz, $J_{7(7'),6}$ = $J_{7(7'),5}$ = $J_{7(7'),4}$ ≈ 1.7 Hz, 1 H, 7(7')-H), 2.45 (dddd, $J_{7'(7),7(7')}$ = 16.6 Hz, $J_{7'(7),6}$ = $J_{7'(7),5}$ = $J_{7'(7),4}$ ≈ 2.4 Hz, 1 H, 7'(7)-H), 2.91 (md, $J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 4.84–4.91 (m, 2 H, 9-H), 5.55 (mc, $J_{8,4}$ = 9.0 Hz, 1 H, 8-H), 5.67 (dddd, $J_{5(6),6(5)}$ = 5.9 Hz, $J_{5(6),4}$ = $J_{5(6),7(7')}$ = $J_{5(6),7'(7)}$ = 2.2 Hz, 1 H, 5(6)-H), 5.83 (dddd, $J_{6(5),5(6)}$

(29) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Thieme: Stuttgart, 1979; p 152.

(30) We thank Prof. Dr. M. Christl for a sample of **4a**.

= 5.9 Hz, $J_{6(5),4} = J_{6(5),7(7')} = J_{6(5),7'(7)}$ = 2.1 Hz, 1 H, 6(5)-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 9.79, 14.2 (t, C-1, C-2), 23.6 (s, C-3), 42.6 (t, C-7), 56.4 (d, C-4), 113.9 (t, C-9), 131.1, 133.8, 139.7 (d, C-5, C-6, C-8); GC-MS (70 eV) m/e 120 (3, M^+), 105 (22), 93 (7), 92 (84), 91 (100), 79 (16), 78 (7), 77 (18), 66 (6), 65 (14), 63 (5), 53 (6), 51 (10), 44 (7), 41 (9), 39 (21). Capillary GC conditions for GC-MS analysis: 30 m SE 30 column; helium gas flow of 1.0 kp/cm^2; oven, injector, and interface temperatures of 50, 180, and 175 °C; t_R = 10.5 min.

Dispiro(cyclopropane-1,3'-tricyclo[3.2.0.0^{2,7}]heptane-6',1''-cyclopropane) (2c). A sample of 470 mg (3.21 mmol) of 2c was pyrolyzed as earlier at 540 °C (17 Torr) to afford 150 mg (41%) of a complex mixture, which consisted of at least seven dozen components, as established by capillary GC. When a sample of 365 mg (2.50 mmol) of 2c was pyrolyzed at 510 °C (17 Torr), 195 mg (53%) of a complex mixture of more than three dozen components was detected, while pyrolysis of 390 mg (2.67 mmol) of 2c at 480 °C (17 Torr) led to recovery of 370 mg (95%) starting tricycloheptane.

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Synthesis of α-Halocinnamate Esters via Solvolytic Rearrangement of Trichloroallyl Alcohols

William J. Kruper, Jr.,* and Albert H. Emmons

Organic Chemicals and Polymers Laboratory, Central Research, Dow Chemical U.S.A., Midland, Michigan 48674

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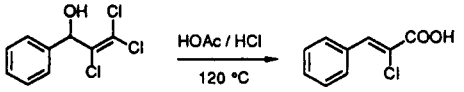
Aryl trichlorovinyl ketones undergo regioselective reduction to the corresponding carbinols with sodium borohydride in alcoholic solvents and are transformed to the (*Z*)-α-chlorocinnamate ester derivatives via an acid-catalyzed allylic rearrangement. Michael addition of ammonia to these ester derivatives affords *cis*- and/or *trans*-aziridine amides. The facile rearrangement allows the synthesis of *d,l*-phenylalanine derived from perchloroethylene and toluene.

Introduction

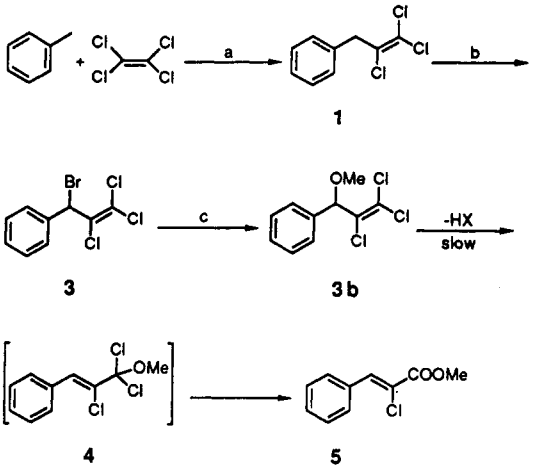
During the course of our investigations into the use of perchloroethylene as an inexpensive, commodity precursor to halogenated dienes and new, flame retardant epoxides,[1] we noted its potential as a two-carbon annelating agent for the benzyl radical (Scheme I), resulting in the formation of 1.[2] The trichlorovinyl group has served as a valuable precursor to substituted acetylenes[3] and other compounds of agricultural interest.[4] In addition, the similar oxidation state of 1 and phenylalanine prompted us to consider simple approaches to the selective hydrolysis of the trichlorovinyl group of this substrate; however, no practical methods for this transformation have been reported.[5] A related hydrolysis involving an acid-catalyzed rearrangement of 1-hydroxy-1-phenyl-2,3,3-trichloro-2-propene (2) to α-chlorocinnamic acid in low yield has been described by Zakharkin and co-workers.[6]



(1)

2 2b

Scheme I[a]



[a] Key: a Cl_2 initiator, 625 °C quartz hot tube; b, Br_2, CCl_4, AIBN; c, MeOH, H_2SO_4, 105 °C.

Since α-halocinnamate esters are useful in the preparation of aziridines,[7] optically active α-halo esters,[8] amino acids,[9] and other heterocyclic systems,[10] facilitation of this

(1) (a) Kruper, W. J., Dow Chemical Co. U.S. Patent 4,668,832, 1987. (b) Pawloski, C. E.; Kruper, W. J., Dow Chemical Co. U.S. Patent 4,668,710, 1987.

(2) Schemerling, L.; West, J. P. *J. Am. Chem. Soc.* **1953**, *75*, 6098-6104.

(3) Liese, T.; Splellstaben, G.; de Meijere, J. *Tetrahedron Lett.* **1982**, *23*, 3241-44.

(4) (a) Gajewski, R. P.; Jackson, J. L.; Jones, N. D.; Swartzendruber, J. K.; Deeter, J. B. *J. Org. Chem.* **1989**, *54*, 3311-3317. (b) Hackett, A. G.; Kotyk, J. J.; Fujiwara, H.; Logusch, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 3669-3671.

(5) The acid-catalyzed addition of vinylidene chloride to tertiary carbocations occurs with hydrolysis to afford the tertiary alkylacetic acids and esters: (a) Randriamahefa, S.; DesChamps, P.; Gallo, R.; Grangette, H. *Synthesis* **1985**, *5*, 493-495. (b) Bott, K.; Helman, H. *Angew Chem., Int. Ed. Engl.* **1966**, *5*, 870-874. The analogous reaction with trichloroethylene or substituted trichloroethylenes is considerably more difficult and has its limitations: Bott, K. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 171-178.

(6) Zakharkin, L. I. *Acad. Sci. U.S.S.R.; Bull. Div. Chem. Sci.* **1956**, 303-310. The difficulty encountered in the rearrangement of (trichlorovinyl)carbinols of α-haloalkenoic acids has also been observed by others: Pochat, F.; Levas, E. *Bull. Chem. Soc. Fr.* **1972**, *10*, 3846-3855. In contrast to this observation, there are recent reports of facile, low temperature, acid-catalyzed rearrangement of the analogous (trifluorovinyl)carbinol (see refs 14 and 15).

(7) (a) Chari, R. U. J.; Wemple, J. *Tetrahedron Lett.* **1979**, *2*, 111-114. (b) Nakamura, I.; Harada, K. *Heterocycles* **1978**, *9*, 473-480. (c) Lown, J. W.; Itoh, J.; Ono, N. *Can. J. Chem.* **1973**, *51*, 856-859. (d) Woller, P. B., Cromwell, N. H. *J. Org. Chem.* **1970**, *35*, 892-898. (e) Fanta, P. E. In *Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1968; Part A, pp 535-537 and references therein.

(8) Servi, S. *Synthesis*, **1990**, *1*, 1-25.

(9) (a) McDonald, I. A.; Lacoste, J.; Bey, P.; Wagner, M.; Zreida, M.; Palfreyman, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 3354-3356. (b) For the original, low-yield synthesis of phenylalanine that was based upon hydrogenolysis of 2-carboxy-3-phenylaziridine (presumed to be the enamine), see: Yakawa, H.; Kimura, S. *Nippon Kagaku Zasshi* **1955**, *78*, 454-458.

0022-3263/91/1956-3323$02.50/0