catalyst in methanol at room temperature and a pressure of 50 p.s.i. gave a mixture [n^{20}_{D} 1.4660, $[\alpha]_{\mathrm{D}}$ +2.15° (*c* 10.0, MeOH); lit.[4c,10] n^{20}_{D} 1.4665, $[\alpha]_{\mathrm{D}}$ −4.32°] of **3** and **4** in the ratio 3:7 (v.p.c.). The two alcohols were separated by preparative gas chromatography, using a 20-ft. Carbowax column (30% on Chromosorb W 60/80) and a temperature of 180°. Compound **4** showed n^{20}_{D} 1.4675, $[\alpha]^{29}_{\mathrm{D}}$ +38.0° (*c* 6.4 MeOH); lit.[4c,7] n^{20}_{D} 1.4676, $[\alpha]^{17}_{\mathrm{D}}$ +34.7°. Compound **3** was obtained 95% pure (v.p.c.), n^{20}_{D} 1.4623, $[\alpha]^{29}_{\mathrm{D}}$ −22.0°; lit.[4c,7,16] n^{20}_{D} 1.4617, $[\alpha]^{15}_{\mathrm{D}}$ −26.35°. The 3,5-dinitrobenzoate of **3** showed m.p. 105–107°, $[\alpha]_{\mathrm{D}}$ −51.6°; lit.[4c,10,14] m.p. 107°, $[\alpha]^{13}_{\mathrm{D}}$ −52.8°. The 3,5-dinitrobenzoate of **4** gave m.p. 71°, $[\alpha]_{\mathrm{D}}$ +15.5°; lit.[4c,10,11,18a] m.p. 71°, $[\alpha]_{\mathrm{D}}$ +16°. When obtained from its 3,5-dinitrobenzoate, **4** had n^{20}_{D} 1.4675, $[\alpha]^{25}_{\mathrm{D}}$ +39.2° (*c* 9.2, MeOH).

(+)-**Isocarvomenthol** (**1**) **and** (+)-**Neocarvomenthol** (**2**).—Hydrogenation of (−)-*trans*-carveol (**5**) similar to that described above for (−)-*cis*-carveol (**9**) gave a mixture [n^{20}_{D} 1.4658, $[\alpha]_{\mathrm{D}}$ +33.6° (*c* 7.2, MeOH); lit.[4c] n^{19}_{D} 1.4658, $[\alpha]_{\mathrm{D}}$ +12.25°] of **1** and **2** in the ratio 28:72. (v.p.c.). The two alcohols were separated by preparative gas chromatography. Compound **1** showed n^{20}_{D} 1.4660, $[\alpha]^{29}_{\mathrm{D}}$ +19.5° (*c* 2.8, MeOH); lit.[4c,7,25] n^{20}_{D} 1.4662, $[\alpha]^{16}_{\mathrm{D}}$ +17.72°. Compound **2** gave n^{20}_{D} 1.4641, $[\alpha]^{29}_{\mathrm{D}}$ +43.7° (*c* 6.1, MeOH); lit.[4c,7] n^{20}_{D} 1.4632, $[\alpha]^{21}_{\mathrm{D}}$ +41.7°. The 3,5-dinitrobenzoate of **1** showed m.p. 111°, $[\alpha]^{25}_{\mathrm{D}}$ +28°; lit.[4c,6,10,14] m.p. 111°, $[\alpha]_{\mathrm{D}}$ +26.7°.

V.p.c. analysis of mixtures of all four isomers was effected at 140°. The order of the alcohols in terms of increasing retention times was **2**, **3**, **1**, and **4**. Compounds **3** and **1** were not completely separated.

Allylic alcohols **5–12** were obtained in pure form (as indicated by v.p.c.) from saponification of the following esters[9,10,53d,60] on a small scale. Their properties are reported elsewhere.[9,10,53d]

(−)-*trans*-**Carvotanacetol** (**6**).—The 3,5-dinitrobenzoate gave m.p. 117°, $[\alpha]^{23}_{\mathrm{D}}$ −188.5°; lit.[6] m.p. 115–116° $[\alpha]_{\mathrm{D}}$ −201°. The *p*-nitrobenzoate gave m.p. 86°, $[\alpha]^{23}_{\mathrm{D}}$ −228°; lit.[6] m.p. 86–87°, $[\alpha]_{\mathrm{D}}$ −226°. The *p*-nitrobenzoate described in ref. 45 is not the ester of pure (−)-*trans*-carvotanacetol.[53d]

(+)-*p*-**Mentha-1**(**7**),**8-dien**-*trans*-**2-ol** (**7**).—The 3,5-dinitrobenzoate showed m.p. 70–71°, $[\alpha]_{\mathrm{D}}$ +33°; lit.[12,45] m.p. 69–71°. The *p*-nitrobenzoate gave m.p. 114–115°, $[\alpha]_{\mathrm{D}}$ +49.3°. The phenylurethane showed m.p. 80°, $[\alpha]_{\mathrm{D}}$ +21.4°; lit.[12,13,45] m.p. 80°, $[\alpha]_{\mathrm{D}}$ +21°.

(+)-*p*-**Menth-1**(**7**)-**en**-*trans*-**2-ol** (**8**).—The *p*-nitrobenzoate gave m.p. 110°, $[\alpha]_{\mathrm{D}}$ +74.0° (lit.[45] m.p. 107–108°, $[\alpha]_{\mathrm{D}}$ +155.8°), the rotation probably being twice the true value.

(−)-*cis*-**Carvotanacetol** (**10**).—The 3,5-dinitrobenzoate showed m.p. 91°, $[\alpha]_{\mathrm{D}}$ +33.2°; lit.[61,62] m.p. 88.5–90°, $[\alpha]_{\mathrm{D}}$ +33.3°.

(+)-*p*-**Mentha-1**(**7**),**8-dien**-*cis*-**2-ol** (**11**).—The 3,5-dinitrobenzoate gave m.p. 76°, $[\alpha]_{\mathrm{D}}$ −60°.

(+)-*p*-**Menth-1**(**7**)-**en**-*cis*-**2-ol** (**12**).—The 3,5-dinitrobenzoate showed m.p. 118°, $[\alpha]_{\mathrm{D}}$ −59.4°; lit.[46] m.p. 116.5°, $[\alpha]^{20}_{\mathrm{D}}$ −54.3°. The *p*-nitrobenzoate gave m.p. 84°, $[\alpha]_{\mathrm{D}}$ −55.1°; lit.[46] m.p. 83.5°, $[\alpha]_{\mathrm{D}}$ −51.5°.

N.m.r. Spectra.—The n.m.r. spectra were measured on a Varian HR-60 instrument at 60 Mc./sec. in 5–20% CCl_4 solutions with TMS as internal standard. The chemical shifts (in c.p.s.) were averaged from repeated up- and downfield scans and are reproducible to at least ±2 c.p.s. Chemical shifts for the carbinol proton in the saturated alcohols are given in Table I; those in the unsaturated alcohols are given in Table II (along with the shifts for the olefinic protons).

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(60) We are indebted to Professor Dr. G. O. Schenck, Mülheim, Ruhr, Germany, for samples.

(61) J. Read and G. Swann, *J. Chem. Soc.*, 239 (1937).

(62) J. A. Mills, *ibid.*, 4976 (1952).

Photodecomposition of 1,2,3-Triazolines. A New Entry into the Aziridine Series

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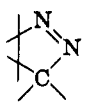
Photolysis of solutions of 1,2,3-triazolines results in loss of nitrogen and the formation of aziridines. A variety of triazoline structures have been found to undergo photodecomposition. The specificity of reaction path in the photolysis contrasts strikingly with the thermal decomposition of triazolines.

The chemical and structural similarity of 1-pyrazolines (**1**) and 1,2,3-Δ^2-triazolines (**2**), *e.g.*, thermal decomposition with loss of nitrogen and isoelectronic structures, prompted an investigation of the light-induced decomposition of triazolines. Van Auken and Rinehart have recently reported this mode of reaction in the 1-pyrazoline series.[2] It has been found that 1,2,3-triazolines readily decompose under the influence of ultraviolet light.



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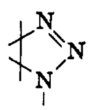

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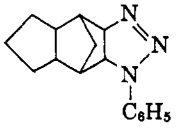
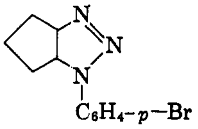
To determine the scope of the photodecomposition reaction, a variety of triazoline structures were prepared and irradiated. In all instances a quantitative evolution of nitrogen (1 mole/mole of triazoline) was observed. The diversity of substrates employed indicates that the photodecomposition of 1,2,3-triazolines, resulting in the loss of nitrogen, is a general reaction for this class of compounds. Compounds **3–8** are typical of those that have been photolytically decomposed.[3]



3[7]



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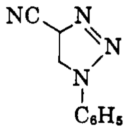
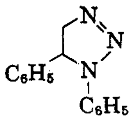
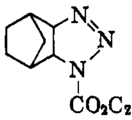


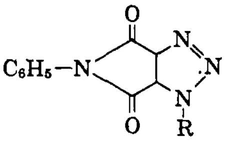
5[9]



6[15]



7



8a,[5] R = C_6H_5
b, R = *n*-C_4H_9

Although the thermal decomposition of certain 1-aryl-1,2,3-triazolines has been reported to produce the corresponding aziridines,[4-6] Alder and Stein's comprehensive study has shown that aziridine formation is

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[1] Socony Mobil Oil Co., Princeton, N. J.

[2] T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962); **82**, 5251 (1960).

[3] Thiatriazolinethione has also been photolyzed in acetone solvent. The decomposition products are nitrogen, sulfur, and thiocyanic acid; *cf.* E. Lieber, E. Oftedahl; and C. N. R. Rao, *J. Org. Chem.*, **28**, 194 (1963).

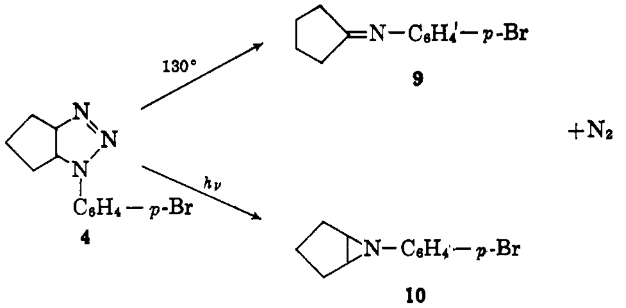
[4] F. D. Chattaway and G. D. Parkes, *J. Chem. Soc.*, **127**, 1307 (1925).

[5] A. Mustafa, S. M. A. D. Zayed, and S. Khattab, *J. Am. Chem. Soc.*, **78**, 145 (1956).

[6] P. Scheiner and W. R. Vaughan, *J. Org. Chem.*, **26**, 1923 (1961).

usually complicated, and frequently excluded, by the formation of isomeric anil compounds.[7] The thermal decomposition of triazolines is therefore not a generally useful route to aziridines.[8,9] A somewhat similar situation prevails with regard to the pyrolysis of 1-pyrazolines; extensive formation of unsaturated compounds limits the utility of this reaction as a cyclopropane preparation. Photolysis of pyrazolines, on the other hand, produces cyclopropanes relatively free from the contaminating olefins.[2] In view of the above-mentioned analogy, a comparison of the specificity of reaction path in the thermal and photolytic decompositions of 1,2,3-triazolines was undertaken.

Pyrolysis of the *p*-bromophenyl azide–cyclopentene adduct (**4**) at 130° gave the anil (**9**), as previously reported.[7] The anil, the only product isolated, was obtained in 67% yield. A strong band at 1673 cm.$^{-1}$, characteristic of the C=N group,[10] was observed in the infrared spectrum of **9**. Contrasting with this result, the photolysis of **4** in acetone gave a quantitative yield of the aziridine (**10**). Compound **10**, isomeric with **9**, did not absorb in the C=N region, but exhibited a peak at 1190 cm.$^{-1}$ characteristic of ring-fused aziridines.[11] Acid hydrolysis of **10** produced an amino alcohol (infrared), while similar treatment of **9** resulted in cyclopentanone and *p*-bromoaniline.



It is of interest that the anil **9** does not arise *via* rearrangement of the aziridine **10** in the course of the pyrolysis. A sample of **10** was recovered unchanged after being subjected to the conditions of the thermal decomposition.

Contrary to earlier reports,[5,12] it has been found that the pyrolysis of the phenyl azide–N-phenylmaleimide adduct (**8a**) gives rise to both aziridine and olefinic products.[13] Photolysis of **8a**, however, produces the aziridine, uncontaminated by side products. Similarly, the photodecomposition of **3** yields only the corresponding aziridine.[7]

The pyrolyses mentioned above (**3**, **4**, and **8a**) were conducted without solvent. To examine the influence of solvent on the reaction course, the photo- and thermal decompositions of the *p*-bromophenyl azide–norbornene adduct (**11**) were investigated in solvent phenetole. Although the major product was **12** in either case, the analytical data obtained by infrared analysis of the product mixtures (Table I) clearly indicate the greater specificity for aziridine formation in the photolytic process. Here again the aziridine was shown to be stable under the pyrolytic conditions.

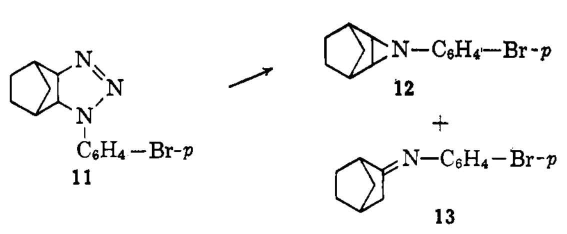


TABLE I

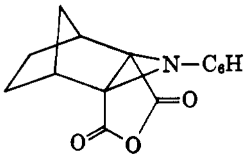
DECOMPOSITIONS OF 11 IN PHENETOLE

	Products, %^{a}	
	12	**13**
Pyrolysis^b	53	20
Photolysis^c	100	1

^{a} ±4%. ^{b} Refluxing phenetole, 171°. ^{c} General Electric sunlamp.

The aziridine structure **12** was assigned on the basis of the elemental analysis and the infrared and n.m.r. spectra. A characteristic ring-fused aziridine absorption[11] was observed at 1190 cm.$^{-1}$ in the spectrum of **12**, but not in **11** or **13**. The n.m.r. spectrum of **12** was similar to that of **11**, except that the proton signals at τ 5.4 and 6.3 (one proton each) in the latter were replaced by a single peak (two protons, τ 7.8) in the former. This change reflects the differing environments experienced by the ring protons adjacent to nitrogen in **11** and **12**. As in the case of triazoline **3**, photodecomposition does not appear to result in the rearrangement of the bicyclic structure. Compound **13** was independently prepared from norcamphor and *p*-bromoaniline.

As a synthetic route to aziridines, the photodecomposition is a promising new method. Particularly noteworthy are the ease of operation and the mildness of reaction conditions. Compound **14**, for example, was readily synthesized by this method, but would otherwise be difficult to obtain. (Triazoline pyrolysis gives mainly tar in this case.) Since syntheses of 1,2,3-Δ^2-triazolines (addition of azides to olefinic bonds,[14] addition of diazomethane to anils,[15] and rearrangement of 1-arylazoaziridines[16]) are available, it seems likely that the photodecomposition reaction may permit the preparation of presently inaccessible aziridines.



14

Experimental[17]

Photolyses. General Method.—Solutions of the triazolines (0.08–0.60 *M*) in inert solvents (acetone, toluene, and *p*-dioxane)

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[7] K. Alder and G. Stein, *Ann.*, **501**, 1 (1933).

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[9] S. M. Gurvich and A. P. Terentev, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, **1**, 409 (1953).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1958; p. 268.

[11] J. B. Patrick, R. P. Williams, W. E. Meyer, W. Fulmor, D. B. Cosulich, R. W. Broschard, and J. S. Webb, *J. Am. Chem. Soc.*, **86**, 1889 (1964).

[12] S. J. Davis and C. S. Rondestvedt, *Chem. Ind.* (London), 848 (1956).

[13] W. I. Awad, S. M. A. R. Omran, and F. Nagieb, *Tetrahedron*, **19**, 1591 (1963).

[14] J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).

[15] G. D. Buckley, *J. Chem. Soc.*, 1850 (1954).

[16] H. W. Heine and D. A. Tomalia, *J. Am. Chem. Soc.*, **84**, 993 (1962).

[17] Melting points (Fisher-Johns block) and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 237 Infracord. Ultraviolet spectra were obtained with a Cary Model 15 spectrophotometer. N.m.r. spectra were obtained with a Varian A-60 spectrometer.

were irradiated with a General Electric sunlamp. The reaction vessel, a large Pyrex test tube with a gas outlet side arm, was equipped with an internal cold-finger condenser immersed in the solution. Magnetic stirring was maintained throughout each run. Under these conditions, with the lamp about 10 cm. from the reaction vessel, the temperature of the reacting solutions did not exceed 35°. The volume of nitrogen evolved was measured at atmospheric pressure by means of a gas buret.

The beginning of each run was marked by a 1- or 2-min. induction period, during which time no gas evolution was observed. In the course of the runs nitrogen evolution abruptly ceased when the radiation was interrupted. After evolution of the theoretical volume further gas evolution was not observed.

Compounds **7** and **8b** decomposed extremely slowly in the apparatus described above. These compounds were efficiently decomposed, however, by irradiation of their solutions in a 50-ml. flask fitted with an internal ultraviolet light source (Delmar Scientific Laboratories, DM-580). External cooling was provided by means of a water bath. The ultraviolet spectra of **7** and **8b** (ethanol, 95%) showed λ_{max} at 243 and 266 mμ, respectively; other triazolines (**3**, **4**, **8a**, and **11**) exhibited λ_{max} in the 295–320-mμ region.

Preparation and Photolysis of 3-Carbethoxy-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (7).—Ethyl azidoformate,[18] 3.6 g. (0.031 mole), and norbornene (Aldrich), 2.9 g. (0.031 mole), were dissolved in 10 ml. of pentane and allowed to stand (tightly stoppered flask) at room temperature for 1 week. Two layers formed at that time. Removal of the solvent at room temperature and under reduced pressure afforded 6.1 g. (94%) of colorless fragrant liquid. This material decomposed when heated above 70°; attempts to purify it by distillation were therefore abandoned. The infrared spectrum of the product showed that no ethyl azidoformate or norbornene were present.

A 1.00-g. (0.0048-mole) sample of **7** was dissolved in 25 ml. of acetone and irradiated. After completion of the gas evolution, the solvent was removed and 0.82 g. (95%) of a pale yellow liquid was obtained. Distillation (larger sample) of this material occurred at 99–100° (2.4 mm.), $n^{25}\text{D}$ 1.4841. The infrared spectrum of this compound (3-carbethoxy-3-azatricyclo[3.2.1.0^{2,4}]octane) showed no absorption in the C=N region.[10]

Anal. Calcd. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.43; H, 8.56; N, 7.98.

2-Butyl-7-phenyl-2,3,4,7-tetraazabicyclo[3.3.0]oct-3-ene-6,8-dione (8b).—A solution of 1.98 g. (0.020 mole) of *n*-butyl azide[19] and 3.14 g. (0.020 mole) of N-phenylmaleimide[20] in 40 ml. of ethyl acetate was refluxed for 6 hr. After removal of about one-half of the original solvent, dilution with 25 ml. of petroleum ether (60–90°), and cooling, a yield of 4.72 g. (92%) was obtained, m.p. 100–105°. Two crystallizations from petroleum ether–benzene (1:1) afforded 3.00 g. of product, m.p. 119.5–120.5°.

Anal. Calcd. for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.69; H, 6.03; N, 20.50.

2-*p*-Bromophenyl-2,3,4-triazabicyclo[3.3.0]oct-3-ene (4) was prepared as previously described[7] in 44% yield, m.p. 122° dec. as reported.[7]

Photolysis of 4. 6-*p*-Bromophenyl-6-azabicyclo[3.1.0]hexane (10).—A solution of 3.85 g. (0.0145 mole) of **4** in 25 ml. of acetone was irradiated as described above until nitrogen evolution ceased. A volume of 359 ml. was observed (theoretical volume, 362 ml.). Removal of the solvent under reduced pressure gave 3.38 g. of pale yellow solid, m.p. 66–69°. Three crystallizations from pentane (Dry Ice–acetone bath cooling) gave 2.12 g. of white solid, m.p. 73–74°.

Anal. Calcd. for $C_{11}H_{12}BrN$: C, 55.49; H, 5.08; N, 5.88. Found: C, 55.73; H, 5.38; N, 5.84.

The infrared spectrum of **10** showed no significant absorption in the 1600–1700-cm.$^{-1}$ region, but did show absorption at 1190 cm.$^{-1}$.

In a test tube, a 0.20-g. sample of **10** was heated (oil bath) at 130–140° for 1 hr. The infrared spectrum of the resulting slightly discolored material was identical with that of **10**.

A 1.25-g. sample of **10** was refluxed with 70 ml. of dilute sulfuric acid for 1 hr. After cooling, the solution was made basic to litmus with 10% sodium hydroxide solution and extracted with three 20-ml. portions of ether. The dried extracts (magnesium sulfate) were evaporated to dryness, yielding 1.16 g. of viscous oil. The infrared spectrum (3% in chloroform) showed peaks at 3615 and 3430 cm.$^{-1}$, with no absorption in the carbonyl region.

Pyrolysis of 4. Cyclopentylidene-*p*-bromoaniline (9).—To a flask immersed in an oil bath at 130–140°, 10.2 g. (0.038 mole) of **4** was added in small portions. The solid melted with vigorous gas evolution and a dark brown oil was obtained. Heating was discontinued after 1 hr. Distillation of the crude product afforded 6.1 g. (67%) of yellow oil, b.p. 110–111° (0.4 mm.), lit.[7] b.p. 173° (20 mm.). The infrared spectrum showed a strong peak at 1672 cm.$^{-1}$.

A 0.79-g. sample of **9** was refluxed with 50 ml. of dilute sulfuric acid for 2 hr. Extraction of the hydrolysate with three 20-ml. portions of ether, followed by drying the extracts (magnesium sulfate) and evaporation, gave a brown oil. The infrared spectrum showed this material to be a mixture of cyclopentanone and **9**. The aqueous solution (above) was made basic with 10% sodium hydroxide solution and extracted with two 20-ml. portions of ether; the extracts were dried over magnesium sulfate. Evaporation of the solvent gave a tan solid (m.p. 58–62°) whose infrared spectrum was identical with that of authentic *p*-bromoaniline.

3-*p*-Bromophenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (11).—A solution of 19.8 g. (0.10 mole) of *p*-bromophenyl azide[21] and 9.4 g. (0.10 mole) of norbornene (Aldrich) in 100 ml. of petroleum ether was refluxed for 3 hr. On cooling, the solution deposited 25.6 g. (88%) of product, m.p. 120–123°. A sample recrystallized twice from *n*-heptane melted from 123 to 124°.

Anal. Calcd. for $C_{13}H_{14}BrN_3$: C, 53.44; H, 4.83; N, 14.38. Found: C, 53.39; H, 4.92; N, 14.32.

Photolysis of 11. 3-*p*-Bromophenyl-3-azatricyclo[3.2.1.0^{2,4}]octane (12).—A solution of 8.2 g. (0.028 mole) of **11** in 40 ml. of acetone was irradiated for 24 hr. Removal of the solvent afforded yellow-brown crystals, m.p. 101–110°. Recrystallization from petroleum ether (30–60°) gave 6.4 g. (86%) of white crystals, m.p. 113–115°. Three additional crystallizations from the same solvent gave the analytical sample, m.p. 115–116°.

Anal. Calcd. for $C_{13}H_{14}BrN$: C, 59.10; H, 5.34; N, 5.30. Found: C, 59.28; H, 5.31; N, 5.27.

2-Norbornylidene-*p*-bromoaniline (13).—Norcamphor (Aldrich), 11.0 g. (0.10 mole), *p*-bromoaniline, 17.2 g. (0.10 mole), and 0.5 ml. of concentrated hydrochloric acid were refluxed with 100 ml. of toluene for 23 hr. A Dean–Stark trap was used to remove water formed during the reaction. Fractional distillation (15-cm. Vigreux column) gave a main fraction of 20.0 g. (76%), b.p. 127–130° (0.4–0.5 mm.). On standing in the refrigerator this material solidified and was further purified by crystallization from pentane. The compound melted from 32 to 33°.

Anal. Calcd. for $C_{13}H_{14}BrN$: C, 59.10; H, 5.34; N, 5.30. Found: C, 59.00; H, 5.16; N, 5.45.

Pyrolysis and Photolysis of 11 in Phenetole.—A solution (0.177 *M*) of **11** was prepared by accurately weighing 2.587 g. into a 50-ml. volumetric flask and filling with phenetole (reagent grade redistilled). One-half of the solution was refluxed (*ca.* 171°) for 5 hr., at which time nitrogen evolution had ceased. The remainder of the solution was photolyzed as previously described. The infrared spectra of the product solutions were obtained (0.1-cm. NaCl cell, phenetole reference) and compared with a series of spectra of reference solutions. The reference solutions (eleven) contained **12** and **13** in concentrations varying from 0.201 *M* to 0.0 *M* for each component; the total concentration (**12** and **13**) was 0.201 in all cases. Comparison of peak heights was made at 1680 (anil) and 1370 cm.$^{-1}$ (aziridine). The photolysis solution was estimated to be 0.180 *M* in **12** and 0.002 *M* in **13**; pyrolysis solution was estimated to be 1.80 *M* in **12** and 0.002 *M* in **13**; pyrolysis solution, 0.094 *M* in **12** and 0.036 *M* in **13**. These results, converted to per cent yields, appear in Table I. In the pyrolysis, the formation of additional product(s) was suggested by the dark red-brown appearance of the product solution. Infrared analysis of a 0.20 *M* solution of **12** before and after a 5-hr. reflux period showed that **12** was stable under the pyrolytic conditions.

3-Phenyl-3-azatricyclo[3.2.1.0^{2,4}]octane-2,4-dicarboxylic Acid Anhydride (14).—The corresponding triazoline (3-phenyl-3,4,5-triazatricyclo [5.2.1.0^{2,6}]dec-4-ene-2,6-dicarboxylic acid anhydride) was prepared in 75% yield as previously described, m.p. 153–154°, lit.[7] m.p. 154°. A sample, 3.01 g. (0.0106 mole), of the triazoline was photolyzed in 25 ml. of acetone. After evolution of nitrogen

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was completed, the solvent was evaporated and the product was collected, 2.70 g., m.p. 155–160°. Three crystallizations from petroleum ether (60–90°)–ethyl acetate (1:1) gave a product melting from 161–162°. The infrared spectrum showed no absorption in the C=N region, but did absorb at 1185 cm.$^{-1}$. In addition to the aromatic protons, the n.m.r. spectrum showed a single peak (two protons, bridgehead) at τ 6.9 and a complex multiplet (six protons) from τ 7.6–8.7.

Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.57; H, 5.32; N, 5.78.

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Unsaturated Neopentyl Compounds. The Acetolysis of 2,2-Dimethyl-3-buten-1-yl and 2,2,4-Trimethyl-3-penten-1-yl *p*-Bromobenzenesulfonates. π-Electron Delocalization in the Absence of Steric Strain[1]

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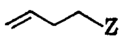
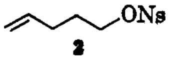
The acetolysis of 2,2-dimethyl-3-buten-1-yl *p*-bromobenzenesulfonate is about 60 times as rapid at 100° as that of 2,2-dimethylbutyl *p*-bromobenzenesulfonate, and yields a mixture of 2-methylpentadienes, 2-methyl-4-penten-2-yl acetate, and 4-methyl-3-penten-1-yl acetate. Evidence is presented that this rate enhancement is the result of π-electron delocalization in the absence of steric strain, and that vinyl is almost as good a "neighboring group" as phenyl. The anchimerically assisted solvolysis of 2,2,4-trimethyl-3-penten-1-yl *p*-bromobenzenesulfonate in anhydrous acetic acid at 25° yields a mixture of 2,5-dimethylhexadienes and 2,5-dimethyl-4-hexen-2-yl acetate. The nature of the transition state and intermediates in the acetolysis of these and other unsaturated primary arenesulfonates is discussed, and an explanation is offered for the *gem*-dimethyl effect in the solvolyses of homoallylically unsaturated neopentyl derivatives.

It is now a well established fact that the solvolytic displacement reactions of many cyclic and bicyclic esters may be markedly accelerated by an appropriately situated, nonconjugated double bond.[2] Winstein has provided the most generally accepted explanation of such rate enhancements by suggesting that they are the result of increased π-electron delocalization in the transition state of the rate-limiting step.[2b,3] Although there are ample theoretical reasons for suggesting such delocalization,[4] this experimental interpretation has recently been questioned by H. C. Brown[5] who points out that, in every unambiguous case of enhanced solvolysis by an isolated, nonconjugated double bond, this bond is either exocyclic to, or an integral part of, a cyclic or bicyclic ring. Such systems, he suggests, may derive their greater driving force from relief of steric strain in the transition state rather than from an electronic effect. Brown's interpretation, though certainly valid in many instances, would be rendered less generally condemning to the concept of π-electron delocalization if it could be shown that similar rate enhancements occur in systems where such steric effects are negligible.

Attempts to demonstrate solvolytic rate enhancements in the reactions of appropriately unsaturated acyclic derivatives have met with little success. The solvolysis of allylcarbinyl chloride (**1a**) in 50% aqueous ethanol at 100°[6] is only about one-third as rapid as that of *n*-propyl chloride,[7] while the ethanolysis of allylcarbinyl benzenesulfonate (**1b**) at 55°[8] is one-half as fast as that of *n*-butyl benzenesulfonate.[9] The acetolysis of 4-penten-1-yl (**2**) and 4-hexen-1-yl (**3**) *p*-nitrobenzenesulfonates are only seven-tenths as fast as that of the *n*-hexyl ester under the same conditions.[2c,10] Apparently in these cases the double bond provides little or no additional driving force, and, even in cases which do show a small rate enhancement, it is doubtful that electron delocalization is the cause. For example, the rate of acetolysis of 5-hexen-1-yl *p*-nitrobenzenesulfonate (**4**) is about one and one-half times that of the *n*-hexyl ester, but may not be a simple first-order reaction.[2c,10] Similarly, the acetolysis of allylcarbinyl *p*-toluenesulfonate (**1c**) is markedly accelerated by the addition of sodium acetate.[11]



1a, Z = Cl
b, Z = OBz
c, Z = OTs



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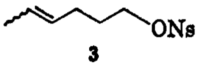

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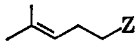
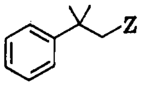
4



5a, Z = OH
b, Z = OAc
c, Z = OTs
d, Z = 2,4-DNB



6a, Z = OBs
b, Z = OTs

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