J. Org. Chem. 1981, 46, 5324-5328

***trans*-1-(Formylamino)-2-(3-methoxyphenyl)cyclohexane (16)** was obtained by refluxing **15** in ethylformate during 18 h.[16] After distillation at 164–166 °C (0.04 torr), a light yellow oil is obtained in 95% yield: IR (NaCl, film) 3270 (NH), 1660 (CO); NMR ($CDCl_3$) shows *Z* (77%) and *E* (23%) rotamers about the amide bond, δ 7.85 (CHO (*Z*), d, $J_{NH-CHO} = 0.9$ Hz), 7.59 (CHO (*E*), d, $J_{NH-CHO} = 11.7$ Hz); mass spectrum *m/z* (relative intensity) 233 (2, $M^{+\cdot}$), 188 (100).

7-Methoxy-*trans*-1,2,3,4,4a,10b-hexahydrophenanthridine (17) was obtained as byproduct in the synthesis of the 9-methoxy isomer **18**. A 10.5-g sample of **16** was heated with 105 g of polyphosphoric acid at 115 °C for 5 h. After cooling, the reaction mixture was poured into 400 mL of ice–water and carefully made basic with NaOH. After extraction with ether, drying over $MgSO_4$ and evaporation of the solvent, the residue was distilled at 117.5 °C (0.04 torr). The ^1H NMR spectrum of the colorless oil indicates a mixture of 7-methoxy (15%) and 9-methoxy (85%) derivatives (H_6 integration). By column chromatography on alumina (Merck Co., activity II–III) with petroleum ether–ether (90/10) elution, both compounds can be separated. One obtains 0.75 g of **17** and 6.18 g of **18**.

17: mp 100–101 °C; IR (KBr) 1615 (C=N); mass spectrum, *m/z* (relative intensity) 215 (91, $M^{+\cdot}$, $C_{14}H_{17}NO$), 186 (100, $C_{12}H_{12}NO$); NMR δ 8.70 (H_6, d, $J = 3.1$ Hz), 7.32–6.79 (3 H_{arom}), 3.86 (OCH_3), 2.84 (H_{4a}), 2.43–1.28 (H_{alif}).

18: mp ($HClO_4$) 184–185 °C; IR (KBr) 1625 (C=N); mass spectrum, *m/z* (relative intensity) 215 (100, $C_{14}H_{17}NO$), 186 (99, $C_{12}H_{12}NO$); NMR δ 8.22 (H_6, d, $J = 3.1$ Hz), 7.22–6.77 (3 H_{arom}), 3,84 (OCH_3), 2.88 (H_{4a}), 2.41–1.25 (H_{alif}).

Indole N-Methylation. The procedure of Morrison[17] was followed on 100-mg samples of the parent compounds.[3,16,18,19] The compounds were purified by column chromatography on alumina with ether elution; yield 80–85%. After crystallization from ethanol the following compounds were obtained: **1b**, mp 186–187 °C. Anal. Calcd for $C_{24}H_{26}N_2$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.10; H, 7.53; N, 8.26. **6b**, mp 158–158.9 °C. Found: C, 84.30; H, 7.55; N, 8.29. **8b**, mp 182–184 °C. Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72. Found: C, 83.12; H, 7.05; N, 9.90.

4b,5,6,7,8,8a,10,11,16,16b-Decahydro-1-methoxydibenz[*f*,*h*]indolo[2,3-*a*]quinolizine (10). Tryptophyl bromide (210 mg) and **17** (215 mg) were heated for 4 h at 100–120 °C. Glacial acetic acid (10 mL) was added, and the solution was refluxed overnight. The precipitated hydrobromide salt was filtered, and the free base was liberated with dilute NaOH. Crystallization from ethanol gave 57% of **10**: mp 175–175.5 °C; mass spectrum, *m/z* (relative intensity) 358 (100, $C_{24}H_{26}N_2O$). Anal. Calcd for $C_{24}H_{26}NO$: C, 80.45; H, 7.26; N, 7.82. Found: C, 80.32; H, 7.15; N, 8.01.

Registry No. **1b**, 79549-36-3; **6b**, 79549-37-4; **8b**, 79517-39-8; **10**, 79517-40-1; **15**, 32948-96-2; **15**·HCl, 32928-84-0; **16**, 79517-41-2; **17**, 79517-42-3; **18**, 79517-43-4; *trans*-1-(3-methoxyphenyl)-2-nitrocyclohexane, 32928-86-2; tryptophyl bromide, 3389-21-7.

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[16] G. Van Binst and D. Tourwé, *J. Heterocycl. Chem.*, 9, 895 (1972).

[17] G. C. Morrison, W. A. Cetenko, and J. Shavel, Jr., *J. Org. Chem.*, 32, 2768 (1967).

[18] I. W. Elliott and Y. G. Bryant, *J. Heterocycl. Chem.*, 4, 127 (1967).

[19] Note added in proof in ref 4.

Photochemistry of Vinyl Halides. Formation of Benzofurans by Photolysis of β-(*o*-Methoxyphenyl)vinyl Bromides

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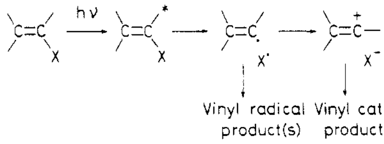
Photolysis of β,β-bis(*o*-methoxyphenyl)-substituted vinyl bromides gave benzofuran derivatives which are derived from an intramolecular nucleophilic attack of the methoxyl group on an intermediate vinyl cation. With α-aryl-substituted vinyl bromides, only one type of benzofuran derivative was detected. However, when the α substituent was a hydrogen or a methyl group, two isomeric benzofurans were formed, one via the unrearranged vinyl cation and the other via an (*o*-methoxyphenyl)-rearranged vinyl cation. Irradiation of α-methyl-β,β-bis(*o*-methoxyphenyl)vinyl bromide in nucleophilic solvent, i.e., methanol, did not result in solvent-incorporated products. In the photolysis of β-(*o*-methoxyphenyl)-substituted vinyl bromides a selectivity–reactivity relationship between the cyclization and the rearrangement of the intially formed vinyl cation was observed.

It is well-known that irradiation of vinyl halides gives products derived from vinyl radicals as the reactive intermediates.[1] However, it was recently found that an ionic itermediate, i.e., a vinyl cation, was also generated in the course of the photolysis of vinyl halides.

We reported that in the photolysis of 1,1-diaryl-2-haloethylenes[2] and 1,1-diaryl-2-halopropenes[3] the corresponding vinyl cations were generated by an internal electron transfer in the vinyl radical pairs which were initially formed by homolytic fission of the carbon–halogen bond (eq 1). McNeely and Kropp reported that solvent-incorporated products were obtained in the photolysis of alicyclic vinyl halides and suggested that vinyl cations which were formed by an electron transfer were the product-forming intermediates.[4] Likewise, Sket and Zupan also suggested that the photolysis of 1,1-diphenyl-2-haloethylenes gave diphenylacetylene via a vinyl cation.[5]



(1)

Solvolytically generated vinyl cations have been extensively studied since 1964.[6] In this field, we reported that the solvolysis of α-aryl-β,β-bis(*o*-methoxyphenyl)vinyl halides gave two isomeric benzofuran derivatives (eq 2).[7]

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[1] Sammes, P. G. "Chemistry of The Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

[2] Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 180.

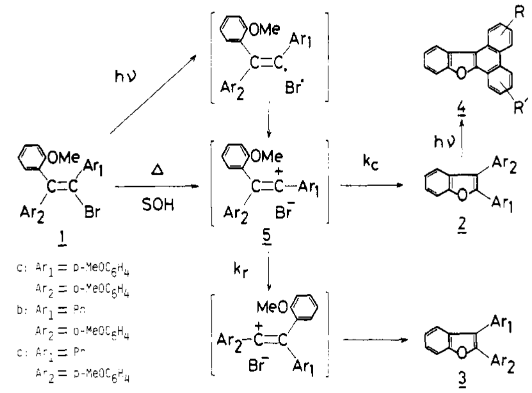
[3] Kitamura, T.; Kobayashi, S.; Taniguchi, H., submitted for publication in *J. Org. Chem.*

[4] McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319.

[5] Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1979**, 752.

[6] Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.

0022-3263/81/1946-5324$01.25/0



(2)

Therefore, the corresponding photoinduced vinyl cations might also give benzofuran derivatives. Such a photochemical method might be very useful for organic synthesis, since the vinyl cations are generated from any vinyl halides even at room temperature in various solvents in contrast to the thermal solvolysis which usually requires an α-activating group, high temperatures, and highly ionizing solvents. Moreover, various vinyl cations where the α substituent is hydrogen, alkyl, and aryl are easily generated by photolysis of vinyl halides.

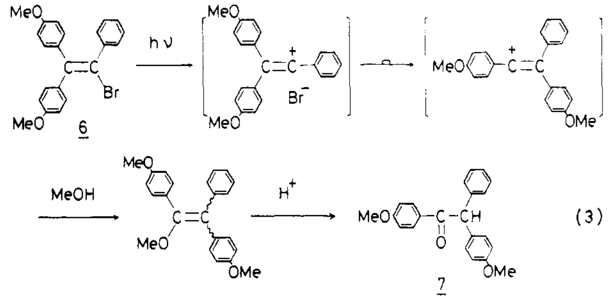
Therefore, we carried out the photolysis of β-(o-methoxyphenyl)-substituted vinyl halides in order to probe the scope of the utility of the photoinduced vinyl cations for the synthesis of benzofuran derivatives.

Results and Discussion

Photolysis of α-Aryl-β-(o-methoxyphenyl)vinyl Bromides. Irradiation of the vinyl bromide **1a** was carried out in THF by using 100-W high-pressure mercury lamp through a Pyrex filter. The products obtained were benzofuran **2a** and a trace of benzofuranophenanthrene **4a** (eq 2). Since the benzofuran **2a** is identical with the solvolysis product of **1a**,[7] the photolysis of **1a** probably produces the same intermediate vinyl cation which gives **2a** by an intramolecular cyclization. When **1a** was irradiated without a Pyrex filter or when the benzofuran **2a** was further irradiated, the benzofuranophenanthrene **4a** was obtained.

Irradiation of the vinyl bromide **1b** in benzene gave the benzofuran **2b** as major product together with a trace of the benzofuranophenanthrene **4b**. In the photolysis the generated vinyl cation undergoes intramolecular cyclization without a 1,2 aryl shift. In contrast, in the solvolysis of **1b** in 50% EtOH, 7% of the rearranged benzofuran **3b** was produced along with 93% of the benzofuran **2b**.[7]

A change of the β-(o-methoxyphenyl) group to a β-(p-methoxyphenyl) group results in a large difference in the extent of rearrangement, as also found in the solvolysis. Namely, although **1b** specifically undergoes intramolecular cyclization without a 1,2 arryl shift, the para isomer, that is, β,β-bis(p-methoxyphenyl)-α-phenylvinyl bromide (**6**), gives the only rearrangement products both in photolysis in methanol (eq 3)[8] and in solvolysis in TFE.[9] This implies that the cyclization by an o-methoxyphenyl group is very fast compared with the rearrangement of β-methoxyphenyl groups across the double bond.



(3)

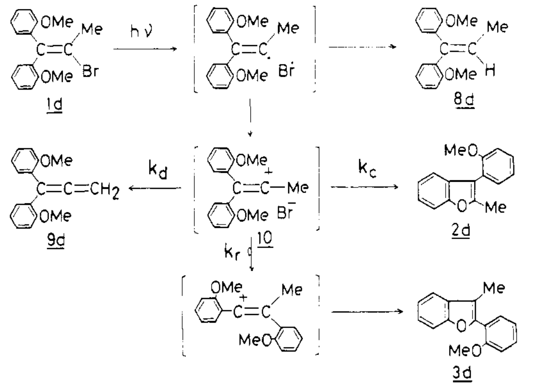
When the vinyl bromide **1c** was similarly irradiated in benzene only the unrearranged benzofuran **2c** was formed (eq 2). Again, in the solvolysis of **1c** in AcOH–AgOAc 9% of the benzofuran **3c** which is derived from a β-aryl-rearranged cation was formed along with 91% of the benzofuran **2c**.[10]

Consequently, the photolysis of α-aryl-β-(o-methoxyphenyl)vinyl bromides gives exclusively benzofuran derivatives with unrearranged skeletons.

If the cyclization and the rearrangement processes are irreversible, the ratio of **2** to **3** represents the ratio of rate constants for the cyclization (k_c) and the rearrangement (k_r) of the initially formed vinyl cation **5**. The photoinduced vinyl cations behave somewhat differently from the solvolytically generated vinyl cations, as seen from the ratio of k_r and k_c: $k_r/k_c = 0$ in photolysis and $k_r/k_c \approx 0.1$ in solvolysis.

Photolysis of α-Methyl-β,β-bis(o-methoxyphenyl)vinyl Bromide. α-Methyl-β,β-diarylvinyl bromides do not undergo solvolysis under usual conditions. For example, a 1:1 mixture of (*E*)- and (*Z*)-β-(o-methoxyphenyl)-β-(p-methoxyphenyl)-α-methylvinyl bromide was refluxed in AcOH with 10 equiv of AgOAc for 11 h, but the starting materials were recovered unchanged.[10] Consequently, photolysis becomes a significant and convenient method for the formation of vinyl cation **10**.

Irradiation of **1d** in methanol containing pyridine as a buffer yielded the benzofurans **2d** (27%) and **3d** (23%), the propene **8d** (6%), and the allene **9d** (11%) (eq 4). The same products, **2d** (25-26%), **3d** (28%), and **8d** (13%), except for the allene **9d**, were formed when the irradiation was carried out in benzene or benzene containing zinc powder.



(4)

We suggest that photolysis of **1d** leads initially to a homolytic cleavage of the carbon–halogen bond to form a radical pair. The propene **8d** is formed by the abstraction of a hydrogen atom by the vinyl radical. Electron transfer in the vinyl radical pair gives the vinyl cation **10**, which is involved in the competing routes leading to **2d**,

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(7) Sonoda, T.; Kobayashi, S.; Taniguchi, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2560.

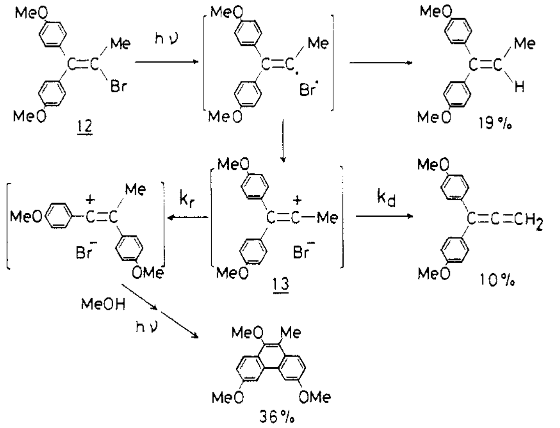
(8) Kobayashi, S.; Suzuki, T.; Taniguchi, H. Annual Symposium on Photochemistry in Japan; Fukuoka, Japan, Oct 1976; p 155. Photolysis of **6** in methanol was carried out for 1.5 h through a Pyrex filter with a high-pressure mercury lamp. The products formed were a mixture of (*E*)- and (*Z*)-1,2-bis(p-methoxyphenyl)-1-methoxy-2-phenylethylenes and a trace of their photocyclized products. Acid hydrolysis of the product mixture gave **7** in 78% yield.

(9) (a) Rappoport, Z.; Gal, A.; Houminer, Y. *Tetrahedron Lett.* **1973**, 641. (b) Rappoport, Z.; Houminer, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1506.

(10) Sonoda, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1976**, 389. Sonoda, T. Ph.D Thesis, Kyushu University, 1978.

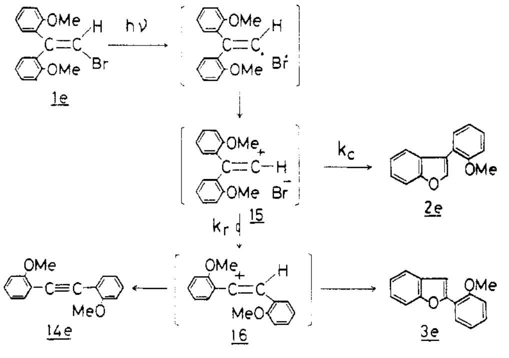
3d, and **9d**. The allene **9d** is formed in methanol by deprotonation of the methyl group of **10** by either the basic sovlent or the pyridine, but it is not formed when the photolysis was carried out in benzene. The possibility of hydrogen abstraction from the methyl group by the bromine atom to form the allene **9d** is rejected since in the photolysis in benzene, where the radical product **8d** is formed, the allene **9d** is not obtained. The benzofuran **2d** is formed by cyclization of the unrearranged vinyl cation **10**. However, β-*o*-methoxyphenyl rearrangement leads to the more stable α-arylvinyl cation **11**. Cyclization of the cation **11** gives the benzofuran **3d**.

Consequently, if the three processes are irreversible, the ratio of **2d**, **3d**, and **9d** represents the ratio of the cyclization (k_c), the rearrangement (k_r), and the deprotonation (k_d) rate constants of the cation **10**. In the photolysis of the vinyl bromide **1d**, $k_c/k_r/k_d = 27/23/11$ in methanol. For the photolysis of β,β-(*p*-methoxyphenyl)-α-methylvinyl bromide (**12**) in which the intially formed vinyl cation **13** undergoes both rearrangement and deprotonation, the ratio (k_r/k_d) is 3.6 (eq 5).[3] The ratio is relatively lower in the case of β,β-bis(*o*-methoxyphenyl)-substituted vinyl bromide **1d**, in which the deprotonation also competes with the cyclization of the cation **10** to the unrearranged benzofuran **2d**. The rearrangement in the photolysis of **1d** also competes with the cyclization to **2d**, since the α-methylvinyl cation is less stable than the α-arylvinyl cation.[11] The ratio of k_r/k_c is nearly equal to 1.



(5)

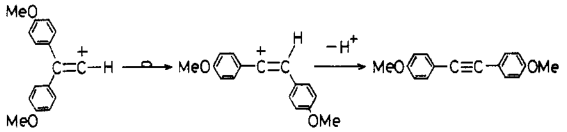
Photolysis of β,β-Bis(*o*-methoxyphenyl)vinyl Bromide. In the photolysis of the vinyl bromide **1e** in benzene the products obtained were the benzofurans **2e** (14%) and **3e** (30%) and the acetylene **14e** (53%). In this case, the initially formed vinyl cation **15** is very unstable.[10] Rearrangement to a more stable α-arylvinyl cation, **16**, is the favored route. Vinyl cation **16** is then cyclized to the benzofuran **3e** or deprotonated to the acetylene **14e** (eq 6). Consequently, the k_r/k_c of 5.9 is larger than in the case of the vinyl bromides **1b** and **1d**. In contrast, the β,β-bis(*p*-methoxyphenyl)-substituted vinyl cation **17** leads exclusively to rearrangement since a cyclization product cannot be formed (eq 7).[2]



(6)

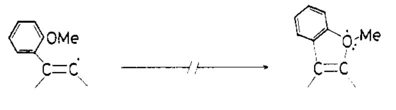
Table I. Comparison of the Competing Processes of Eq 10

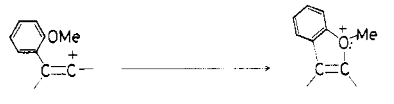
R	solvent	k_c	k_r	k_d
p-MeOC$_6$H$_4$	THF	100	0	
Ph	benzene	100	0	
Me	MeOH	40	40	20
Me	benzene	50	50	
H	benzene	15	85	



(7)

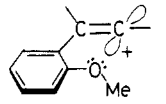
Intramolecular Cyclization in the Photolysis of β-(*o*-Methoxyphenyl)-Substituted Vinyl Bromides. In the photolysis of the vinyl bromides there are two reactive intermediates, i.e., the vinyl radical–bromine atom pair and the vinyl cation–bromide anion pair. Since cyclization via the vinyl radical does not obey the octet rule (eq 8), we assume it occurs exclusively via the vinyl cation (eq 9), and therefore the formation of benzofurans serves as evidence for the intervention of the vinyl cation.


(8)


(9)

When the vinyl bromide **1d** was photolyzed in methanol, solvent-incorporated products were not formed. A similar behavior was observed in the solvolysis,[7] suggesting that cyclization is much faster than attack by an external nucleophile.

Vinyl cations usually have linear geometry with sp hybridization at the α-carbon. The vacant p orbital is in the molecular plane and in close vincinity to the lone pair on the oxygen atom of the *o*-methoxyphenyl group(s) (see structure **18**). Consequently, this structure leads to easy intramolecular cyclization. The attack of the nucleophilic solvent on the vinyl cation will result in the formation of a sterically hindered tetrasubstituted olefin, while the intramolecular cyclization leads to a less sterically hindered benzofuran. Indeed, β-(*o*-methoxyphenyl)-substituted vinyl cations cyclize intramolecular faster than they react with a nucleophile.


18

Competition between Cyclization and Rearrangement. The initially formed vinyl cation undergoes three processes, i.e., cyclization (k_c), rearrangement (k_r), and deprotonation (k_d), as summarized in eq 10. The yields of the products which reflect the relative rate constants are given in Table I.

The k_c/k_r ratios are dependent on the nature of the α substituent of the initially formed vinyl cation, whereas the deprotonation rate is dependent on the solvent basicity.

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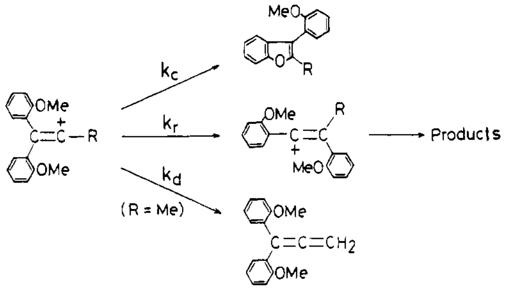
(11) Apeloig, Y; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* 1977, *42*, 3004.



(10)

Apeloig et al. calculated the following order of efficiency of α substituents in stabilizing the vinyl cation: $C_6H_5 \gg$ c-$C_3H_5 \simeq HC{=}CH_2 \gg C{\equiv}CH \simeq CH_3 \gg H$, in the gas phase.[11] The relative k_c/k_r values of Table I are correlated with the stability of the initially formed vinyl cation. Hence, a reactivity–selectivity relationship holds: the more stable the vinyl cation is the higher the extent of cyclization and the lower the extent of rearrangement.

Conclusion

The photolysis of β-(*o*-methoxyphenyl)-substituted vinyl bromides give various benzofuran derivatives. With α-aryl-substituted systems (Ar = *p*-$MeOC_6H_4$ and C_6H_5) the benzofuran is derived exclusively from the unrearranged vinyl cation, but when the α substituent is methyl or hydrogen, the benzofuran derived from the rearranged vinyl cation is also formed. These results reflect the different stabilities of the initially formed vinyl cations. The photolysis β-(*o*-methoxyphenyl)-substituted vinyl bromides provides a simple and useful method of the synthesis of benzofuran derivatives.

Experimental Section

Melting points are uncorrected. NMR spectra were taken on JNM-MH-60 and HITACHI R-24B spectrometers. Mass spectra were obtained with a JEOL JMS-07 spectrometer. Ultraviolet spectra were recorded on a Shimadzu UV-200S spectrometer. IR spectra were obtained with a Shimadzu IR-400 spectrometer. High-pressure liquid chromatography was carried out with a Shimadzu 840 liquid chromatograph.

Materials. The vinyl bromides were prepared according to the literature methods: **1a** and **1b**,[7] **1c**,[10] and **1e**.[12]

β,β-Bis(*o*-methoxyphenyl)-α-methylvinyl Bromides (1d). *o*-Methoxyphenylmagnesium bromide prepared from *o*-bromoanisole and magnesium in dry ethyl ether was allowed to react with ethyl propionate. After the usual treatment, the 1,1-bis(*o*-methoxyphenyl)propanol was obtained, which was recrystallized from hexane: mp 102–103 °C; NMR (CCl_4) δ 0.77 (t, J = 7 Hz, 3 H), 2.27 (q, J = 7 Hz, 2 H), 3.31 (s, 6 H), 4.12 (br s, 1 H), 6.45–7.54 (m, 8 H). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.85; H, 7.38. The propanol was converted to 1,1-bis(*o*-methoxyphenyl)propene (**8d**) by refluxing it for 90 min with 85% phosphoric acid. The propene **8d** was recrystallized from ethanol: mp 86–88 °C; NMR ($CDCl_3$) δ 1.68 (d, J = 7 Hz, 3 H), 3.61 (s, 3 H), 3.74 (s, 3 H), 6.08 (q, J = 7 Hz, 1 H), 6.67–7.30 (m, 8 H). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.01; H, 7.14. The vinyl bromide **1d** (mp 107–108 °C), which was recrystallized from ethanol, was obtained by bromination of the propene **8d** in CCl_4: NMR ($CDCl_3$) δ 2.20 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 6.59–7.12 (m, 8 H). Anal. Calcd for $C_{17}H_{17}O_2Br$: C, 61.28; H, 5.14. Found: C, 61.07; H, 5.23.

Photolysis of Vinyl Bromide 1a. A solution of **1a** (300 mg) in THF (100 mL) was irradiated under a nitrogen atmosphere at 5 °C for 8 h through a Pyrex filter with a 100-W high-pressure mercury lamp. The solvent was removed under reduced pressure, and the crude photoproducts were obtained by elution with benzene through an alumina column. Fractionation recrystallization from benzene–hexane gave the benzofuran **2a** (140 mg, mp 126–128 °C), which was identified by comparison with an authentic sample,[6] and few crystals of compound (mp 179–182 °C) which was assigned as benzofuranophenanthrene **4a** on the basis of the spectral data: NMR (CCl_4) δ 4.07 (s, 3 H), 4.25 (s, 3 H), 7.10–8.10 (m, 10 H); UV (cyclohexane) λ_{max} 225 nm (log ϵ 4.75), 319 (4.34), 332 (4.34), 358 (4.11), 376 (4.06). Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.61; H, 4.98.

Irradiation of **2a** (300 mg) in THF (100 mL) with a Pyrex filter for 9 days under similar conditions gave 160 mg of **4a** (70% conversion). Irradiation of **1a** (850 mg) in THF (110 mL) without a Pyrex filter for 6.5 h gave 185 mg of **4a** which was separated by column chromatography on alumina with benzene–hexane as the eluant. Large amounts of yellow powder (150 mg, mp 155–180 °C) were obtained from the ether–ethanol eluate and assigned as a mixture of reaction products of **1a** with THF by the NMR spectrum.

Photolysis of Vinyl Bromides 1b, c. A solution of **1b** (33.6 mg) in benzene (1 mL) was irradiated in a Pyrex NMR tube through hard glass with a 100-W high-pressure mercury lamp. The reaction was followed by NMR. After 6 h of irradiation the disappearance of **1b** was checked, and the photoproducts were analyzed by high-pressure liquid chromatography (column, silica gel; solvent, methylene chloride/hexane, 5/95 (v/v); pressure, 50 kg/cm^2). The major product was 2-phenyl-3-(*o*-methoxyphenyl)benzofuran (**2b**), which was identified by comparison with an authentic sample.[6] A trace of benzofuranophenanthrene **4b** was also detected.

A solution of **1c** (33.7 mg) in benzene (1 mL) was similarly irradiated in a Pyrex NMR tube for 4.5 h. The photoproducts were analyzed by high-pressure liquid chromatography. It was found by comparison with an authentic sample[10] that the major product was 2-phenyl-3-(*p*-methoxyphenyl)benzofuran (**2c**), and a trace of benzofuranophenanthrene **4c** was also detected.

In the above photoproduct analyses, the benzofuranophenanthrenes **4b** and **4c** were detected by comparison of the retention times with those of the authentic samples which were prepared by the irradiation of **2b** and **2c** with the same preparative method as for the preparation of **4a** from **2a**. **4b**: mp 155–158 °C (from EtOH–benzene); NMR (CCl_4) δ 4.10 (s, 3 H), 7.10–8.76 (m, 11 H). Anal. Calcd for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.69; H, 4.68. **4c**: mp 144–147 °C (from EtOH–benzene); NMR ($CDCl_3$) δ 3.94 (s, 3 H), 7.07–8.60 (m, 11 H). Anal. Calcd for $C_{21}H_{14}O_2$: C, 84,54; H, 4.73. Found: C, 84.79; H, 4.68.

Photolysis of Vinyl Bromide 1d. A solution of **1d** (2 mmol, 666 mg) in methanol (100 mL) containing pyridine (0.2 mL) was irradiated directly under a nitrogen atmosphere at 10 °C by using a 100-W high-pressure mercury lamp. The solvent was removed under reduced pressure, and then the residue was chromatographed over alumina. Elution with 40% benzene–hexane gave benzofuran **2d**: mp 60–61 °C (from EtOH); NMR(CCl_4) δ 2.34 (s, 3 H), 3.59 (s, 3 H), 6.59–7.31 (m, 8 H); UV (EtOH) λ_{max} 253 nm (log ϵ 4.13), 277 (3.89), 284 (3.86); mass spectrum, m/e 238 (M^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.31; H, 5.98. Elution with 60% benzene–hexane gave benzofuran **3d** as the major product along with small amounts of benzofuran **2d**. Further repeated chromatography of this fraction gave **3d**. Mass and NMR spectra showed that **3d** was a constitutional isomer of **2d**. The structure of **3d** was assigned as 2-(*o*-methoxyphenyl)-3-methylbenzofuran by the following spectra. The benzofuran **3d** should have absorption a longer wavelength than **2d** in the UV spectrum because **3d** has a longer conjugated system than **2d**:[12] NMR (CCl_4) δ 2.16 (s, 3 H), 3.74 (s, 3 H), 6.72–7.42 (m, 8 H); UV(EtOH) λ_{max} 282, 299; mass spectrum, m/e 238 (M^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.20; H, 5.96. Elution with 80% benzene–hexane gave propene **8d**, which was identified by comparison of its NMR spectrum with that of an authentic sample obtained as described at the beginning of the Experimental Section. Elution with benzene gave the allene **9d** as an oil. The purification of **9d** by column chromatography was failed, but the structure was assigned by use of the following spectral data: NMR (CCl_4) δ 3.60 (s, 6 H), 4.85 (s, 2 H), 6.67–7.20 (m, 8 H); IR 1938 cm^{-1} ($C{=}C{=}C$).

The product distribution was determined by the NMR spectrum of the crude mixture with *tert*-butylbenzoic acid as an internal standard.

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[12] (a) Cardillo, G.; Cricchio, R.; Merlin, L. *Tetrahedron* **1971**, *22*, 1875. (b) Angeloni, A. S.; Delmoro, F.; Tramontini, M. *Ann. Chim. (Rome)* **1963**, *53*, 1751.

Similar irradiation experiments of **1d** (2 mmol, 666 mg) in benzene (100 mL) or benzene (100 mL) containing zinc powder (131 mg) gave **2d**, **3d**, and **8d** but did not give the allene **9d**.

Photolysis of Vinyl Bromide 1e. A solution of **1e** (500 mg) in benzene (200 mL) was directly irradiated by using a 100-W high-pressure mercury lamp at 10 °C for 4 h. After evaporation of the solvent the crude photoproducts were chromatographed over alumina and separated into three fractions. The first fraction (elution with 20% benzene–hexane) gave an oil which contained **2e** and **3e**. Complete separation by repeated chromatography on alumina with hexane as the eluant failed. The early fraction contained mainly **2e**, and the latter fraction contained mainly **3e**. The structure of **3e** [NMR (CCl_4) δ 3.98 (OMe); UV (cyclohexane) λ_{max} 312, 326 nm] was confirmed as 2-(*o*-methoxyphenyl)benzofuran by comparison of its spectra of an authentic sample.[10] The structure of **2e** which was a constitutional isomer of **3e** [NMR (CCl_4) δ 3.84 (OMe); UV (cyclohexane) λ_{max} 254, 260, 283 nm], having shorter wavelength wavelength absorption in UV spectrum, and was assigned as 3-(*o*-methoxyphenyl)benzofuran but could not be purified for analysis. The second fraction (elution with 30% benzene–hexane) gave a crystalline compound which was confirmed as the starting material **1e** by the mixture melting point (114–115 °C). The third fraction (elution with 50% benzene–hexane) gave bis(*o*-methoxyphenyl)acetylene (**14e**):[13] mp 127–128 °C; NMR (CCl_4) δ 3.88 (s, 6 H), 6.67–7.53 (m, 8 H). The product distribution was determined by the NMR spectrum of each of the fractions.

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Registry No. 1a, 62378-29-4; **1b**, 62378-32-9; **1c**, 79517-71-8; **1d**, 79517-72-9; **1e**, 5293-93-6; **2a**, 62378-40-9; **2b**, 62378-28-3; **2c**, 25433-77-6; **2d**, 79517-73-0; **2e**, 28226-83-7; **3d**, 79517-74-1; **3e**, 42926-53-4; **4a**, 79534-26-2; **4b**, 79534-27-3; **8d**, 79517-75-2; **9d**, 79517-76-3; **14e**, 5293-78-7; *o*-methoxyphenyl bromide, 578-57-4; 1,1-bis(*o*-methoxyphenyl)propanol, 79517-77-4; 1,1-bis(*p*-methoxyphenyl)propene, 4663-13-2; 1,1-bis(*p*-methoxyphenyl)propadiene, 39179-88-9; 10-methyl-3,6,9-trimethoxyphenanthrene, 79534-14-8.

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[13] Coleman, G. H.; Holst, W. H.; Maxwell, R. D. *J. Am. Chem. Soc.* **1936**, *58*, 2310.

Synthesis and Bridgehead Reactivities of 1-Substituted Tricyclo[3.2.1.0^{3,6}]octanes

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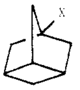
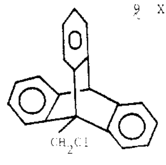
Ten bridgehead 1-substituted tricyclo[3.2.1.0^{3,6}]octanes were conveniently synthesized by our newly developed route. Thus, 5-allyl-5-(carboethoxy)cyclopentenone was irradiated to give a mixture of the tricyclic keto esters **5a** and **5b**, which were converted to 1-(carboethoxy)tricyclo[3.2.1.0^{3,6}]octane by the reduction of the corresponding thioketals. The ester function was then transformed to various substituents. The pK_a of the bridgehead carboxylic acid was determined. The bridgehead radical reactivity was also examined. The results were compared with those of the related systems.

In our previous communication,[1] we reported a facile synthesis of 1-tricyclo[3.2.1.0^{3,6}]octylmethyl *p*-toluenesulfonate (**1**; Scheme I). The solvolytic behavior of **1** is of particular interest. Significant solvent participation in the acetolysis of **1** was noted, which appears to be unusual in the bridgehead neopentyl system. Since the bridgehead ester **3** can be readily synthesized by our route as outlined in Scheme I, we have prepared various bridgehead substituted tricyclo[3.2.1.0^{3,6}]octanes **7–13** and undertaken a complementary investigation of the bridgehead reactivities of these highly strained tricyclooctane derivatives.



7 $X=CO_2H$
8 $X=CO_3Bu^t$
9 $X=H$
10 $X=NH_2 \cdot HCl$
11 $X=Br$
12 $X=Cl$
13 $X=CH_2Cl$



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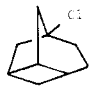

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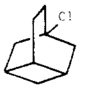

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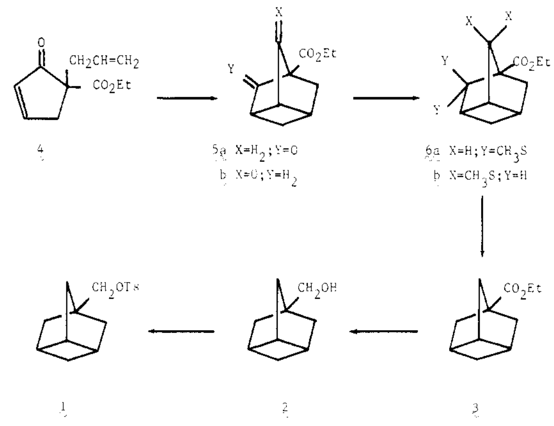
Scheme I



Results and Discussion

Synthesis. The synthetic details of **3** from **4** are described in the Experimental Section. The carboxylic acid **7** was obtained from the base hydrolysis of **3**. Thermal decomposition of **8**, readily synthesized by the usual manner,[2] afforded the hydrocarbon **9**, which exhibits identical properties with those described in the literature.[3]

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[1] Luh, T.-Y.; Lei, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 214.

[2] Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271.

[3] Sauers, R. R.; Parent, R. A.; Damle, S. B. *J. Am. Chem. Soc.* **1966**, *88*, 2257.

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