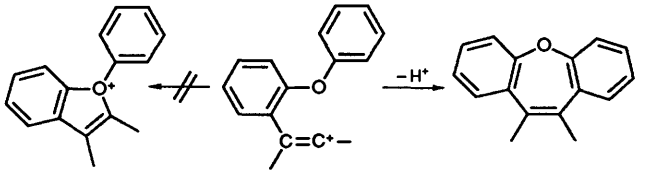
Electrophile-induced Intramolecular Cyclization of *ortho*-(Aryloxy)phenylalkynes to Dibenz[*b,f*]oxepines

Tsugio Kitamura,* Tatsuya Takachi, Hironobu Kawasato and Hiroshi Taniguchi*
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812, Japan

Reaction of *o*-(aryloxy)phenylalkynes with electrophiles such as perchloric acid, tetrafluoroboric acid, benzenesulfenyl chloride, and iodine monochloride yielded dibenz[*b,f*]oxepine derivatives. Cyclization to the dibenz[*b,f*]oxepines competed with 1,2-addition of the electrophiles. The effect of substituents on the alkyne is also discussed.

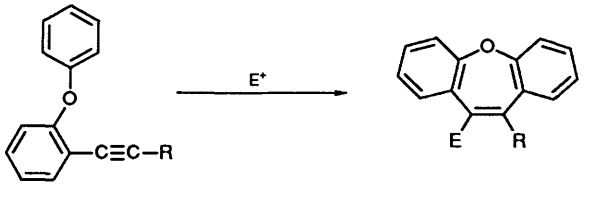
Mechanistic and synthetic aspects of the reactive intermediate vinyl cations have been investigated.[1] When the vinyl cation has a heteroatom at the appropriate position, intramolecular cyclization proceeds preferentially to yield heterocyclic compounds.[2] This process is a noted method for the preparation of substituted heterocycles because the intermediate vinyl cation, stabilized by an α-aryl group, has potent utility for the intramolecular cyclization in these cases.[2]

In a previous study,[3] vinyl cations bearing an aryloxy group at the *ortho* position of the β-aryl group were found to undergo intramolecular cyclization of the vinyl cations on the aryl ring instead of the oxygen atom to produce seven membered heterocycles, dibenz[*b,f*]oxepines (Scheme 1). This process is highly selective in the case of stabilized α-arylvinyl cations.



Scheme 1

On the other hand, electrophilic addition to carbon–carbon triple bonds is another method for the generation of vinyl cations [1,4] and in this case the reaction can be conducted under mild conditions. If electrophilic addition to the carbon–carbon triple bond is applicable to the preparation of dibenz[*b,f*]-oxepine derivatives, this procedure is much improved with respect to the reaction conditions and also provides functionalized dibenz[*b,f*]oxepines by using appropriate electrophiles (Scheme 2). Thus, we have investigated intramolecular

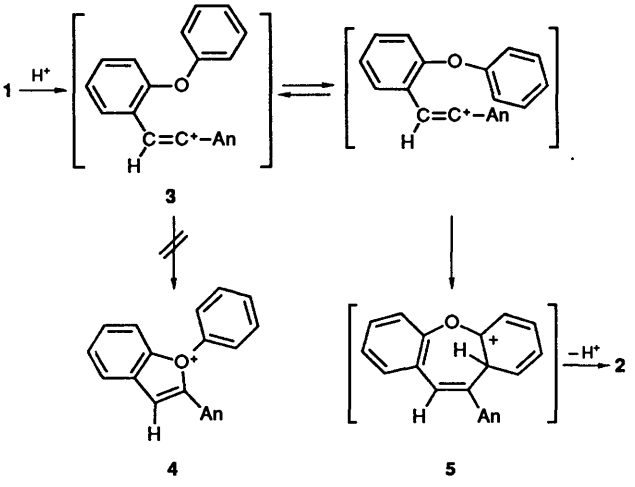


Scheme 2

cyclizations by electrophilic addition of *o*-(aryloxy)phenyl-substituted alkynes[5] and the effects of various electrophiles and substituents on the cyclization.

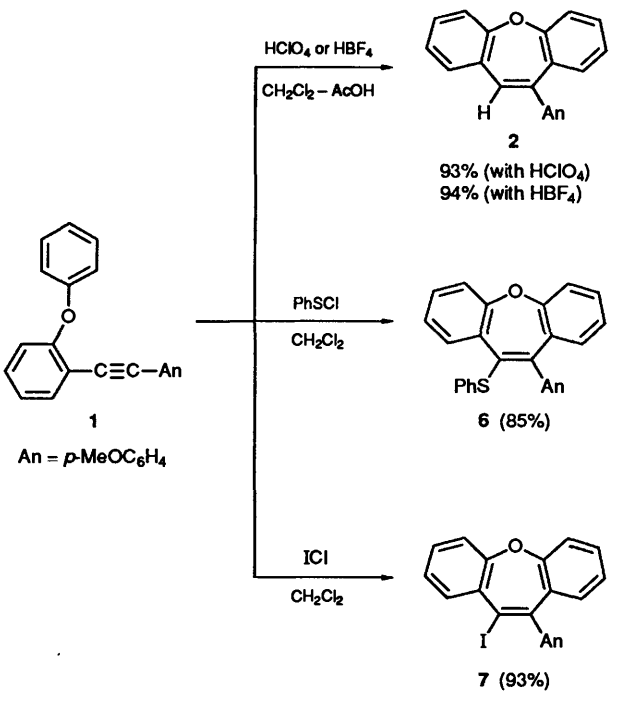
Tandem Electrophilic Addition–Cyclization Reactions of 1-(p-*Methoxyphenyl*)-2-(o-*phenoxyphenyl*)*ethyne* **1** *with Electrophiles.*—Treatment of 1-(*p*-methoxyphenyl)-2-(*o*-phenoxyphenyl)ethyne **1** with Brönstead acids such as perchloric acid ($HClO_4$) and tetrafluoroboric acid (HBF_4) in dichloromethane–acetic acid gave 5-(*p*-methoxyphenyl)dibenz[*b,f*]oxepine **2** in high yields, respectively.

Protonation at the carbon–carbon triple bond produces the vinyl cation **3** stabilized by the α-anisyl group, which readily undergoes intramolecular vinylation of the *ortho*-aryloxy group to yield dibenz[*b,f*]oxepine **2**. A similar type of intermolecular vinylation of aromatic compounds has been studied on vinyl cations generated from vinyl triflates[6] and bromides.[7] Vinyl cations bearing a methoxy group as the *ortho*-substituent,[2f–i] instead of an aryloxy group, afford benzofuran derivatives by attack of the oxygen atom at the cationic carbon followed by removal of the methyl group. In the present case, the attack of the oxygen atom produces unstable 1-phenylbenzo[*b*]furanium ion **4**.[3b] Accordingly, electrophilic aromatic substitution leading to **2** is the most preferable process. In addition, the activation of the aromatic ring by oxygen atom and the proximity to the cationic centre accelerate the generation of the most stable ion **5** (Scheme 3).



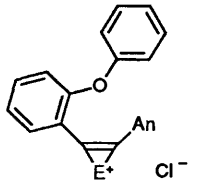
Scheme 3

Similar treatment of alkyne **1** with benzenesulfenyl chloride or iodine monochloride in dichloromethane afforded 5-(*p*-methoxyphenyl)-6-(phenylthio)dibenz[*b,f*]oxepine **6** or 5-iodo-6-(*p*-methoxyphenyl)dibenz[*b,f*]oxepine **7**, respectively, in 85 or 93% yield (Scheme 4). Electrophilic addition of benzenesulfenyl chloride to alkynes produces a stable bridged thiirenium ion,[4] which collapses to an (*E*)-alkenyl chloride by attack of chloride anion. The same behaviour is found for the reaction of iodine monochloride with alkynes. However, in the present case, no alkenyl chlorides were formed. This result means that intramolecular arylation is predominant over inter-



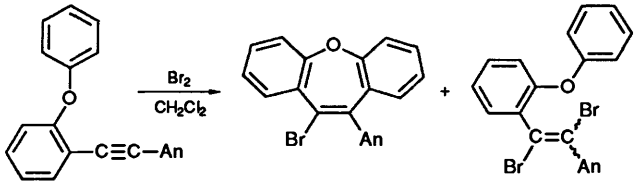
Scheme 4

molecular attack of chloride anion in the bridged thiirenium ion **8a** or in the bridged iodonium ion **8b**.



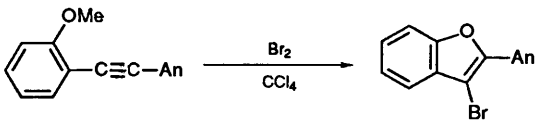
8a E = PhS
8b E = I

The reaction with bromine was found to be somewhat different from that with perchloric acid, tetrafluoroboric acid, benzenesulfenyl chloride, or iodine monochloride. Interaction of alkyne **1** with bromine in dichloromethane led to a mixture of 5-bromo-6-(*p*-methoxyphenyl)dibenz[*b*,*f*]oxepine **9** (56%) and (*E*)- and (*Z*)-1,2-dibromo-1-(*p*-methoxyphenyl)-2-(*o*-phenoxyphenyl)ethenes **10** (44%) (Scheme 5). The aryloxy-substituted



Scheme 5

system lacks the selectivity to bromine-induced intramolecular cyclization compared with the corresponding *ortho*-methoxyphenyl-substituted alkyne which yields a benzofuran derivative quantitatively on treatment with bromine (Scheme 6).[8] Formation of a 3:2 mixture of (*E*)- and (*Z*)-1,2-dibromoethenes **10** suggests that the intermediate cation is an open cation where

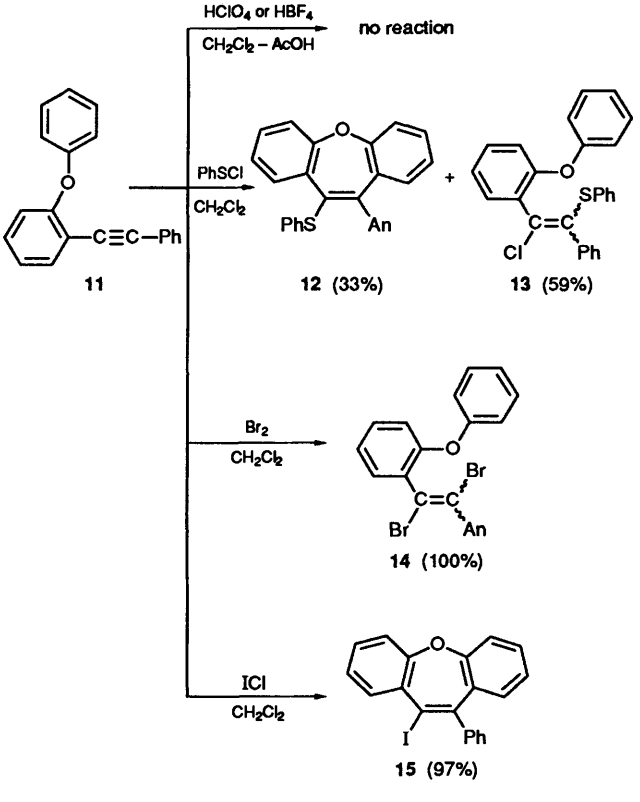


Scheme 6

the positive charge is localized on the carbon attached to the anisyl group, rather than a complete bridged bromonium ion. Furthermore, the relatively strong nucleophilicity of bromide anion decreases the selectivity to cyclization.

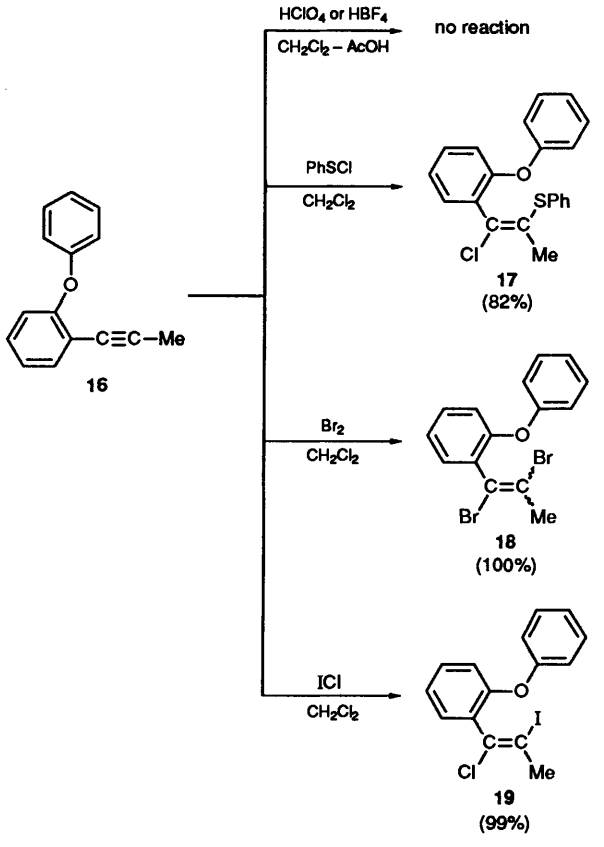
Effect of Substituents on Tandem Electrophilic Addition–Cyclization Reactions.—Substituents are important factors affecting organic reactions. In the present reactions, a large substituent effect is expected.

Treatment of 1-phenyl-2-(*o*-phenoxyphenyl)ethyne **11** with perchloric acid or tetrafluoroboric acid resulted in recovery of the starting alkyne **11**. This is attributable to the relatively low reactivity of phenyl-substituted alkynes compared with *p*-methoxyphenyl-substituted alkynes.[9] On the other hand, interaction with benzenesulfenyl chloride yielded 5-phenyl-6-(phenylthio)dibenz[*b*,*f*]oxepine **12** (33%) and alkenyl chloride **13** (59%). Treatment with bromine afforded 1,2-dibromoethenes **14** (100%). However, reaction with iodine monochloride yielded 5-iodo-6-phenyldibenz[*b*,*f*]oxepine **15** quantitatively (Scheme 7).



Scheme 7

No cyclized products were obtained in the case of the propyne derivative **16**. Treatment of 1-(*o*-phenoxyphenyl)prop-1-yne **16** with perchloric acid or tetrafluoroboric acid resulted in recovery of the starting propyne **16**. Reactions with benzenesulfenyl chloride, bromine, or iodine monochloride gave 1,2-adducts, that is, alkenyl chloride **17**, 1,2-dibromoethene **18**, or chloroiodoethene **19**, respectively (Scheme 8). The outcome of the stereochemistry concerning 1,2-adducts is deduced on the basis of the known behaviour of the electrophiles toward alkynes.[4] Namely, benzenesulfenyl chloride and iodine mono-



Scheme 8

chloride add stereoselectively to yield the (*E*)-isomers but bromine adds non-stereoselectively.

In summary, electrophilic addition to *o*-phenoxyphenyl-substituted alkynes can be summarized as follows: (1) an electrophile such as proton, PhS^+, Br^+ or I^+ attacks the carbon–carbon bond to form a bridged cation or a vinyl cation; (2) the resulting cation undergoes intramolecular arylation to produce a dibenz[*b*,*f*]oxepine rather than intramolecular nucleophilic attack by the oxygen atom to form a 1-phenylbenzo[*b*]furanium ion; (3) a *p*-methoxyphenyl group as the substituent facilitates the intramolecular arylation, while other substituents favour intermolecular addition; (4) benzenesulfenyl chloride and iodine monochloride are better reagents to obtain seven-membered dibenz[*b*,*f*]oxepine derivatives.

Therefore, it is concluded that electrophilic addition to *o*-(aryloxy)phenylalkynes proceeds under mild conditions and provides a substituted dibenz[*b*,*f*]oxepine and a 1,2-adduct. This process can be applied to the preparation of dibenz-[*b*,*f*]oxepine derivatives when the alkyne is substituted by aryl groups.

Experimental

M.p.s are uncorrected. NMR spectra were taken on Hitachi R 600, Bruker AC-250, and JEOL GSX 400 machines and *J*-values are given in Hz. IR spectra were obtained with a Hitachi 270-30 instrument. Mass spectra were obtained with a Shimadzu GCMS-7000 machine.

Copper(I) acetylides were prepared according to the method described by Castro *et al.*[10] Benzenesulfenyl chloride was prepared by the reaction of diphenyl disulfide with SO_2Cl_2.[11]

o-Iodophenyl Phenyl Ether.—To a solution of diphenyl ether (15.9 cm^3, 0.10 mol) in THF (80 cm^3) was added dropwise BuLi (1.6 mol dm^{-3} in hexane; 100 cm^3, 0.16 mol) at 0 °C under a nitrogen atmosphere. After being stirred for 4 h, the mixture was cooled to −70 °C and a solution of iodine (30 g, 0.12 mol) in THF (tetrahydrofuran) (50 cm^3) was added. The mixture was warmed to room temperature with stirring and then quenched with aqueous sodium thiosulfate. The product was extracted with diethyl ether and the organic layer was washed and dried (Na_2SO_4). Evaporation of the solvent gave crystals, which were filtered off and washed with methanol. Recrystallization from methanol yielded 9.83 g (33%) of *o-iodophenyl phenyl ether*; m.p. 51–53 °C (lit.,[12] m.p. 55–56 °C); δ_H(60 MHz; $CDCl_3$) 6.66–7.96 (m, ArH).

Preparation of 1-(p-*Methoxyphenyl*)-2-(o-*phenoxyphenyl*)-*ethyne* **1**.—A mixture of *o*-iodophenyl phenyl ether (2.96 g, 10 mmol) and copper(I) *p*-methoxyphenylacetylide (2.34 g, 12 mmol) was refluxed in pyridine (40 cm^3) for 12 h. To the cooled mixture was added dilute HCl and aqueous NH_4Cl and the product was extracted with diethyl ether. The organic layer was washed successively with aqueous sodium thiosulfate, dilute HCl, water and saturated aqueous NaCl, and dried (Na_2SO_4). After evaporation of the solvent the product was purified by column chromatography on alumina with hexane–dichloromethane as the eluent. Recrystallization from methanol gave white crystals (2.51 g, 83%); m.p. 84.5–85.5 °C (Found: C, 83.9; H, 5.3. $C_{21}H_{16}O_2$ requires C, 83.98; H, 5.37%); δ_H(60 MHz; $CDCl_3$) 3.76 (s, OMe) and 6.69–7.48 (m, ArH); δ_C(100 MHz; $CDCl_3$) 55.24, 83.83, 94.58, 113.86, 115.36, 116.51, 118.02, 119.81, 122.83, 123.71, 129.32, 129.61, 133.03, 133.45, 156.92, 157.63 and 159.64; ν_{max}(Nujol)/cm^{-1} 2224 (C≡C).

Preparation of 2-(o-*Phenoxyphenyl*)-1-*phenylethyne* **11**.—In the manner described above, *o*-iodophenyl phenyl ether (4.44 g, 15 mmol) and copper(I) phenylacetylide (2.47 g, 15 mmol) were allowed to react in pyridine (40 cm^3). The crude product was recrystallized from methanol to yield white crystals (3.07 g, 76%); m.p. 85–87 °C (Found: C, 88.6; H, 5.2. $C_{20}H_{14}O$ requires C, 88.86; H, 5.22); δ_H(60 MHz; $CDCl_3$) 6.83–7.66 (m, ArH); ν_{max}(Nujol)/cm^{-1} 2228 (C≡C).

Preparation of 1-(o-*Phenyoxyphenyl*)*prop*-1-*yne* **16**.—To a solution of diphenyl ether (15.9 cm^3, 0.10 mol) in THF (100 cm^3) was added BuLi (1.6 mol dm^{-3} in hexane; 61.9 cm^3, 0.10 mol) at room temperature under a nitrogen atmosphere and the mixture was stirred for 2 h. The mixture was cooled to −70 °C and propionaldehyde (7.2 cm^3, 0.10 mol) was added dropwise. The mixture was warmed to room temperature with stirring and quenched with water. The product was extracted with diethyl ether and the organic layer was washed with water and saturated NaCl, and dried (Na_2SO_4). After evaporation of the solvent the crude mixture was submitted to column chromatography on alumina. Elution with dichloromethane–ethanol gave 1-(*o*-phenoxyphenyl)propan-1-ol as a pale yellow oil (12.96 g, 57%); δ_H(60 MHz; $CDCl_3$) 0.88 (t, *J* 7, Me), 1.71 (quint., *J* 7, CH_2), 2.47 (br s, OH), 4.80 (t, *J* 7, CH) and 6.55–7.53 (m, ArH). This propanol was used for the next step without further purification. 1-(*o*-(Phenoxyphenyl)propan-1-ol (12.17 g, 53.3 mmol) was dissolved in acetone (10 cm^3) and cooled to 0 °C. A solution of chromium(VI) oxide (3.50 g, 35 mmol), water (10 cm^3), and conc. sulfuric acid (3 cm^3) was added under a nitrogen atmosphere and the mixture was stirred for 1 h. The mixture was diluted with water and extracted with diethyl ether. The organic layer was washed successively with aqueous $NaHCO_3$, water, and saturated NaCl, and dried (Na_2SO_4). After evaporation of the solvent, the crude product was submitted to column chromatography on alumina. Elution with hexane–dichloromethane gave *o*-phenoxypropiophenone as a pale yellow oil (7.22, 60%); δ_H(60 MHz; $CDCl_3$) 1.13 (t, *J* 7, Me), 3.02 (q, *J* 7, CH_2) and 6.73–7.96 (m, ArH); ν_{max}(neat)/cm^{-1} 1680

(C=O). This propiophenone was used for the next step without further purification. A solution of *o*-phenoxypropiophenone (7.22 g, 31.9 mmol) and phosphorus pentachloride (6.73 g, 31.0 mmol) in benzene (30 cm^3) was refluxed for 12 h. The mixture was poured into ice-water and extracted with diethyl ether. The organic layer was washed successively with aqueous $NaHCO_3$, water, and saturated NaCl, and dried (Na_2SO_4). After evaporation of the solvent the crude product was submitted to column chromatography on alumina. Elution with dichloromethane gave 1-chloro-1-(*o*-phenoxyphenyl)prop-1-ene as a pale yellow oil (7.47 g, 95%); δ_H(60 MHz; $CDCl_3$) 1.81 (d, *J* 7, Me), 6.04 (q, *J* 7, =CH) and 6.67–7.57 (m, ArH). This chloropropene was used for the next dehydrochlorination without further purification. To a stirred suspension of potassium *tert*-butoxide (4.40 g, 39.2 mmol) in THF (30 cm^3) was added at 0 °C a solution of 1-chloro-1-(*o*-phenoxyphenyl)prop-1-ene (7.44 g, 30.4 mmol) in THF (20 cm^3) and the mixture was stirred at room temperature for 12 h. The mixture was diluted with water and extracted with diethyl ether. The organic layer was washed with water and saturated NaCl, and dried (Na_2SO_4). After evaporation of the solvent the product mixture was submitted to column chromatography on alumina. Elution with hexane–dichloromethane gave o-*phenoxyphenylprop*-1-*yne* **16** as white crystals, which were recrystallized from methanol to yield 2.07 g (33%); m.p. 60–61 °C (Found: C, 86.3; H, 5.9. $C_{15}H_{12}O$ requires C, 86.51; H, 5.81); δ_H(60 MHz; $CDCl_3$) 1.91 (s, Me) and 6.69–7.57 (m, ArH); ν_{max}(Nujol)/cm^{-1} 2240 (C≡C).

Reaction of 1-(p-*Methoxyphenyl*)-2-(o-*phenoxyphenyl*)*ethyne* **1**.—*With perchloric acid or tetrafluoroboric acid.* Alkyne **1** (0.300 g, 1.0 mmol) was dissolved in dichloromethane (2 cm^3) and acetic acid (8 cm^3) and 60% perchloric acid (0.15 cm^3, 1.5 mmol) was added at room temperature. The mixture was stirred at room temperature for 12 h, diluted with water, and extracted with dichloromethane. The dichloromethane extract was washed with water and dried (Na_2SO_4). Evaporation of the solvent gave white crystals, which were filtered off and washed with methanol to yield 5-(p-*methoxyphenyl*)*benz*[b,f]*oxepine* **2** (0.273 g, 93%); m.p. 130–131 °C (Found: C, 83.8; H, 5.35. $C_{21}H_{16}O_2$ requires C, 83.98; H, 5.37); δ_H(60 MHz; $CDCl_3$) 3.82 (s, OMe) and 6.83–7.47 (m, ArH); δ_C(100 MHz; $CDCl_3$) 55.28, 113.77, 120.78, 121.46, 124.51, 124.80, 127.22, 129.25, 129.39, 130.07, 130.12, 130.46, 130.86, 132.19, 134.91, 141.76, 153.91, 158.51 and 159.38.

In the manner described for the reaction with perchloric acid, alkyne **1** (0.300 g, 1.0 mmol) was treated with 42% tetrafluoroboric acid (0.24 cm^3, 1.0 mmol) in dichloromethane (2 cm^3)–acetic acid (8 cm^3). The same dibenz[*b,f*]oxepine **2** was obtained (0.281 g, 94%).

With benzenesulfenyl chloride. To a solution of alkyne **1** (0.300 g, 1.0 mmol) in dichloromethane (10 cm^3) was added dropwise a solution of benzenesulfenyl chloride (0.145 g, 1.0 mmol) in dichloromethane (2 cm^3) and the mixture was stirred at room temperature for 12 h. Evaporation of the solvent gave white crystals which were recrystallized from ethanol to yield 5-(p-*methoxyphenyl*)-6-(*phenylthio*)*dibenz*[b,f]*oxepine* **6** (0.347 g, 85%); m.p. 120–123 °C (Found: C, 79.5; H, 4.95. $C_{27}H_{20}O_2S$ requires C, 79.38; H, 4.93); δ_H(60 MHz; $CDCl_3$) 3.75 (s, OMe) and 6.69–7.79 (m, ArH); *m/z* 408 (M^+, 100%), 393 (M^+ – Me, 14) and 299 (M^+ – PhS, 19).

With iodine monochloride. To a solution of alkyne **1** (0.300 g, 1.0 mmol) in dichloromethane (10 cm^3) was added a solution of iodine monochloride (0.162 g, 1.0 mmol) in dichloromethane (2 cm^3) and the mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was crystallized from methanol to give 5-*iodo*-6-(p-*methoxyphenyl*)*dibenz*[b,f]-*oxepine* **7** as crystals (0.398 g, 93%); m.p. 147–149 °C (Found: C, 59.1; H, 3.6. $C_{21}H_{15}IO_2$ requires C, 59.17; H, 3.55); δ_H(250 MHz; $CDCl_3$) 3.83 (s, OMe), 6.79–6.96 (m, ArH), 7.12–7.26 (m, ArH) and 7.70–7.74 (m, ArH); δ_C(62.9 MHz; $CDCl_3$) 55.20, 101.68, 113.57, 120.19, 120.75, 124.58, 124.77, 129.97, 130.51, 131.04, 131.38, 131.49, 134.73, 134.91, 139.97, 147.24, 157.66, 158.91 and 159.09; *m/z* 426 (M^+, 79%) and 299 (M^+ – I, 100).

With bromine. To a solution of alkyne **1** (0.030 g, 1.0 mmol) in dichloromethane (10 cm^3) was added a solution of bromine (0.160 g, 1.0 mmol) in dichloromethane (2 cm^3) and the mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was crystallized from hexane to give white crystals (0.214 g, 56%) of 5-*bromo*-6-(p-*methoxyphenyl*)-*dibenz*[b,f]*oxepine* **9**; m.p. 182–184 °C (hexane–benzene) (Found: C, 66.65; H, 4.0. $C_{21}H_{15}BrO_2$: 66.51; H, 3.99); δ_H(60 MHz; $CDCl_3$) 3.83 (s, OMe) and 6.67–7.90 (m, ArH); *m/z* 380 (M^+ + 2, 90%), 378 (M^+, 90) and 299 (M^+ – Br, 100). From the mother liquor, a mixture of (*E*)- and (*Z*)-1,2-*dibromo*-1-(p-*methoxyphenyl*)-2-(o-*phenoxyphenyl*)*ethene* **10** as an oil (0.201 g, 44%) (Found: C, 54.9; H, 3.5. $C_{21}H_{16}Br_2O_2$: C, 54.81; H, 3.50); δ_H(60 MHz; $CDCl_3$) 3.64 (s, OMe), 3.73 (s, OMe) and 6.46–7.53 (m, ArH); *m/z* 463 (M^+ + 2, 2), 460 (M^+, 4), 458 (M^+ – 2, 2), 381 (M^+ – 79, 19), 379 (M^+ – 81, 20) and 300 (M^+ – Br_2, 100).

Reaction of 1-*Phenyl*-2-(o-*phenoxyphenyl*)*ethyne* **11**.—*With benzenesulfenyl chloride.* In the manner described for the reaction of alkyne **1**, alkyne **11** (0.270 g, 1.0 mmol) was treated with benzenesulfenyl chloride (0.145 g, 1.0 mmol). After work-up of the reaction mixture, the products were separated by column chromatography on silica gel and preparative HPLC with hexane–dichloromethane as the eluent. 5-*Phenyl*-6-(*phenylthio*)*dibenz*[b,f]*oxepine* **12** was obtained as white crystals (0.126 g, 33%); m.p. 143–145 °C (Found: C, 82.65; H, 4.85. $C_{26}H_{18}OS$ requires C, 82.51; H, 4.79); δ_H(60 MHz; $CDCl_3$) 6.65–7.86 (m, ArH); *m/z* 378 (M^+, 100%), 301 (M^+ – Ph, 8) and 269 (M^+ – PhS, 36). 1-*Chloro*-1-(o-*phenoxyphenyl*)-2-*phenyl*-2-(*phenylthio*)*ethene* **13** was obtained as an oil (0.246 g, 59%) (Found: C, 75.35; H, 4.7. $C_{26}H_{19}ClOS$ requires C, 75.26; H, 4.61); δ_H(60 MHz; $CDCl_3$) 6.81–7.57 (m, ArH); *m/z* 414 (M^+, 76%), 379 (M^+ – Cl, 24), 320 (67) and 285 (100).

With bromine. In the manner described for the reaction of alkyne **1**, alkyne **11** (0.270 g, 1.0 mmol) was treated with bromine (0.160 g, 1.0 mmol). After work-up, the crude products were purified by column chromatography on silica gel with hexane–dichloromethane as the eluent to yield a mixture of (E)- and (Z)-1,2-*dibromo*-2-(o-*phenoxyphenyl*)-1-*phenylethenes* **14** as an oil (0.429 g, 100%) (Found: C, 55.85; H, 3.3. $C_{20}H_{14}Br_2O$ requires C, 55.85; H, 3.28); δ_H(60 MHz; $CDCl_3$) 6.44–7.53 (m, ArH); *m/z* 432 (M^+ + 2, 1%), 430 (M^+, 2), 428 (M^+ – 2, 1), 351 (M^+ – 79, 22), 349 (M^+ – 81, 24) and 270 (M^+ – 2 Br, 100). One of the isomers was crystallized to give white crystals, m.p. 109–111 °C (MeOH).

With iodine monochloride. In the manner described for the reaction of alkyne **1**, alkyne **11** (0.270 g, 1.0 mmol) was treated with iodine monochloride (0.162 g, 1.0 mmol). Similar work-up gave 5-*iodo*-6-*phenyldibenz*[b,f]*oxepine* **15** as crystals (0.385 g, 97%); m.p. 126–128 °C (Found: C, 60.55; H, 3.3. $C_{20}H_{13}IO$ requires C, 60.63; H, 3.31); δ_H(250 MHz; $CDCl_3$) 6.78–6.93 (m, ArH), 7.12–7.44 (m, ArH) and 7.71–7.74 (m, ArH); δ_C(62.9 MHz; $CDCl_3$) 101.66, 120.33, 120.79, 124.62, 124.82, 127.79, 128.32, 129.63, 130.00, 130.61, 131.18, 134.58, 134.86, 147.38, 147.55, 157.61 and 158.90; *m/z* 396 (M^+, 67%) and 269 (M^+ – I, 100).

Reaction of 1-(o-*Phenoxyphenyl*)*prop*-1-*yne* **16**.—*With benzenesulfenyl chloride.* In the manner described for the reaction of alkyne **1**, alkyne **16** (0.208 g, 1.0 mmol) was treated with benzenesulfenyl chloride (0.145 g, 1.0 mmol). After work-up, white crystals of (E)-1-*chloro*-1-(o-*phenoxyphenyl*)-2-(*phenylthio*)*prop*-1-*ene* **17** were obtained, which were recrystallized

from methanol to yield 0.270 g (82%); m.p. 84–86 °C (Found: C, 71.2; H, 4.95. $C_{21}H_{17}ClOS$ requires C, 71.48; H, 4.86); δ_H(60 MHz; $CDCl_3$) 2.10 (s, Me) and 6.70–7.67 (m, ArH); *m/z* 352 (M^+, 57%), 259 (M^+ − OPh, 62) and 224 (259 − Cl, 100).

With bromine. In the manner described for the reaction of alkyne **1**, alkyne **16** (0.208 g, 1.0 mmol) was treated with bromine (0.160 g, 1.0 mmol). After work-up, the crude products were purified by column chromatography on alumina. Elution with hexane–dichloromethane gave a mixture of (E)- and (Z)-1,2-*dibromo*-1-(o-*phenoxyphenyl*)*prop*-1-*enes* **18** as an oil (0.367 g, 100%) (Found: C, 49.1; H, 3.25. $C_{15}H_{12}Br_2O$ requires C, 48.95; H, 3.29); δ_H(60 MHz; $CDCl_3$) 2.18 (s, Me), 2.50 (s, Me) and 6.69–7.51 (m, ArH); *m/z* 370 (M^+ + 2, 2%), 368 (M^+, 4), 366 (M^+ − 2, 2), 289 (M^+ − 79, 20), 287 (M^+ − 81, 23) and 208 (M^+ − 2 Br, 100). Integration of methyl protons of (*E*)- and (*Z*)-isomers in the ^1H NMR spectrum showed a ratio of 1:2.

With iodine monochloride. In the manner described for the reaction of alkyne **1**, alkyne **16** (0.208 g, 1.0 mmol) was treated with iodine monochloride (0.162 g, 1.0 mmol). After work-up, the crude product was purified by a preparative TLC (silica gel) with dichloromethane–hexane to give 1-*chloro*-2-*iodo*-1-(o-*phenoxyphenyl*)*prop*-1-*yne* **19** as an oil (0.369 g, 99%) (Found: C, 48.15; H, 3.25. $C_{15}H_{12}ClIO$ requires C, 48.61; H, 3.26); δ_H(250 MHz; $CDCl_3$) 2.65 (s, Me), 6.80–6.85 (m, ArH), 7.00–7.11 (m, ArH) and 7.21–7.36 (m, ArH); δ_C(62.9 MHz; $CDCl_3$) 30.48, 94.96, 118.41, 119.59, 122.95, 123.58, 125.86, 129.59, 130.34, 131.11, 133.02, 154.34 and 156.64; *m/z* 372 (M^+ + 2, 3%), 370 (M^+, 11), 254 (34), 243 (M^+ − I, 100), 208 (M^+ − I − Cl, 91) and 207 (91).

References

1 (*a*) M. Hanack, *Carbokationes, Carbokation-Radikale*, Thieme Verlag, Stuttgart, 1990; (*b*) Z. Rappoport, in *Reactive Intermediates*, ed. R. A. Abramovitch, Plenum, New York, 1983, vol. 3; (*c*) P. J. Stang, Z. Rappoport, M. Hanack and L. R. Subramanian, *Vinyl Cations*, Academic Press, New York, 1979.

2 (*a*) G. Capozzi, G. Melloni, G. Modena and M. Piscitelli, *Tetrahedron Lett.*, 1968, 4039; (*b*) G. Capozzi, G. Melloni, G. Modena and U. Tonellato, *J. Chem. Soc., Chem. Commun.*, 1969, 1520; (*c*) G. Modena and U. Tonellato, *J. Chem. Soc. B*, 1971, 381; (*d*) G. Capozzi and G. Modena, *J. Chem. Soc., Perkin Trans. 1*, 1972, 216; (*e*) G. Capozzi, G. Modena and L. Ronzini, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1136; (*f*) T. Sonoda, M. Kawakami, T. Ikeda, S. Kobayashi and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1976, 612; (*g*) T. Sonoda, S. Kobayashi and H. Taniguchi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2560; (*h*) T. Suzuki, T. Sonoda, S. Kobayashi and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1976, 180; (*i*) T. Suzuki, T. Kitamura, T. Sonoda, S. Kobayashi and H. Taniguchi, *J. Org. Chem.*, 1981, **46**, 5324.

3 (*a*) T. Kitamura, S. Kobayashi and H. Taniguchi, *Chem. Lett.*, 1984, 547; (*b*) T. Kitamura, S. Kobayashi, H. Taniguchi and K. Hori, *J. Am. Chem. Soc.*, 1991, **113**, 6240.

4 G. H. Schmid, in *The Chemistry of the Carbon–Carbon Triple Bond*, ed. S. Patai, Wiley, Chichester, 1978, ch. 8.

5 For a preliminary report, see: T. Kitamura, T. Takachi, H. Kawasato, S. Kobayashi and H. Taniguchi, *Tetrahedron Lett.*, 1989, **30**, 7445.

6 P. J. Stang and A. G. Anderson, *Tetrahedron Lett.*, 1977, 1485; *J. Am. Chem. Soc.*, 1978, **100**, 1520.

7 T. Kitamura, S. Kobayashi, H. Taniguchi and Z. Rappoport, *J. Org. Chem.*, 1982, **47**, 5003.

8 M. Matsumoto, Master Thesis, Kyushu University, Japan, 1985. Treatment of 1-(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)ethyne with bromine in carbon tetrachloride gave 3-bromo-2-(*p*-methoxyphenyl)benzofuran quantitatively.

9 (*a*) D. S. Noyce and M. D. Schiavelli, *J. Am. Chem. Soc.*, 1968, **90**, 1020; (*b*) R. C. Bott, C. Eaborn and D. R. M. Walton, *J. Chem. Soc.*, 1965, 384.

10 C. E. Castro, E. J. Gaughan and D. C. Owsley, *J. Org. Chem.*, 1966, **31**, 4071.

11 W. H. Mueller and P. E. Butler, *J. Org. Chem.*, 1968, **33**, 1533.

12 S. Buchan and H. McCombie, *J. Chem. Soc.*, 1931, 137.

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