The reaction is ca. 2.5 times faster in nitrobenzene than in chlorobenzene under similar conditions. (4) Rearrangement cannot be observed in hydroxylic solvents; rather, the allylic group is cleaved. (5) The α-methylallyl methyl ester **4** undergoes isomerization to the crotyl methyl ester **3** at 130°, but at a rate ca. 20 times slower than the isomerization of **2** to **1** at the same temperature and concentration; this reaction is accelerated by the free acid **2**.

One intriguing mechanistic possibility for the isomerization is a 3,3-sigmatropic shift. This pathway has been demonstrated in the isomerization of allylic thiophosphates in which the oxygen to sulfur migration is accompanied by inversion of the allylic group.[6] An allyl phosphinate was found not to undergo such Claisen-type rearrangements,[4] but a monoallyl phosphonate such as **2** bears a labile acidic proton. The more nucleophilic oxygens in the anion of **2** might be more prone to initiate the sigmatropic shift.

The data clearly eliminate this possibility, however; the inhibition by pyridine indicates that the anion is inert, while the concentration dependence and effect of trifluoroacetic acid require that the reactive species is either the neutral or protonated **2**.

An ionic mechanism involving C–O cleavage to produce allylic cations is completely consistent with the observations. In hydroxylic solvents, the cations are intercepted without internal return and no isomerization is observed. The rate increase in nitrobenzene over chlorobenzene also supports this conclusion. The function of acid may be merely to prevent ionization of the strong phosphonic acid; in this case the neutral acid **2** would dissociate to an ion pair.[7] The isomerization of the neutral methyl ester **4** under nonacidic conditions shows that such a pathway is likely. On the other hand, the much slower isomerization of **4** suggests that **2** may react in a protonated form to produce a neutral phosphonic acid and an allylic cation which then recombine; such a mechanism seems required for the acid catalysis of isomerization of **4**. Cleavage in both neutral and protonated forms has been suggested for dibenzyl phosphate[8] and it appears that both mechanisms occur with rather similar energies for the allylic esters under the conditions described herein.

It thus appears that ionic mechanisms direct the isomerization of allyl phosphonates even in chlorobenzene. The detection of this rearrangement is a special case in a nonnucleophilic solvent; the possible significance of such rearrangements in biological systems remains unknown.

Experimental Section

Preparation of 3-Buten-2-yl Phenylphosphonate (2). A solution of phenylphosphonodichloridate (19.5 g) and pyridine (19 g) in anhydrous ether (300 ml) was stirred in an ice bath under argon while 3-buten-2-ol (6.0 g) was added over 15 min. After warming to room temperature, the mixture was poured into ice water containing 4 g of NaOH. The organic layer was separated, extracted with bicarbonate, and discarded. The aqueous layer and bicarbonate extract were acidified to pH <1 with concentrated HCl and extracted thrice with 75 ml of chloroform. Evaporation of the chloroform extracts gave a colorless oil which was treated[9] with a solution of 12 g of barium hydroxide in 120 ml of water. Ethanol (100 ml) was added and the precipitate was removed. The filtrate was concentrated on a vacuum pump to about one-half the volume, then adjusted to pH <1 with concentrated HCl and extracted with ether (3 × 50 ml). The organic layers were combined, dried, and evaporated to give 7.4 g of a viscous oil.

Anal. Calcd for $C_{10}H_{13}O_3P$: C, 56.58; H, 6.18. Found: C, 56.31; H, 5.93.

The NMR ($CDCl_3$, Varian A-60A) showed complex multiplets centered at δ 7.7 (2 H) and 7.3 (3 H) (aromatic protons) and at 5.7 (1 H) and 5.0 ppm (3 H) (vinyl and methine protons) plus a doublet for the methyl group at 1.31 ppm.

The 2-buten-1-yl phenylphosphinate **1**, a known compound,[10] was prepared from crotyl alcohol by a similar procedure. Its NMR spectrum ($CDCl_3$) showed multiplets at 7.7 (2 H) and 7.3 (3 H) (aromatic protons), 5.57 (2 H) (vinyl) and 4.5 (2 H) (methylene), and a broad doublet at 1.58 ppm (3 H) for the methyl group.

Equilibrations. Weighed samples of **2** or **1** in a NMR tube were diluted with 0.60 ml of chlorobenzene or nitrobenzene and immersed in a constant-temperature bath at 79.9°. The samples were withdrawn and NMR spectra recorded at regular intervals. Effects of pyridine, D_2O, and trifluoroacetic acid were determined by adding a known amount of each to the initial sample.

On one occasion, to confirm that **1** was the product from **2**, the equilibrated sample after 15 hr in chlorobenzene at 80° was pumped to dryness on a vacuum pump and put through the extraction sequence described above in the preparation of **2**. The NMR remained that of a mixture of **1** plus **2**.

Methyl 3-Buten-2-yl Phenylphosphonate (4). A solution of phenylphosphonodichloridate (25.4 g), pyridine (21 g), and 300 ml of ether was stirred in an ice bath under argon while first methanol (4.5 g) and then 3-buten-2-ol (8 g) were added dropwise. The mixture was filtered and the filtrate was washed with bicarbonate, dried over $MgSO_4$, and evaporated to give 15 g of colorless oil. The oil was fractionated by Kugelrohr distillation to give 9 g of **3** at 130° (0.01 mm).

Anal. Calcd for $C_{11}H_{15}O_3P$: C, 58.38; H, 6.69. Found: C, 58.14; H, 6.60.

Registry No.—**1**, 53940-78-6; **2**, 53940-79-7; **3**, 53940-80-0; **4**, 53940-81-1; phenylphosphonodichloridate, 824-72-6.

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New Syntheses of Functional Arenesulfonyl Azides

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The synthesis of light-sensitive polymers containing sulfonyl azide groups requires functional monomers, which can be readily prepared from inexpensive starting materials. For the construction of these polymers two principles can be used: (a) reaction of an arenesulfonyl azide containing two functional groups with another difunctional monomer to produce addition or condensation polymers, and (b) reaction of a monofunctional arenesulfonyl azide with a multifunctional linear polymer. Mono-, as well as difunctional, arenesulfonyl azides were prior to our investigation virtually unknown.[1]

A readily available starting material for the synthesis of functional arenesulfonyl azides is 4-isocyanatobenzenesulfonyl chloride (**1**), which is obtained in high yield by phosgenation of sulfanilic acid.[4] In order to achieve a completely selective functionalization of **1**, it was treated with excess ethylene glycol or triols at room temperature in acetonitrile

Table I
Arenesulfonyl Azides

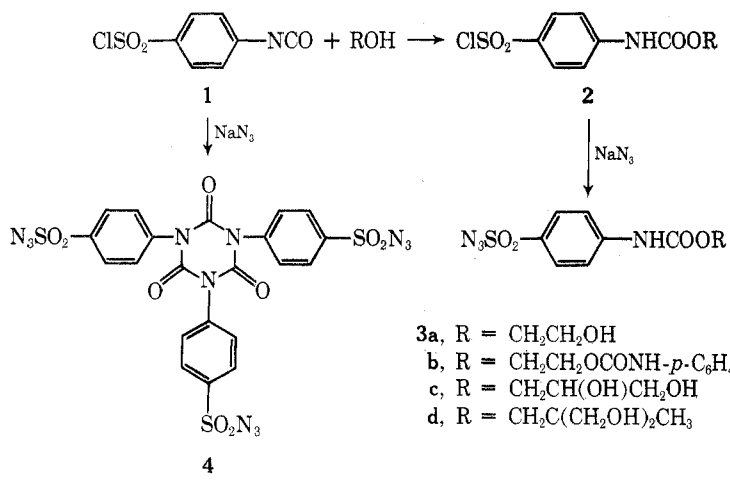
Compd	Arenesulfonyl azide	Mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N[c]
3a	N_3SO_2—C$_6$H$_4$—$NHCOOCH_2CH_2OH$	120–122	91	$C_9H_{10}N_4O_5S$	37.76	3.52	19.57	37.60	3.73	17.13
3b	(N_3SO_2)—C$_6$H$_4$—$(NHCOOCH_2)_2$	170–172	45	$C_{16}H_{14}N_8O_8S_2$	37.65	2.75	21.96	37.45	2.82	20.92
3c	N_3SO_2—C$_6$H$_4$—$NHCOOCH_2CH(OH)CH_2OH$	121	72	$C_{10}H_{12}N_4O_6S_2$	37.97	3.80	17.72	37.69	4.04	16.74
3d	N_3SO_2—C$_6$H$_4$—$NHCOOCH_2C(CH_2OH)_2CH_3$	*a*	~100	$C_{12}H_{16}N_4O_6S$	41.86	4.68	16.27	41.58	4.51	15.82
4	(N_3SO_2)—C$_6$H$_4$—$(NCO)_3$	*b*	89	$C_{21}H_{12}N_{12}O_9S_3$	37.50	1.80	24.99	37.55	1.84	22.48

[a] Viscous liquid. [b] Decomposition at approximately 200° (see Table II). [c] Lower percentages of nitrogen were observed in the elemental analyses because of violent thermal decomposition.

to give the 2-hydroxyalkyl 4-chlorosulfonylcarbanilates (**2**) exclusively. Under the mild reaction conditions no reaction of the chlorosulfonyl group with the excess di- or triol is observed.

The progress of the reaction of **1** with the alcoholic hydroxyl group is monitored by infrared spectroscopy. After disappearance of the isocyanato group, sodium azide is added to the reaction mixture, which causes rapid conversion of **2** to give hydroxyalkyl 4-azidosulfonylcarbanilates (**3**). It is essential that all of the isocyanate has reacted prior to the addition of the sodium azide, because unreacted **1** is readily trimerized by the basic sodium azide. For example, treatment of **1** with sodium azide in acetonitrile at room temperature produces the novel tris(4-azidosulfonylbenzene)isocyanurate (**4**) exclusively (Scheme I).

Scheme I



Reaction of 2 equiv of **1** with ethylene glycol gives rise to the formation of the bis carbamate **3b** (see Table I). Attempts to achieve selective reaction of **1** with aliphatic amines failed, because there is not a sufficient differential in rates of reaction of amines with both functional groups in **1**. The infrared spectra of the carbanilates **3** show a SO_2N_3 stretching at 2083 cm^{-1} and a C=O stretching at 1739 cm^{-1}, while **4** shows a SO_2N_3 stretching at 2132 cm^{-1} and a C=O stretching at 1698 cm^{-1}.

Arenesulfonyl azides undergo photolytic and thermal degradation with evolution of nitrogen gas. All carbanilates **3** have defined melting points, but violent decomposition occurs at 180–200°. The isocyanurate **4** has no sharp melting point, and violent decomposition is observed at approximately 200°. The thermal decomposition temperature of all arenesulfonyl azides is somewhat dependent on the rate of heating (see Table II). The carbanilate monomer **3a** has been grafted to anhydride copolymers to give light-sensitive polycarboxylic acids.[5] In order to prepare light-sensitive polycarboxylic acids by a reverse scheme, i.e., reaction of an azidosulfonyl group containing anhydride with hydroxy group containing linear polymers, the novel 4-azidosulfonylphthalic anhydride (**7**) has been synthesized by the route outlined in Scheme II. The required precursor, 4-chlorosulfonylphthalic anhydride (**6**), is obtained by the reaction of 4-sulfophthalic anhydride (**5**) with phosphorus pentachloride. Reaction of **7** with hydroxy group containing polymers gives rise to the formation of light-sensitive polycarboxylic acids.[6]

Scheme II

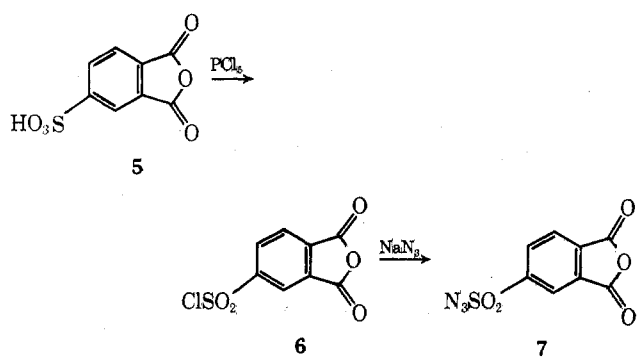


Table II
Thermal Decomposition of Arenesulfonyl Azides by Differential Scanning Calorimeter

Compd	T_m	T_d (40°/min)	T_d (80°/min)
3a	120–122	180	215
3b	170–172	192	212
3c	121	190	210
4		198	208

Experimental Section[7]

2-Hydroxyethyl 4-Azidosulfonylcarbanilate (3a). To an amount of 50.4 g (0.8 mol) of ethylene glycol in 500 ml of acetonitrile with cooling and stirring a solution of 43.2 g (0.2 mol) of 4-isocyanatobenzenesulfonyl chloride in 100 ml of acetonitrile was added over a period of 10 min at 2–8°. After disappearance of the N=C=O stretching in the infrared spectrum of the reaction mixture, 13 g (0.2 mol) of sodium azide was added and the reaction mixture was stirred at room temperature for 60 min. The precipitated sodium chloride was removed by filtration, and on evaporation of most of the solvent under vacuum and addition of water 52 g (91%) of 2-hydroxyethyl 4-sulfonylazidocarbanilate, mp 115–118°, was precipitated. Recrystallization from acetonitrile raises the melting point to 120–122°. The azidocarbanilates **3b–d** were prepared similarly.

Tris(4-azidosulfonylbenzene)isocyanurate (4). To 26 g (0.4 mol) of sodium azide suspended in 400 ml of acetonitrile a solution of 87 g (0.4 mol) of 4-isocyanatobenzenesulfonyl chloride[4] was added over a period of 20 min at 4–10°. After stirring at room temperature for 3 hr 600 ml of water was added to precipitate a mixture of product and sodium chloride, which was washed several times with water to remove the salt. Thus 79.7 g (89%) of 4 was obtained: mp ~200° (violent dec); ir (acetonitrile) 2132 (SO_2N_3), 1698 cm^{-1} (C=O).

4-Chlorosulfophthalic Anhydride (6). To 229.35 g (1.1 mol) of phosphorus pentachloride suspended in 1000 ml of acetonitrile, 228 g (1 mol) of 4-sulfophthalic anhydride (obtained from molten phthalic anhydride and sulfur trioxide) was added. The reaction mixture was refluxed for 150 min and the solvent was evaporated under vacuum. The residue was dissolved in 1000 ml of methylene chloride and washed twice with 300 ml of water. The organic layer was dried with magnesium sulfate, the solvent was evaporated, and vacuum distillation of the residue gave 163.2 g (66.2%) of 4-chlorosulfonylphthalic anhydride: bp 170° (0.5 mm); mp 91–92° (CCl_4); ir ($CHCl_3$) 1869, 1786 cm^{-1} (C=O).

Anal. Calcd for $C_8H_3ClO_5S$: C, 38.95; H, 1.22; Cl, 14.37. Found: C, 38,80; H. 1.53; Cl, 14.16.

4-Azidosulfonylphthalic Anhydride (7). To a solution of 12.3 g (0.05 mol) of 4-chlorosulfonylphthalic anhydride in 125 ml of acetonitrile, 3.25 g (0.05 mol) of sodium azide was added. After stirring for 4 hr at room temperature the precipitated sodium chloride was removed by filtration and the solvent was removed under vacuum. Trituration of the residue with diethyl ether gave 8.8 g (69.5%) of **7**: mp 93–94°; ir ($CHCl_3$) 2137 (SO_2N_3), 1869 and 1786 cm^{-1} (C=O).

Anal. Calcd for $C_8H_3N_3O_5S$: C, 37.94; H, 1.18; N, 16.60. Found: C, 38.27; H, 1.09; N, 16.23.

Registry No.—**1**, 6752-38-1; **3a**, 33780-21-1; **3b**, 34280-60-9; **3c**, 34235-62-6; **3d**, 34235-60-4; **4**, 31328-33-3; **5**, 134-08-7; **6**, 39871-41-5; **7**, 37696-57-4; ethylene glycol, 107-21-1; 1,2,3-propanetriol, 56-81-5; 2-(hydroxymethyl)-2-methyl-1,3-propanediol, 77-85-0; sodium azide, 26628-22-8.

References and Notes

(1) The use of isocyanatobenzenesulfonyl azides[2] and 3-sulfonylazidobenzoyl chloride[3] to graft onto hydroxy group containing linear polymers are the only reported examples.
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Preparation and Anodic Peak Potentials of Salts of Coordination Compounds Derived from Boric Acid and Polyhydric Phenols

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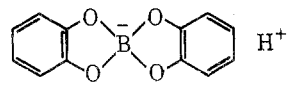
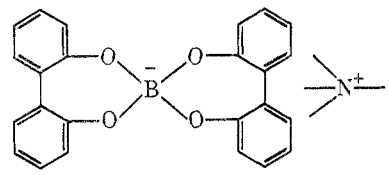
The coordination compounds derived from boric acid and dihydric phenols have the spiran structure shown in I,



I



II

for the compound from boric acid and catechol. They have been studied since the late 19th century, and this work has been reviewed in a comprehensive manner by Steinberg.[1] Salts of these coordination compounds are now being used extensively as the solute in the electrolyte of electrolytic capacitors.[2] As a result we have had occasion to prepare the salts listed in Table I.

Alkali metal and amine salts have been reported previously,[1] but quaternary ammonium salts have been described only in the patent literature.[2] The bis-2,2′-dihydroxybiphenylborate salts are of special interest, since they have the structure, shown in II, where the spiran rings about the boron atom are seven-membered, and the four aromatic rings are very probably forced into two planes, one perpendicular to the other. These geometrical requirements, the seven-membered spiran rings and the largely planar configuration for the two biphenyl ring systems, do not result in any difficulty in the preparation of these salts, since they are readily obtained in high yield and are extremely stable once formed.

Peak potentials for the anodic oxidation of the free phenols and the salts were determined at a platinum anode by cyclic voltammetry at a scan rate of 200 mV/sec in dimethyl sulfoxide containing 0.1 *M* tetrabutylammonium fluoroborate as the supporting electrolyte. The results are shown in Table II. Since in each case studied there is no significant change in potential in going from the free phenol to the salt, the initial anodic process must be the same for both the free phenol and the salt and must consist of an electron transfer from an aromatic ring to form a cation radical. This must be true for the salts even though the negative charge is centered on the boron atom. It also follows that the change from free phenol to coordination compound is not accompanied by any significant perturbation of the electronic structure of the aromatic rings.

The current functions, $i_p/V^{1/2}\,C^*$, where i_p is the peak current, V is the scan rate, and C^* is the bulk concentration of the electroactive species, decreased with increasing scan rate. This is indicative of a chemical reaction coupled with the electron transfer. It is highly probable that catechol, 2,3-naphthalenediol, and 2,2′-dihydroxybiphenyl are electrochemically equivalent, since the observed current function values were similar. Catechol and 4-methylcatechol have been reported to undergo a two-electron oxidation coupled with a nucleophilic addition reaction.[3] The current function values for the complexes were consistently