showed four protons from the water at δ 3.6, which **4d** did not. After D_2O exchange, the spectra were identical: ir (KBr) 2.96 (NH), 3.3–3.35 (aliphatic CH), 6.00 and 6.40 (amide bands), 8.6 μ (P=O); NMR (mixture of $CDCl_3$–Me_2SO-d_6) δ 1.3 [s, 27 H, $(CH_3)_3C$], 3.6 (**4u**, m, 10 H, PCH_2, 2 H_2O), 3.6 (**4d**, m, 6 H, PCH_2), 5.8 (broad s, 3 H, NH), 6.4 (broad s, 3 H, NH); after D_2O exchange δ 1.3 [s, 27 H, $(CH_3)_3C$], 3.65 (m, 6 H, PCH_2). The elemental analyses of **4d** and **4u** indicated that 2 mol of water was lost on drying.

Anal. Calcd for $C_{18}H_{39}N_6O_4P$: C, 49.75; H, 9.05; N, 19.34; P, 7.13. Found for **4d**: C, 49.71; H, 8.86; N, 19.17; P, 7.19.

Anal. Calcd for $C_{18}H_{39}N_6O_4P\cdot 2H_2O$: C, 45.94; H, 9.21; N, 17.86; P, 6.58. Found for **4u**: C, 45.86; H, 9.12; N, 17.55; P, 6.57.

Tris(4-phenylureidomethyl)phosphine Oxide (5). Method A gave a 53% yield of white solid after only 48 h in refluxing ethanol.

Method B afforded a 37% yield of solid. Recrystallization from *dimethyl sulfoxide–water* gave the analytical sample, **5**: ir (KBr) 2.99 (NH), 3.25 (aromatic CH), 3.4 (aliphatic CH), 6.03, 6.24, 6.5, and 6.7 (overlapping amide bands and aromatic C=C), 8.59 μ (P=O); NMR (Me_2SO-d_6, 80°) δ 3.7 (d of d, J_{PCH} = J_{NHCH} = 5 Hz, 6 H, PCH_2), 6.56 (t, J = 5 Hz, 3 H, CH_2NH), 6.7–7.65 (m, 15 H, aromatics), 8.81 (s, 3 H, PhNH); after D_2O exchange, δ 3.74 (d, J_{PCH} = 5 Hz, 6 H, PCH_2), 6.7–7.65 (m, 15 H, aromatics).

Anal. Calcd for $C_{24}H_{27}N_6O_4P$: C, 58.29; H, 5.50; N, 17.00; P, 6.27. Found: C, 58.34; H, 5.60; N, 16.99; P, 6.28.

Tris(4,4-diphenylureidomethyl)phosphine Oxide (6). Method A yielded 38% of white solid after 10 days reflux. However, on cooling to ambient temperature, the first solid collected from the reaction mixture was diphenylurea. Addition of water to the ethanolic reaction mixture was necessary to precipitate **6**, which was recrystallized from acetone–ethanol and then from ethyl acetate–ethanol to yield the analytical sample, **6**: ir (KBr) 2.98 (NH), 3.24 (aromatic CH), 3.39 (aliphatic CH), 5.98 and 6.7 (amide bands), 8.65 μ (P=O); NMR ($CDCl_3$) δ 3.67 (m, 6 H, PCH_2), 5.6 (m, 3 H, NH), 7.23 (m, 30 H, aromatics); after D_2O exchange δ 3.73 (d, J = 5 Hz, 6 H, PCH_2), 7.23 (m, 30 H, aromatics). The elemental analysis indicated a dihydrate.

Anal. Calcd for $C_{42}H_{39}N_6O_4P\cdot 2H_2O$: C, 66.48; H, 5.71; N, 11.08; P, 4.08. Found: C, 66.41; H, 5.61; N, 11.00; P, 4.17.

Tetrakis(4,4-diphenylureidomethyl)phosphonium Chloride (11). A mixture of 3.4 g (0.016 mol) of 1,1-diphenylurea, 0.76 g (0.004 mol) of Thpc, and 50 ml of toluene was refluxed for 4.5 h. The reaction mixture was allowed to cool, and the solid that formed was collected (2.0 g, 52% yield). This was recrystallized once from ethanol and twice from acetone–ethanol to yield the analytical sample, **11**: mp 246–247°; ir (KBr) 3.0 (NH), 3.25 (aromatic CH), 3.39 (aliphatic CH), 5.98, 6.27, and 6.7 μ (overlapping amide bands and aromatic C=C); NMR (mixture of $CDCl_3$–Me_2SO-d_6) δ 4.27 (m, 8 H, PCH_2), 6.75 (m, 4 H, NH), 7.3 (m, 40 H, aromatics); after D_2O exchange δ 4.3 (d, J = 4 Hz, 8 H, PCH_2), 7.3 (m, 40 H, aromatics).

Anal. Calcd for $C_{56}H_{52}N_8O_4PCl$: C, 69.52; H, 5.42; N, 11.58; P, 3.20; Cl, 3.67.

However, the elemental analyses indicate a monohydrate of **11**.

Anal. Calcd for $C_{56}H_{52}N_8O_4PCl\cdot H_2O$: C, 68.25; H, 5.52, N, 11.37; P, 3.14; Cl, 3.60. Found: C, 68.13; H, 5.45; N, 11.24; P, 3.20; Cl, 3.95.

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Registry No.—**1**, 57459-44-6; **2**, 57459-45-7; **3**, 57459-46-8; **4**, 57459-47-9; **5**, 57459-48-0; **6**, 57459-49-1; **11**, 57459-50-4; THP, 2767-80-8; methylurea, 598-50-5; ethylurea, 625-52-5; dodecylurea, 2158-09-0; *tert*-butylurea, 1118-12-3; phenylurea, 64-10-8; *N,N*-diphenylurea, 603-54-3; THPC, 124-64-1.

References and Notes

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Reaction of Picryl Azide with Aryloxyallenes[1]

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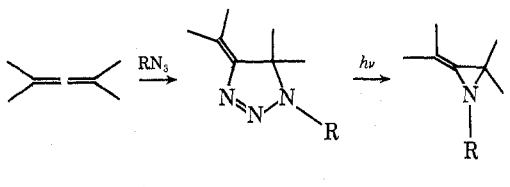
The reaction of aryloxyallenes with picryl azide gives two types of isolated adducts, **2** and **4**. The reaction is proposed to proceed via formation of the unisolated triazoline of type **5**. These compounds undergo an exceptionally facile Claisen rearrangement to yield the adducts of structure **4**, which unless blocked by a substituent at R_5 rapidly tautomerize to the isomeric adducts of type **2**.

As an extension of our work on allene oxides,[2] we have explored several potential synthetic routes to allenimines,[3] the nitrogen analogues of this strained small-ring heterocyclic system. One such approach[4] involves a 1,3-dipolar addition of organoazides to allenes, followed by photochemical expulsion of nitrogen from the adduct to give the desired allenimine (see eq 1). Bleiholder and Shechter[5] have earlier examined the reaction of several azides with alkyl-substituted allenes.[6] Although these authors were able to isolate the desired adducts in several instances,[7] these materials decomposed readily and the ring-contraction step of



(1)

eq 1 was not achieved. In the present study we utilized aryloxyallenes as substrates with the idea that these electron-rich allenes might undergo more facile cycloaddition reactions with azides. In fact, the observed products result from

an unanticipated rearrangement of these primary adducts which involves the activating aryloxy substituent.

The reaction of phenoxyallene (**1a**) with picryl azide at room temperature in chloroform gave a good yield of a yellow, crystalline solid subsequently identified as 4-(2-hydroxybenzyl)-1-picryl-1,2,3-triazole (**2a**). The presence of a phenol function in this product was indicated by its ir spectrum (bands at 3.0 and 8.1 μ), proton exchange with D_2O, and transformation to its acetate. The NMR spectrum of **2a** shows a two-proton singlet at δ 9.25 for the picryl-group protons, a sharp one-proton singlet at δ 8.39, four additional aromatic protons centered at about δ 6.8, and a two-proton singlet at δ 4.00. These data are best accommodated in terms of structure **2a**. In particular, the chemical shift of the downfield one-proton singlet is consistent only with a 4-substituted triazole.[8]

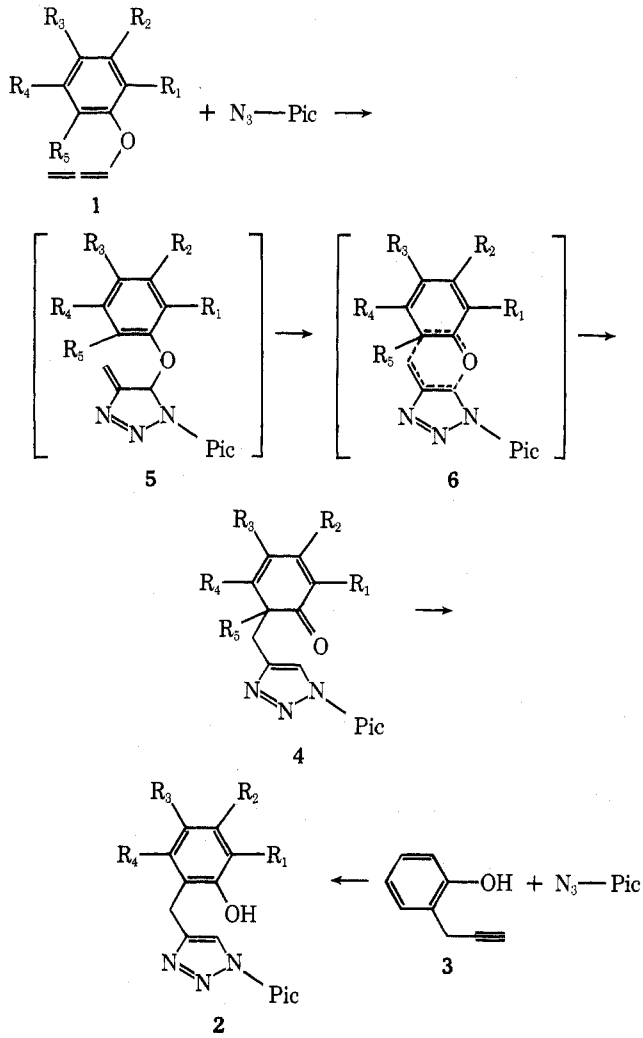
Confirmation of this structure was achieved by an alternate synthesis involving the cycloaddition of picryl azide to *o*-propargylphenol (**3**). Interestingly, only **2a** was observed in this reaction, whereas both regioisomers are usually formed in the addition of azides to terminal acetylenes.[9]

The generality of the reaction of aryloxyallenes with picryl azide was demonstrated by the formation of analogous adducts from allenes **1b** and **1c** in high yield. However, in the instances of **1d**, **1e**, and **1f**, whose aryl groups are blocked by substituents at both ortho positions, the isolated adducts are of the cyclohexadienone type **4**. The NMR spectra of these adducts show a downfield two-proton singlet for the picryl protons, a one-proton singlet appropriate for a C-5 triazole hydrogen, the expected number of olefinic protons for the respective compounds, and a two-proton AB pattern in the range 3.1–4.2 ppm. This latter feature results from the diastereotopic relationship of the benzylic protons owing to the adjacent chiral center. Compound **4f**, in particular, had ir, uv, and NMR spectra which correlated well with the data for model compounds in the literature.[10]

Supporting evidence for these structural assignments was provided by chemical correlation of the two types of adducts. Thus, reduction of the trichlorocyclohexadienone adduct **4d** with 1 equiv of tri-*n*-butyltin hydride[11] resulted in quantitative transformation to the dichloro adduct **2c** by selective removal of the R_5 chlorine substituent. The same adduct was obtained from picryl azide and 2,4-dichloroaryloxyallene (**1c**). Interestingly only the adduct **2c** was obtained in this reaction.

The most straightforward rationalization of the above results invokes a regiospecific 1,3 cycloaddition of the azide to the more electron-rich double bond of the allene to give triazoline **5** as an unisolated intermediate. This species undergoes Claisen rearrangement[12] to produce **4**. In those cases where the 2 and 6 positions of the original aryl group are blocked, the cyclohexadienone adducts **4** can be isolated; otherwise, tautomerization leads to the phenolic adducts **2** in a well-precedented manner.[12] Selective addition to the aryloxy-substituted double bond is expected[9] and the regiospecificity parallels that for the addition of azides to simple enol ethers.[13]

The surprising feature of this reaction is the unusual facility of the Claisen rearrangement of **5**, which proceeds readily at room temperature, rather than requiring the elevated temperatures typical of this type of transformation. However, the exceptional ease of this rearrangement is attributable to the generation of the aromatic[9] triazole system as the immediate product. Consequently, the aromatic character of the aryloxy moiety which is lost in achieving transition state **6** is largely compensated for by the developing aromatic stabilization of the triazole ring. This should result in a substantial lowering of the activation energy relative to a typical Claisen rearrangement.[12]



a, $R_1 = R_2 = R_3 = R_4 = R_5 = H$
b, $R_1 = R_2 = R_4 = R_5 = H$; $R_3 = Cl$
c, $R_2 = R_4 = R_5 = H$; $R_1 = R_3 = Cl$
d, $R_2 = R_4 = H$; $R_1 = R_3 = R_5 = Cl$
e, $R_1 = R_2 = R_3 = R_4 = R_5 = Cl$
f, $R_2 = R_3 = R_4 = H$; $R_1 = R_5 = CH_3$

Attempts to effect the reaction of phenoxyallene with phenyl, *p*-nitrophenyl, *p*-toluenesulfonyl, and carbethoxy azides under similar reaction conditions were unsuccessful in our hands. Nor were products obtained from 1-methyl-1-phenoxyallene, methoxyallene, or 3,3-dimethyl-1-acetoxyallene, even with picryl azide.

Experimental Section

General. NMR spectra were recorded on Varian HR-220 and EM-360 spectrometers; chemical shifts are reported in parts per million downfield from internal Me_4Si. Ir spectra were obtained on KBr pellets or on neat samples using a Perkin-Elmer 137 Infracord. Mass spectra (70 eV) were obtained on Varian MAT CH-7 and AEI MS-9 spectrometers. Analyses were performed by Midwest Microlab, Inc. Anhydrous $MgSO_4$ was routinely used as a drying agent.

Preparation of Aryl Propargyl Ethers. To a solution of 1 equiv of the phenol in ethanol was added 1 equiv of sodium. After hydrogen evolution ceased, 1 equiv of propargyl bromide was added and the reaction mixture was refluxed for 3 hr. The mixture was poured into water and extracted with pentane. The pentane extract was washed with 10% NaOH solution and water, then dried and concentrated. The aryl propargyl ethers were purified by distillation or recrystallization from ethanol.

Phenyl propargyl ether:[14] bp 81–83° (15 mm); ir 3.02 and 4.70 μ; NMR (CCl_4) δ 2.34 (t, 1, J = 2 Hz), 4.52 (d, 2, J = 2 Hz), and 7.0 (m, 5).

4-Chlorophenyl propargyl ether: bp 62–64° (0.75 mm); ir 3.01

and 4.70 μ; NMR (CCl_4) δ 2.42 (t, 1, J = 2 Hz), 4.60 (d, 2, J = 2 Hz), and 7.05 (m, 4).

Exact mass. Calcd for C_9H_7ClO: 166.0186. Found: 166.019.

2,4-Dichlorophenyl propargyl ether: mp 45–46°; ir 3.05 and 4.72 μ; NMR ($CDCl_3$) δ 2.51 (t, 1, J = 2 Hz), 4.74 (d, 2, J = 2 Hz), and 7.2 (m, 3).

Anal. Calcd for $C_9H_6Cl_2O$: C, 53.77; H, 3.01. Found: C, 53.6; H, 3.3.

2,4,6-Trichlorophenyl propargyl ether: mp 99–100°; ir 3.03 μ; NMR ($CDCl_3$) δ 2.57 (t, 1, J = 2 Hz), 4.82 (d, 2, J = 2 Hz), and 7.37 (s, 2).

Anal. Calcd for $C_9H_5Cl_3O$: C, 45.90; H, 2.14. Found: C, 46.1; H, 2.4.

Pentachlorophenyl propargyl ether: mp 137–138°; ir 3.04 and 4.65 μ; NMR ($CDCl_3$) δ 2.59 (t, 1, J = 2 Hz) and 4.90 (d, 2, J = 2 Hz).

Anal. Calcd for $C_9H_3Cl_5O$: C, 35.51; H, 0.99. Found: C, 35.9; H, 1.3.

2,6-Dimethylphenyl propargyl ether: bp 63–64° (0.75 mm); ir 3.03 and 4.65 μ; NMR (CCl_4) δ 2.20 (s, 6), 2.35 (t, 1, J = 2 Hz), 4.35 (d, 2, J = 2 Hz), and 6.84 (s, 3).

Exact mass. Calcd for $C_{11}H_{12}O$: 160.0889. Found: 160.088.

Preparation of Aryloxyallenes. A solution of 50 mmol of the aryl propargyl ether and 2.0 g of potassium *tert*-butoxide in 120 ml of *tert*-butyl alcohol was refluxed for 1–3 h. The reaction mixture was cooled, poured into water, and extracted with pentane. The extract was washed several times with water, dried, and concentrated to give essentially pure allene, free from isomeric acetylene. Distillation of these materials caused decomposition, prompting their use as obtained.

Phenoxyallene:[14] ir 5.08 μ; NMR (CCl_4) δ 5.45 (d, 2, J = 6 Hz), 6.87 (t, 1, J = 6 Hz), and 7.1 (m, 5).

4-Chlorophenoxyallene: ir 5.08 μ; NMR (CCl_4) δ 5.45 (d, 2, J = 6 Hz), 6.82 (t, 1, J = 6 Hz), and 7.13 (m, 4).

Exact mass. Calcd for C_9H_7ClO: 166.0186. Found: 166.019.

2,4-Dichlorophenoxyallene: mp 31–32°; ir 5.10 μ; NMR (CCl_4) δ 5.43 (d, 2, J = 6 Hz), 6.83 (t, 1, J = 6 Hz), and 7.25 (m, 3).

Exact mass. Calcd for $C_9H_6Cl_2O$: 199.9796. Found: 199.980.

2,4,6-Trichlorophenoxyallene: mp 23–24°, ir 5.02 and 5.10 μ; NMR (CCl_4) δ 5.35 (d, 2, J = 6 Hz), 6.98 (t, 1, J = 6 Hz), and 7.34 (s, 2).

Exact mass. Calcd for $C_9H_5Cl_3O$: 233.9406. Found: 233.943.

Pentachlorophenoxyallene: mp 83–85°, ir 5.1 μ; NMR (CCl_4) 5.45 (d, 2, J = 6 Hz) and 7.08 (t, 1, J = 6 Hz).

Exact mass. Calcd for $C_9H_3Cl_5O$: 301.8627. Found: 301.864.

2,6-Dimethylphenoxyallene: ir 5.1 μ; NMR (CCl_4) δ 2.18 (s, 6), 5.18 (d, 2, J = 6 Hz), 6.80 (t, 1, J = 6 Hz), and 6.88 (s, 3).

Exact mass. Calcd for $C_{11}H_{12}O$: 160.0889. Found: 160.091

Reaction of Picryl Azide with Phenoxyallene. Stirring a solution of 1.3 g (5 mmol) of picryl azide and 0.7 g (10 mmol) of phenoxyallene in 40 ml of chloroform at room temperature resulted in finely divided yellow crystals. After 2 days the solid product was collected and washed with chloroform to yield 1.5 g (78%) of pure **2a:** mp 171–173°; ir 3.0, 6.19, 6.48, 7.50, 8.10, and 13.5 μ; NMR (Me_2SO-d_6) δ 4.00 (s, 2), 6.68 (t, 1, J = 7 Hz), 6.79 (d, 1, J = 7 Hz), 7.0 (m, 2), 8.39 (s, 1), and 9.25 (s, 2); mass spectrum *m/e* (rel intensity) 386 (29), 369 (25), 339 (16), 218 (15), 175 (100), 146 (30).

Anal. Calcd for $C_{15}H_{10}N_6O_7$: C, 46.62, H, 2.61; N, 21.77. Found: C, 46.3; H, 2.7, N, 21.7.

Acetylation of 2a. To a 400-mg sample of **2a** in benzene was added 0.8 g of acetyl chloride and 5 drops of pyridine. After refluxing for 1 hr the reaction mixture was poured into water and extracted with ether. The extract was dried and concentrated to give the crude acetate which was purified by recrystallization from methanol: mp 164–165°; ir 5.70, 6.20, 6.48, 7.48, 8.28, and 13.6 μ; NMR ($CDCl_3$) δ 2.23 (s, 3), 4.10 (s, 2), 7.20 (m, 4), 7.45 (s, 1), and 9.00 (s, 2); mass spectrum *m/e* (rel intensity) 428 (1), 386 (57), 131 (45), 119 (26), 118 (14), 107 (11), 91 (26), 43 (100).

Anal. Calcd for $C_{17}H_{12}N_6O_8$: C, 47.67; H, 2.82; N, 19.62. Found: C, 47.8; H, 2.8; N, 19.5.

Reaction of Picryl Azide with *o*-Propargylphenol.[15] A solution of 1.6 g of picryl azide and 0.8 g of *o*-propargylphenol in 30 ml of chloroform was stirred at room temperature for 3 weeks, after which 0.6 g (24%) of yellow, crystalline **2a** was collected, mp 171–172°, mmp 171–173°. This product was spectroscopically identical with the adduct obtained from the reaction of phenoxyallene with picryl azide.

Reaction of Picryl Azide with 4-Chlorophenoxyallene. Stirring a solution of 1.3 g (5 mmol) of picryl azide and 1.7 g (10 mmol) of 4-chlorophenoxyallene in 25 ml of chloroform for 1 day gave 1.4 g (67%) of **2b:** mp 161–163°; ir 3.22, 6.20, 6.47, 7.50, and 12.10 μ; NMR (Me_2SO-d_6) δ 4.00 (s, 2), 6.82 (d, 1, J = 10 Hz), 6.98 (s, 1), 7.05 (d, 1, J = 10 Hz), 8.47 (s, 1), and 9.25 (s, 2); mass spectrum *m/e* (rel intensity) 420 (4), 209 (46), 174 (89), 152 (21), 28 (100).

Anal. Calcd for $C_{15}H_9ClN_6O_7$: C, 42.82, H, 2.16. Found: C, 42.85, H, 2.16.

Reaction of Picryl Azide with 2,4-Dichlorophenoxyallene. Stirring a solution of 1.3 g (5 mmol) of picryl azide and 2.0 g (10 mmol) of 2,4-dichlorophenoxyallene in 30 ml of chloroform for 1 day at room temperature gave 1.8 g (79%) of **2c,** as finely divided yellow crystals: mp 199–200°; ir 3.25, 6.21, 6.50, and 7.50 μ; NMR (Me_2SO-d_6) δ 4.20 (s, 1), 7.08 (d, 1, J = 2 Hz), 7.26 (d, 1, J = 2 Hz), 8.34 (s, 1), and 9.30 (s, 2); mass spectrum *m/e* (rel intensity) 456 (6), 454 (9), 201 (37), 199 (68), 188 (29), 128 (100).

Anal. Calcd for $C_{15}H_8Cl_2N_6O_7$: C, 39.58; H, 1.77; N, 18.46. Found: C, 39.3; H, 1.7; N, 18.5.

Reaction of Picryl Azide with 2,4,6-Trichlorophenoxyallene. A solution of 0.6 g (2.5 mmol) of picryl azide and 1.2 g (5 mmol) of 2,4,6-trichlorophenoxyallene in 15 ml of chloroform was stirred at room temperature for 2 days. The light yellow precipitate was collected and washed with chloroform to give 0.8 g (66%) of **4d:** mp 165–166°; ir 3.21, 5.92, 6.20, 6.50, and 7.50 μ; NMR (acetone-d_6) δ 3.80 (AB q, 2, J = 14 Hz), 6.72 (d, 1, J = 2.5 Hz), 7.35 (d, 1, J = 2.5 Hz), 8.40 (s, 1), and 9.30 (s, 2); mass spectrum *m/e* (rel intensity) 490 (1), 488 (1), 247 (40), 109 (44), 30 (100).

Anal. Calcd for $C_{15}H_7Cl_3N_6O_7$: C, 36.80; H, 1.44; N, 17.16. Found: C, 37.0; H, 1.5; N, 16.7.

Reaction of 4d with Tri-*n*-butyltin Hydride. To a solution of 0.5 g of **4d** in 10 ml of acetone was slowly added 0.5 g of tri-*n*-butyltin hydride in 2 ml of acetone. The reaction mixture was stirred at room temperature for 2 hr, the solvent was removed, chloroform was added, and the resulting crystalline solid was collected and recrystallized from aqueous alcohol to give **2c,** mp 198–201°. The compound was spectroscopically identical with the adduct obtained from the reaction between 2,4-dichlorophenoxyallene and picryl azide in all respects.

Reaction of Picryl Azide with Pentachlorophenoxyallene. A solution of 0.13 g (0.5 mmol) of picryl azide and 0.31 g (1 mmol) of pentachlorophenoxyallene in 5 ml of chloroform was stirred at room temperature for 4 days. The light yellow precipitate was collected and washed with chloroform to give 0.2 g (72%) of **4e:** mp 202–203°; ir 3.23, 5.95, 6.21, 6.50, and 7.50 μ; NMR (acetone-d_6) δ 4.10 (AB q, 2, J = 14 Hz), 8.45 (s, 1), and 9.30 (s, 2); mass spectrum *m/e* (rel intensity) 558 (1), 556 (1), 494 (36), 269 (47), 256 (45), 36 (100).

Anal. Calcd for $C_{15}H_5Cl_5N_6O_7$: C, 32.26; H, 0.90; N, 15.05. Found: C, 31.98; H, 0.93; N, 14.85.

Reaction of Picryl Azide and 2,6-Dimethylphenoxyallene. A solution of 2.5 g (10 mmol) of picryl azide and 3.2 g (20 mmol) of 2,4-dimethylphenoxyallene in chloroform was stirred at room temperature for 1 day, after which the light yellow precipitate was collected and washed with chloroform to give 3.5 g (85%) of **4f:** mp 210–211°; uv λ_{max} 310 nm (ε 4500); ir 3.20, 6.08, 6.11, 6.18, 6.45, and 7.45 μ; NMR (Me_2SO-d_6) δ 1.16 (s, 3), 1.73 (s, 3), 3.05 (AB q, 2, J = 14 Hz), 6.07 (d of d, 1, J = 9 and 6 Hz), 6.25 (d, 1, J = 9 Hz), 6.80 (d, 1, J = 6 Hz), 8.20 (s, 1), and 9.20 (s, 2); mass spectrum *m/e* (rel intensity) 414 (25), 122 (100), 121 (61).

Anal. Calcd: C, 49.28; H, 3.41. Found: C, 48.9; H, 3.5.

Registry No.—**1a,** 1595-40-0; **1b,** 57444-41-4; **1c,** 57444-42-5; **1d,** 57444-43-6; **1e,** 57444-44-7; **1f,** 57444-45-8; **2a,** 57444-46-9; **2a** acetate, 57444-47-0; **2b,** 57444-48-1; **2c,** 57444-49-2; **3,** 39894-71-8; **4d,** 57444-50-5; **4e,** 57444-51-6; **4f,** 57444-52-7; propargyl bromide, 106-96-7; phenol, 108-95-2; 4-chlorophenol, 106-48-9; 2,4-dichlorophenol, 120-83-2; 2,4,6-trichlorophenol, 88-06-2; pentachlorophenol, 87-86-5; 2,6-dimethylphenol, 576-26-1; phenyl propargyl ether, 13610-02-1; 4-chlorophenyl propargyl ether, 19130-39-3; 2,4-dichlorophenyl propargyl ether, 17061-90-4; 2,4,6-trichlorophenyl propargyl ether, 17727-28-5; pentachlorophenyl propargyl ether, 19130-44-0; 2,6-dimethylphenyl propargyl ether, 21078-03-5; picryl azide, 1600-31-3; tri-*n*-butyltin hydride, 688-73-3.

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Solvolysis of Haloallenes. The Question of Nucleophilic Solvent Assistance

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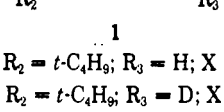
The solvolysis rates of 14 di- and trisubstituted bromoallenes are reported. Solvent effects in ethanol and trifluoroethanol, methyl/hydrogen ratios, and the effect of solvent nucleophilicity on relative rates and α- and β- secondary isotope effects are discussed. Increases in the magnitude of $(k_H/k_D)_\alpha$ and $(k_H/k_D)_\beta$ with decreasing solvent nucleophilicity are analogous to the behavior of highly hindered secondary brosylates. These data are interpreted in terms of a rate-limiting elimination step from an ion-pair intermediate. The relative rate of isomeric propargyl and allenyl systems is also discussed.

In earlier work we have reported that di- and trisubstituted chloro- and bromoallenes exhibit solvolytic behavior typical of an unimolecular bond heterolysis as the slow step.[1] These compounds exhibit m values between 0.80 and 1.06, k_{Br}/k_{Cl} leaving group ratios of 20–58, $\Delta S^{\ddagger}$ of −10 to +9.0 eu, ρ values for aryl-substituted chloroallenes of −2.0, CH_3/H rate ratios in 60E of $10^{4.5}$, and apparently "normal" α and β secondary isotope effects.

Since disubstituted haloallenes exhibit solvolytic reactivity in aqueous ethanol on the order of reactivity of secondary carbinyl systems, we were led to assess the possible involvement of nucleophilic solvent assistance in our system. To this end we have prepared the following substituted haloallenes, **1a–n**, and measured the rates of solvolysis in a variety of solvents. The results of this investigation are compiled in Table I. Tables II and III present the isotope effects based on the data in Table I and the isotopic purity of the deuterated samples. Deuterated and undeuterated compounds were solvolyzed in paired conductance cells. The bridge and digital clock were interfaced with a computer allowing no less than 100 points to be taken per cell. Rate constants were calculated using a nonlinear least-squares program. Each reaction exhibits excellent first-order behavior through better than 4 half-lives.



1

a, $R_1 = R_2 = t\text{-}C_4H_9$; $R_3 = H$; X = Br
b, $R_1 = R_2 = t\text{-}C_4H_9$; $R_3 = D$; X = Br
c, $R_1 = t\text{-}C_4H_9$; $R_2 = CH_3$; $R_3 = H$; X = Br
d, $R_1 = t\text{-}C_4H_9$; $R_2 = CH_3$; $R_3 = D$; X = Br
e, $R_1 = t\text{-}C_4H_9$; $R_2 = CD_3$; $R_3 = H$; X = Br
f, $R_1 = R_2 = CH_3$; $R_2 = H$; X = Br
g, $R_1 = R_2 = CH_3$; $R_3 = D$; X = Br
h, $R_1 = R_2 = CD_3$; $R_3 = H$; X = Br
i, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CH_3$; X = Cl
j, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CD_3$; X = Cl
k, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CH_3$; X = Br
l, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CD_3$; X = Br
m, $R_1 = R_2 = t\text{-}C_4H_9$; $R_3 = CH_3$; X = Br
n, $R_1 = t\text{-}C_4H_9$; $R_2 = R_3 = CH_3$; X = Br

Results and Discussion

The question of nucleophilic solvent assistance has been approached through a study of the effect of solvent nucleophilicity on (a) α and β secondary isotope effects, (b) the CH_3/H ratio, (c) the relative rate of model compounds, and (d) the presence or absence of a rate–product correlation in the presence of azide ion.[2] In this paper we will focus only on the effect of changing solvent nucleophilicity on the reactivity of the haloallenes reported here. The effect of added salts on this reaction will be reported later.

Effect of Solvent Nucleophilicity on Rate. It has been suggested that in those systems where nucleophilic solvent assistance is important (such as secondary carbinyl derivatives) such assistance is manifested in markedly changing rate ratios between solvent assisted substrates and those incapable of assistance usually owing to steric inhibition.[3] An elegant example of this behavior was reported by Schleyer et al. These workers reported 2-propyl tosylate/2-adamantyl tosylate rate ratios which varied from $10^{-1.6}$ in TFA to 10^3 in 100E and interpreted this behavior as consistent with substantial solvent assistance in 2-propyl tosylate not present (or marginally present) in the weakly nucleophilic solvents. The 2-adamantyl tosylate shows no solvent assistance due to steric interactions and is therefore a good model of a nonassisted secondary carbinyl system. On the other hand, *tert*-alkyl halides exhibit a constant rate ratio over a variety of solvents. For example, the *t*-BuCl/1-adamantyl Br rate ratio remains constant throughout 19 solvents of widely varying polarity and nucleophilicity.[4]