was removed in vacuo to give (94%) the crude material, which was eluted through a short-path silica column with first CH_2Cl_2 followed by a 50:50 mixture of $EtOH/CH_2Cl_2$ to obtain (84%) **5**: 600 mg; mp >350 °C; ^1H NMR ($CDCl_3$) δ 1.91 (br s, CH_2C-H_2CH_2Cl, 12 H), 3.60 (br s, CH_2Cl, 6 H), 8.60 (broad s, NH_3, 3 H); IR (KBr) 3400–2575, 2959, 2039, 1518, 652 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 58.5 (H_3NC), 44.1 (CH_2Cl), 33.2 ($CH_2CH_2CH_2Cl$), 25.7 (CH_2CH_2Cl); MS, *m/e* 184 ($M^+ - C_3H_6Cl_2$, 65). Anal. Calcd for $C_{10}H_{21}Cl_4N$: C, 40.40; H, 6.06; N, 4.71. Found: C, 40.67; H, 6.28; N, 4.51.

1-Azoniatricyclo[3.3.3.0]undecane Chloride (6). To a mixture of acetonitrile (300 mL) and K_2CO_3 (2.5 g) was added the amine hydrochloride (**5**; 680 mg, 2.29 mmol). The stirred mixture was refluxed for 24 h; then after cooling to 25 °C, the K_2CO_3 was removed via filtration through a Celite pad. The filtrate was concentrated to yield (86%) azapropellane **6**: 370 mg. The crude material was chromatographed on a short alumina column, eluting with EtOH/EtOAc (50:50) to afford (74%) **6**: 320 mg; mp >350 °C; ^1H NMR (D_2O, dioxane: δ 3.70) δ 1.98 (br s, $CH_2CH_2CH_2N$, 12 H), 3.40 (m, CH_2N, 6 H); IR (KBr) 3470, 3300, 2970, 2100, 1458 cm^{-1}; ^{13}C NMR (CD_3CN: δ 117.7, 1.3) δ 79.2 (*C*N), 64.9, 64.7, 64.5 (CH_2N), 37.0 ($CH_2CH_2CH_2N$), 23.3 (CH_2CH_2N); MS, *m/e* 152 (M^+ - Cl, 9). Anal. Calcd for $C_{10}H_{18}ClN$: C, 64.00; H, 9.60; N, 7.47. Found: C, 63.91; H, 9.60; N, 7.60.

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Registry No. **1**, 116747-79-6; **2**, 1466-48-4; **3**, 59085-15-3; **4**, 116747-80-9; **5**, 116747-81-0; **6**, 116747-82-1; acrylonitrile, 107-13-1; nitromethane, 75-52-5.

A Novel Application of the Friedel–Crafts Reaction to the Synthesis of Differently Substituted Polynuclear Compounds

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The Friedel–Crafts reaction has been studied extensively for more than a century, and numerous compounds have been synthesized through alkylation, acylation, cycliacylation, and other miscellaneous types of reactions.[2,3] Most of the syntheses involve the use of stoichiometric amounts of the substrates, reactants, and the catalysts. Although the influence of temperature and excess amounts of the substrates, reactants, and catalysts in the orientation of alkylation and acylation of aromatic compounds has also been reported and Gore et al.[4-6] described diacylation of naphthalene derivatives by the use of excess amounts of acylating agents, we reported[7] for the first time that when excess amounts of substrates like anisole and phenetole are used, interesting polynuclear compounds are formed as secondary reaction products. Roberts et al.[8,9] also observed similar novelties subsequently. We also demonstrated that formation of the unexpected products depends on the nucleophilicity of the substrate and electrophilicity of the acyl carbonyl group of the initially formed acylated product.[10] In our attempt to synthesize differently substituted polynuclear compounds by the reaction of dichloroacetyl chloride and different pairs of substituted benzenes under Friedel–Crafts conditions, it was contemplated that the initially formed acylated product of one arene might react with the other nucleophile, if present in the reaction mixture, generating the desired compounds. With this aim in view, arenes with varying degrees of nucleophilicity were used as pairs of substrates and it was, indeed, observed that differently substituted polynuclear compounds of choice could conveniently be prepared by regulating the reaction conditions. We believe that our approach to this type of polynuclear compound is notable for its generality, preparative simplicity, and conceptual novelty.

Results and Discussion

The substrates used for the study were mono- and disubstituted benzenes of varying nucleophilicity, e.g., toluene, chlorobenzene, anisole, phenetole, *m*-xylene, and dimethylresorcinol. Initially the reaction was carried out under Friedel–Crafts conditions with the nucleophile of lower reactivity using stoichiometric proportions of the reactants and the catalyst to facilitate the formation of the normal acylated product. Application of higher temperature for stimulating the reaction was found to be necessary for the substrates of lower reactivity. No solvent was used for the initial acylation reaction as all the substrates used were liquids. However, for the reaction of the acylated product and the second substrate, CS_2 was used as solvent.

The normal acylated product of anisole formed initially by the reaction of stoichiometric amounts of anisole, dichloroacetyl chloride, and anhydrous $AlCl_3$ reacted in situ with a unimolar proportion of phenetole to yield 2,2-dichloro-1-(4′-ethoxyphenyl)-1-(4″-methoxyphenyl)ethylene (**1**) (Chart I). The same product could also be obtained by the reaction of the normal acylated product of phenetole on anisole. A minor byproduct characterized as 2,2-dichloro-1-(4′-ethoxyphenyl)-1-(4″-hydroxyphenyl)ethylene (**2**) was also formed, obviously by demethylation of the anisole part. Following a similar experimental protocol, we could also prepare the mixed dimeric products 2,2-dichloro-1-(4′-methoxyphenyl)-1-(2″,4″-dimethoxyphenyl)ethylene (**3**), 2,2-dichloro-1-(4′-methylphenyl)-1-(2″,4″-dimethoxyphenyl)ethylene (**4**), 2,2-dichloro-1-(4′-methylphenyl)-1-(4″-methoxyphenyl)ethylene (**5**), and 2,2-dichloro-1-(4′-chlorophenyl)-1-(4″-methoxyphenyl)-ethylene (**6**) by the use of anisole and dimethylresorcinol, toluene and dimethylresorcinol, toluene and anisole, and chlorobenzene and anisole respectively. The structures of these dimeric products were established by their elemental

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(2) *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1963–1965; Vol. 1–4.
(3) *Friedel-Crafts Chemistry*; Olah, G. A., Ed.; Wiley: New York, 1973.
(4) Gore, P. H.; Thadani, C. K.; Thorburn, S. *J. Chem. Soc. C* **1968**, 2502.
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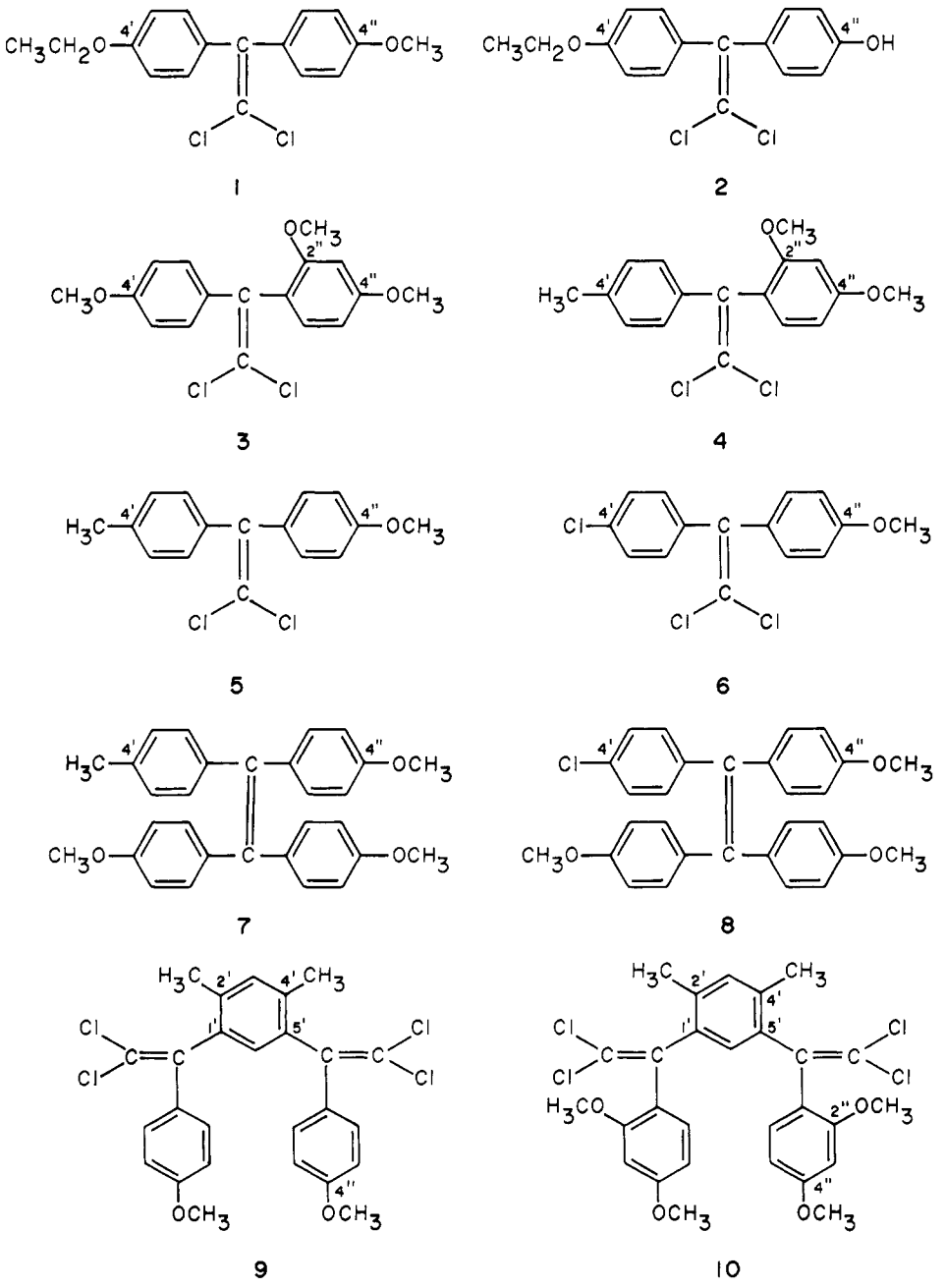
(9) El-Khawaga, A. M.; Roberts, R. M. *J. Org. Chem.* **1984**, *49*, 3832.
(10) Mahato, S. B.; Mandal, N. B.; Pal, A. K.; Maitra, S. K. *Tetrahedron* **1987**, *43*, 4439.

0022-3263/88/1953-5554$01.50/0

Chart I

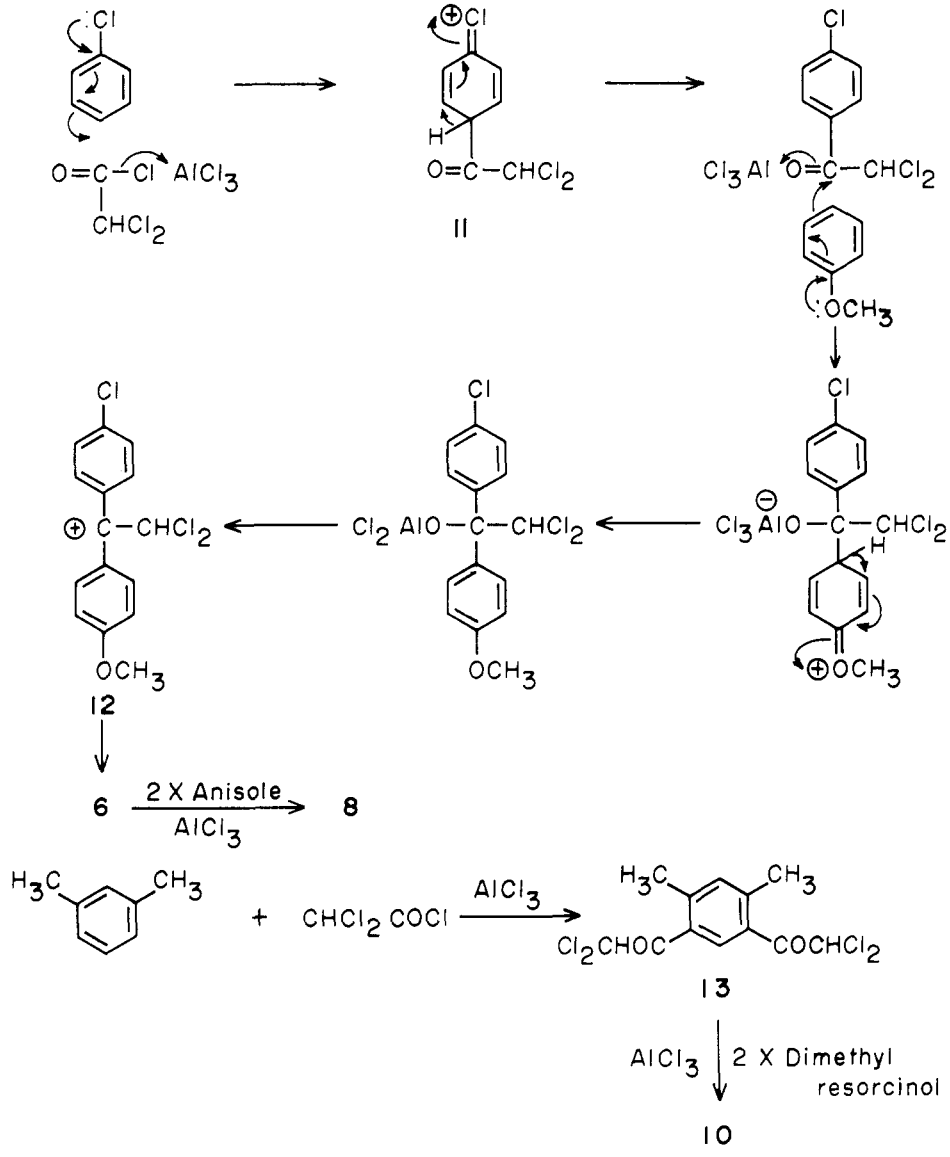


analysis and mass spectral and ^{1}H NMR data.

However, if the proportion of the second substrate used in the later stage of the reaction is increased to bimolar or higher, mixed tetrameric products are obtained in moderate yields. For example, when anisole was used in bimolar or higher proportion after toluene was acylated in the aforesaid manner, the interesting differently substituted tetramer 1,1,2-tris(4″-methoxyphenyl)-1-(4′-methylphenyl)ethylene (**7**) was obtained. In a similar manner the preparation of 1,1,2-tris(4″-methoxyphenyl)-1-(4′-chlorophenyl)ethylene (**8**) could be achieved by the employment of chlorobenzene and anisole as the substrates, the latter being used in higher proportion. Besides mass spectral and ^{1}H NMR analysis, which revealed the structural features of compounds **7** and **8**, the structure of **8** was unequivocally established by single-crystal X-ray analysis. The interesting trimeric products comprising *m*-xylene and anisole as well as *m*-xylene and dimethylresorcinol were produced when the respective pairs of the substrates were subjected to similar treatment in the prescribed reaction conditions. The *m*-xylene, anisole pair yielded 2′,4′-dimethyl-1′,5′-bis[2,2-dichloro-1-(4″-methoxyphenyl)ethenyl]benzene (**9**), and *m*-xylene and dimethylresorcinol afforded 2′,4′-dimethyl-1′,5′-bis[2,2-dichloro-1-(2″,4″-dimethoxyphenyl)ethenyl]benzene (**10**). Although mass and ^{1}H NMR data were of much help in predicting the structures of compounds **9** and **10**, single-crystal X-ray analysis was performed for unambiguous determination of the structure of **10**, and thus the structure of **9**, which is very similar to that of **10** in spectral characteristics, could also be deduced to be as shown. The ORTEP[11] drawings of the molecular structures (less hydrogen atoms) of compounds **8** and **10** are shown in Figure 1, and the schematic drawings with numbering scheme are shown in Figure 2 (supplementary material). The crystallographic data for compounds **8** and **10** are given in Table I (supplementary material).

(11) Johnson, C. K. ORTEP II Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Scheme I



The mechanism of formation of the mixed dimeric products is exemplified by the formation of compound **8** from chlorobenzene and anisole (Scheme I). Chlorobenzene reacts with dichloroacetyl chloride in the presence of anhydrous $AlCl_3$, producing the normal para-acylated product **11**. Further reaction of this acylated product depends on the electrophilicity of the acyl carbonyl group and nucleophilicity of the second arene. The generation of the carbonium ion **12** may reasonably be assumed, which leads to the formation of the dimeric product **6**. The other dimeric products are evidently formed in a similar way. Moreover, these diaryldichloroethylenic compounds may well act as alkylating agents in the presence of $AlCl_3$, producing tetrameric products like **7** and **8**.

The formation of compounds **9** and **10** may be attributed to the presence of two electronically equivalent ortho (or para) positions to the methyl groups in *m*-xylene which facilitates diacylation. Both the electrophilic acyl carbonyls of compound **13** then react with nucleophilic arenes in the presence of $AlCl_3$ to yield novel trimers **9** and **10** (Scheme I).

The results obtained so far have amply demonstrated that dichloroacetyl chloride and various substituted arenes may be utilized under Friedel–Crafts conditions for the convenient synthesis of differently substituted polynuclear compounds of pharmaceutical interest. By proper regulation of reaction parameters, it is possible to synthesize targeted compounds, and the method has potential for wider application.

Experimental Section

All melting points are uncorrected. IR spectra were recorded in Nujol mull on a Shimadzu IR-435 instrument. ^1H NMR spectra were recorded in $CDCl_3$ on a JEOL FT-100 NMR spectrometer operating at 99.6 MHz. All ^1H shifts are reported relative to Me_4Si. Mass spectra were obtained on Hitachi Model RMU-6L and MS-50 A.E.I. mass spectrometers at 70 eV by the direct-insertion method.

General Procedures. The pairs of substrates used for the study were anisole, phenetole; chlorobenzene, anisole; toluene, anisole; toluene, resorcinol dimethyl ether; *m*-xylene, anisole; and *m*-xylene, resorcinol dimethyl ether. Stoichiometric amounts of the substrates, dichloroacetyl chloride, and anhydrous $AlCl_3$ were used for the initial acylation reaction. The substrate of lower nucleophilicity of the pair and anhydrous $AlCl_3$ were taken in a round-bottomed flask fitted with a magnetic stirrer and a dropping funnel. The temperature of the flask was maintained at 0–10 °C. Dichloroacetyl chloride was added to this mixture slowly with constant stirring during a period of 2 h. The requisite amount of CS_2 was then added, and the stirring was continued for a further 1 h. At this stage the reaction mixture was heated on a steam bath for 1 h up to 80–90 °C for the less reactive substrates, e.g.,

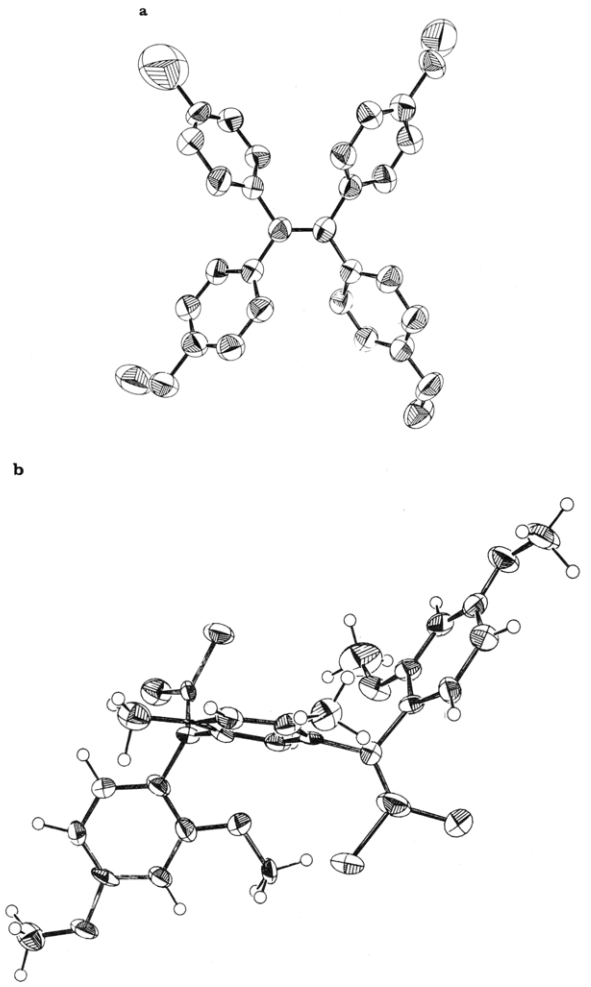


Figure 1. ORTEP stereoviews of (a) compound **8** and (b) compound **10**.

chlorobenzene, toluene, and *m*-xylene, and cooled to 0–10 °C, and to this reaction mixture was added a further 1-molar proportion of anhydrous $AlCl_3$. The heating step was eliminated for the reactive substrates. The flask was again fitted with a dropping funnel containing a 1- or higher molar proportion of the second substrate, which was slowly added to the reaction mixture with stirring during a period of 2 h. The reaction mixture was then left overnight (16 h) at room temperature. The product was decomposed with an ice–HCl mixture and then taken up with ether. The ether solution was washed free from acid and dried under reduced pressure, and the residue was subjected to column chromatography over silica gel. The fractions were monitored by TLC, and those found homogeneous were combined and further purified by crystallization.

2,2-Dichloro-1-(4′-ethoxyphenyl)-1-(4″-methoxyphenyl)ethylene (1). Proportion of reactants: anisole (5.4 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), phenetole (6.1 g) (0.05 mol). Compound **1** was eluted with petroleum ether and crystallized from MeOH: mp 90–91 °C; yield 4.86 g (30%); IR 1601, 1510, 1314, 1272, 1251, 1185, 1050, 966, 871, 837, and 806 cm^{-1}; ^1H NMR δ 1.40 (t, 3 H, J = 7 Hz, C4′-OCH_2CH_3), 3.80 (s, 3 H, 1 × CH_3), 4.00 (q, 2 H, J = 7 Hz, C4′-OCH_2CH_3), 6.80 (dd, 4 H, J = 2, 8 Hz, 3′-H, 5′-H, 3″-H, 5″-H), 7.19 (dd, 4 H, J = 2, 8 Hz, 2′-H, 6′-H, 2″-H, 6″-H); MS, m/z (relative intensity) 324 (M^+ + 2, 4), 322 (M^+, 8), 310 (8), 308 (11), 278 (57), 265 (20), 244 (60), 228 (47), 223 (86), 214 (97), 209 (99), 198 (86), 194 (92), 185 (90), 180 (100), 162 (93), 151 (94). Anal. Calcd for $C_{17}H_{16}Cl_2O_2$: C, 63.17; H, 4.99. Found: C, 63.22; H, 4.92.

2,2-Dichloro-1-(4′-ethoxyphenyl)-1-(4″-hydroxyphenyl)ethylene (2). Proportion of reactants: as for compound **1**. Compound **2** was eluted with chloroform and crystallized from hexane: mp 109 °C; yield 1.23 g (8%); IR 3185 (hydroxyl), 1606, 1508, 1316, 1281, 1245, 1196, 1171, 1112, 1046, 1013, 990, 932, 859, 831, and 792 cm^{-1}; ^1H NMR δ 1.40 (t, 3 H, J = 7 Hz, C4′-OCH_2CH_3), 4.02 (q, 2 H, J = 7 Hz, C4′-OCH_2CH_3), 5.00 (s, 1 H, C4″-OH), 6.76 (d, 2 H, J = 8 Hz, 3″-H, 5″-H), 6.82 (d, 2 H, J = 8 Hz, 3′-H, 5′-H), 7.16 (d, 2 H, J = 8 Hz, 2″-H, 6″-H), 7.18 (d, 2 H, J = 8 Hz, 2′-H, 6′-H); MS, m/z (relative intensity) 310 (M^+ + 2, 11), 308 (M^+, 15), 222 (3), 215 (9), 210 (51), 181 (93), 163 (55), 152 (100), 151 (95), 142 (51), 139 (60), 126 (82), 115 (57), 99 (68), 89 (73). Anal. Calcd for $C_{16}H_{14}Cl_2O_2$: C, 62.15; H, 4.56. Found: C, 62.10; H, 4.51.

2,2-Dichloro-1-(4′-methoxyphenyl)-1-(2″,4″-dimethoxyphenyl)ethylene (3). Proportion of reactants: anisole (5.4 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), dimethylresorcinol (6.905 g) (0.05 mol). Compound **3** was eluted with petroleum ether and crystallized from MeOH: mp 118–119 °C; yield 6.8 g (40.3%); IR 1605, 1572, 1502, 1413, 1298, 1257, 1209, 1155, 1123, 1043, 1021, 968, 916, 846, 815, 793, 765, and 720 cm^{-1}; ^1H NMR δ 3.70, 3.76, 3.78 (each s, 9 H, 3 × OCH_3), 6.44 (d, 1 H, J = 2 Hz, 3″-H), 6.48 (dd, 1 H, J = 2, 8 Hz, 5″-H), 6.80 (d, 2 H, J = 8 Hz, 3′-H, 5′-H), 7.04 (d, 1 H, J = 8 Hz, 6″-H), and 7.26 (d, 2 H, J = 8 Hz, 2′-H, 6′-H); MS, m/z (relative intensity) 340 (M^+ + 2, 42), 338 (M^+, 74), 288 (100), 273 (88), 267 (31), 255 (36), 245 (45), 239 (31), 227 (89), 210 (80), 195 (80), 186 (92), 182 (95), 151 (90), 150 (89), 139 (98), 121 (83). Anal. Calcd for $C_{17}H_{16}Cl_2O_3$: C, 60.19; H, 4.75. Found: C, 60.12; H, 4.71.

2,2-Dichloro-1-(4′-methylphenyl)-1-(2″,4″-dimethoxyphenyl)ethylene (4). Proportion of reactants: toluene (4.6 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), dimethylresorcinol (6.905 g) (0.05 mol). Compound **4** was eluted with petroleum ether–benzene (75:25) and crystallized from MeOH: mp 130 °C; yield 7.2 g (41.6%); IR 1632, 1579, 1306, 1279, 1210, 1167, 1122, 1039, 987, 931, 833, 802, and 765 cm^{-1}; ^1H NMR δ 2.28 (s, 3 H, CH_3), 3.70, 3.76 (each s, 6 H, 2 × OCH_3), 6.44 (d, 1 H, J = 2 Hz, 3″-H), 6.48 (dd, 1 H, J = 2, 8 Hz, 5″-H), 7.06 (dd, 3 H, J = 2, 8 Hz, 3′-H, 5′-H, 6″-H), 7.22 (dd, 2 H, J = 2, 8 Hz, 2′-H, 6′-H); MS, m/z (relative intensity) 324 (M^+ + 2, 60), 322 (M^+, 95), 307 (4), 288 (28), 274 (52), 272 (100), 258 (34), 257 (39), 252 (17), 251 (15), 239 (21), 238 (28), 223 (13), 211 (40), 202 (10), 150 (89). Anal. Calcd for $C_{17}H_{16}Cl_2O_2$: C, 63.17; H, 4.99. Found: C, 63.13; H, 5.02.

2,2-Dichloro-1-(4′-methylphenyl)-1-(4″-methoxyphenyl)ethylene (5). Proportion of reactants: toluene (4.6 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (5.4 g) (0.05 mol). Compound **5** was eluted with petroleum ether and crystallized from MeOH: mp 116–117 °C; yield 6.28 g (43%); IR 1605, 1570, 1415, 1297, 1210, 1160, 1120, 1040, 980, 932, 845, 765, and 720 cm^{-1}; ^1H NMR δ 2.28 (s, 3 H, CH_3), 3.74 (s, 3 H, 1 × OCH_3), 6.78 (d, 4 H, J = 8 Hz, 3′-H, 5′-H, 3″-H, 5″-H), 7.20 (d, 4 H, J = 8 Hz, 2′-H, 6′-H, 2″-H, 6″-H); MS, m/z (relative intensity) 294 (M^+ + 2, 61), 292 (M^+, 100), 257 (10), 222 (50), 207 (12), 192 (18), 151 (22). Anal. Calcd for $C_{16}H_{14}Cl_2O$: C, 65.55; H, 4.81. Found: C, 65.61; H, 4.75.

2,2-Dichloro-1-(4′-chlorophenyl)-1-(4″-methoxyphenyl)ethylene (6). Proportion of reactants: chlorobenzene (5.6 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (5.4 g) (0.05 mol). Compound **6** was eluted with petroleum ether–benzene (75:25) and crystallized from MeOH: mp 109–111 °C; yield 5.3 g (34%); IR 1605, 1297, 1249, 1166, 1124, 1028, 821, and 720 cm^{-1}; ^1H NMR δ 3.74 (s, 3 H, OCH_3), 6.62 (d, 2 H, J = 8 Hz, 3′-H, 5′-H), 6.90 (dd, 4 H, J = 2, 8 Hz, 2′-H, 6′-H, 3″-H, 5″-H), 7.02 (d, 2 H, J = 8 Hz, 2″-H, 6″-H); MS, m/z (relative intensity) 314 (M^+ + 2, 4), 312 (M^+, 6), 242 (8), 238 (11), 228 (19), 224 (58), 211 (89), 196 (60), 184 (42), 169 (56), 166 (40), 153 (100), 141 (88), 137 (91), 113 (55), 109 (54). Anal. Calcd for $C_{15}H_{11}Cl_3O$: C, 57.69; H, 3.55. Found: C, 57.74; H, 3.50.

1,1,2-Tris(4″-methoxyphenyl)-1-(4′-methylphenyl)ethylene (7). Proportion of reactants: toluene (4.6 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (16.2 g) (0.15 mol). Compound **7** was eluted with petroleum ether–benzene (50:50) and crystallized from MeOH: mp 180 °C; yield 9.15 g (42%); IR 1626, 1506, 1320, 1201, 1170, 989, 849, 805, and 777 cm^{-1}; ^1H NMR δ 2.26 (s, 3 H, CH_3), 3.76 (s, 9 H, 3 × OCH_3), 6.62 (d, 8 H, J = 8 Hz, 3″-H, 5″-H, 3′-H, 5′-H), 6.94 (d, 8 H, J = 8 Hz, 2″-H, 6″-H, 2′-H, 6′-H); MS, m/z (relative intensity) 436 (M^+, 100), 421 (M^+ – CH_3, 22), 313 (35), 285 (28), 222 (56), 210 (58), 207 (30), 199 (55). Anal. Calcd for

$C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.49; H, 6.42.

1,1,2-Tris(4''-methoxyphenyl)-1-(4'-chlorophenyl)ethylene (8). Proportion of reactants: chlorobenzene (5.6 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (16.2 g) (0.15 mol). Compound **8** was eluted with petroleum ether–benzene (50:50) and crystallized from acetone: mp 178–180 °C; yield 9.57 g (42%); IR 1619, 1503, 1322, 1292, 1242, 1170, 1105, 1056, 831, 805, and 719 cm^{-1}; ^1H NMR δ 3.76 (s, 9 H, 3 × OCH_3), 6.64 (dd, 6 H, J = 2, 8 Hz, 3''-H, 5''-H), 6.92 (dd, 8 H, J = 2, 8 Hz, 2''-H, 6''-H, 3'-H, 5'-H), 7.0 (d, 2 H, J = 8 Hz, 2'-H, 6'-H); MS, m/z (relative intensity) 458 (M^+ + 2, 16), 456 (M^+, 48), 348 (6), 333 (9), 305 (29), 289 (19), 263 (29), 239 (54), 227 (67), 199 (100), 152 (96). Anal. Calcd for $C_{29}H_{25}ClO_3$: C, 76.22; H, 5.51. Found: C, 76.18; H, 5.45.

2',4'-Dimethyl-1',5'-bis[2,2-dichloro-1-(4''-methoxyphenyl)ethenyl]benzene (9). Proportion of reactants: *m*-xylene (5.3 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), anisole (10.8 g) (0.1 mol). The product was eluted with petroleum ether–benzene (75:25) and crystallized from MeOH: mp 146–147 °C; yield 9.61 g (38%); IR 1603, 1507, 1268, 1177, 1031, 966, 878, 854, 794, 769, and 720 cm^{-1}; ^1H NMR δ 2.12 (s, 6 H, 2 × CH_3), 3.80 (s, 6 H, 2 × OCH_3), 6.84 (d, 4 H, J = 8 Hz, 3''-H, 5''-H), 7.02 (s, 1 H, 3'-H), 7.14 (s, 1 H, 6'-H), 7.30 (d, 4 H, J = 8 Hz, 2''-H, 6''-H); MS, m/z (relative intensity) 510 (M^+ + 4, 52), 508 (M^+ + 2, 100), 506 (M^+, 76), 476 (7), 474 (21), 472 (24), 438 (12), 437 (19), 436 (18), 435 (21), 426 (5), 425 (10), 424 (10), 423 (19), 422 (10), 366 (5), 365 (7), 203 (17), 201 (29). Anal. Calcd for $C_{26}H_{22}Cl_4O_2$: C, 61.66; H, 4.38. Found: C, 61.60; H, 4.31.

2',4'-Dimethyl-1',5'-bis[2,2-dichloro-1-(2'',4''-dimethoxyphenyl)ethenyl]benzene (10). Proportion of reactants: *m*-xylene (5.3 g) (0.05 mol), dichloroacetyl chloride (7.37 g) (0.05 mol), anhydrous $AlCl_3$ (13.35 g) (0.1 mol), dimethylresorcinol (13.8 g) (0.1 mol). Compound **10** was eluted with benzene and crystallized from ethyl acetate: mp 210–211 °C; yield 11.32 g (40%); IR 1608, 1576, 1502, 1414, 1308, 1287, 1211, 1175, 1127, 1086, 1033, 962, 917, 876, 849, 811, and 722 cm^{-1}; ^1H NMR δ 2.20 (s, 6 H, 2 × CH_3), 3.72, 3.80 (each s, 12 H, 4 × OCH_3), 6.42 (d, 2 H, J = 2 Hz, 3''-H), 6.46 (dd, 2 H, J = 2, 8 Hz, 5''-H), 6.94 (s, 1 H, 3'-H), 7.06 (s, 1 H, 6'-H), 7.18 (d, 2 H, J = 8 Hz, 6''-H); MS, m/z (relative intensity) 570 (M^+ + 4, 53), 568 (M^+ + 2, 100), 566 (M^+, 78), 534 (10), 533 (10), 532 (12), 531 (8), 500 (10), 498 (8), 497 (10), 496 (8), 495 (9), 365 (5), 363 (8), 284 (8), 283 (6), 161 (8), 148 (21). Anal. Calcd for $C_{28}H_{26}Cl_4O_4$: C, 59.36; H, 4.62. Found: C, 59.42; H, 4.57.

Crystallization and X-ray Experiments. Suitable single crystals of compound **10** were grown from ethyl acetate, and those of compound **8** were obtained from acetone. Crystal quality check and space-group determination were made from preliminary rotation and Weissenberg photographs.

Precise lattice constants and the intensity data of a quadrant were measured on a Stoe four-circle diffractometer with Ni-filtered Cu Kα radiation. The reflection intensities were recorded by the θ–2θ scan technique with variable scan range and variable scan speed. Two standard reflections which were measured every 90 min showed no significant variations during the whole data collection. A summary of crystallographic data is given in Table I (supplementary material).

Structure Determination and Refinement. Phase determination was carried out successfully with direct methods. SHELXS-86[12] was used for compound **10** and MULTAN[13] for compound **8**. Least-squares refinements were executed with the corresponding subprograms of the XTAL[14] (compound **10**) and XRAY[15] system (compound **8**). For compound **10**, hydrogens (in parts from difference syntheses and in parts on calculated positions) were included in the final stages of anisotropic refinement of non-H atoms. For compound **8**, hydrogens were not determined. For this structure a disorder of the chlorine and the terminal methoxy groups was observed. The positions given in Figure 1 are the most probable ones; however, there is some evidence for the chlorine to occupy in parts two further of the methoxy positions and that a methoxy group contributes also in parts to the present chlorine site. No attempt was made to investigate this disorder problem in detail. The final atomic parameters with Ueq values for compounds **8** and **10** are given in Tables II and III respectively (supplementary material).

Supplementary Material Available: All X-ray data for compounds **8** and **10**, Tables I–III, as well as listings of complete atomic parameters with U_{ij} values, bond lengths, and bond angles (14 pages). Ordering information is given on any current masthead page.

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Direct Synthesis of β-Keto Methylenetriphenylphosphoranes from Readily Available Phosphonium Salts

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Thermolysis of β-keto methylenetriphenylphosphoranes **1** to give disubstituted acetylenes **2** and triphenylphosphine oxide (Scheme I), first investigated by Trippett and Walker,[1] is a particularly useful method for the preparation of (perfluoroalkyl)-substituted electron-deficient acetylenes.[2] The resultant acetylenes are valuable synthetic intermediates and can be employed in a variety of reactions as dipolarophiles[2c] or dienophiles[2g] for the preparation of fluorinated compounds. Reported methods for preparation of the phosphorane precursors, however, are rather cumbersome, requiring two steps from the readily available phosphonium salts and affording a mixture of the desired phosphorane and a phosphonium salt. An excellent method has been developed for the preparation of (β-ketoalkyl)phosphonates; however, this did not seem to us to be directly applicable to type **1** phosphoranes.[3] In order to prepare suitable quantities of the acetylenes, we endeavored to find a more convenient route to phosphoranes **1**.

Typically, phosphoranes **1** are prepared by treatment of mono-α-substituted methylenephosphoranes **4** with acid chlorides or anhydrides to afford an equimolar mixture of the desired phosphorane **1** and phosphonium salt **6** (Scheme II). Acylation of phosphorane **4** affords intermediate phosphonium salt **5**, which, via transylidation,[4]

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