shift the equilibrium to the right, thereby stabilizing the hydrogen bonded complex.

In the more dipolar solvents, however, factor c and d become increasingly important, and the phenomenon which destabilizes the hydrogen bonded complex with increasing HBA dipolarity is the dipolar interaction between the HBA base and the solvent, which shifts the equilibrium to the left. Thus, we can rationalize stabilization of the hydrogen bonded complex with decreasing solvent dipolarity and with either increasing or decreasing solute dipolarity.

As a concluding comment, it seems fair to state that certain associated species, previously referred to as hydrogen bonded complexes, might more properly be designated as hydrogen bonded dipolar complexes.

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Unusual Products from the Reactions of Anhydrous Hydrogen Chloride with Arylacetylenes[1]

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Liquid-phase reactions of anhydrous hydrogen chloride with *p*-methyl-, *p*-methoxy-, *p*-fluoro-, and unsubstituted phenylacetylene afforded cyclic trimers, tetramers, and pentamers of the corresponding arylacetylenes. Phenylacetylene gave additionally 1-methyl-1-phenyl-3-chloroindene. The reactions proceeded via the corresponding HCl diadducts, i.e., via 1-aryl-1,1-dichloroethanes as intermediates.

Reactions of monosubstituted acetylenes with hydrogen chloride have been examined under various aspects and a variety of conditions.[2] From the published data it appears that both in the gas phase and in organic solvents the corresponding mono- and/or diadducts are formed. By contrast, reactions of monoalkylacetylenes with anhydrous hydrogen chloride in the liquid phase and in the absence of a solvent provided a greater variety of products. In particular, [2 + 2] cycloadditions to yield the corresponding 1,3-dialkyl-1,3-dichlorocyclobutanes have been observed in all cases examined.[3] To our knowledge, reactions of monosubstituted arylacetylenes under such conditions have not been reported.[4,5] In this paper we describe the results of the reactions of neat hydrogen chloride with phenylacetylene (**1a**) and with *p*-methyl-(**1b**), *p*-methoxy-(**1c**), and *p*-fluorophenylacetylene (**1d**) in the liquid phase and at ambient temperatures.

Reaction Products. Phenylacetylene (1a). Reactions of **1a** with HCl in a molar ratio of 1:5 afforded entirely different products, depending on the reaction time (Scheme I). Termination of the reaction after 1 and after 3 days afforded in each case mobile liquids, whereas after 7 days a highly viscous liquid was obtained, after 13 days a semisolid was obtained, and after 27 days a solid reaction product was obtained. ^1H NMR analyses showed that in each case the starting material **1a** had been consumed. Diadduct **4a** was the major reaction product after short reaction times. Its proportion of the total products decreased, however, from 82% (1 day), via 68% (3 days), 20% (7 days), and 11% (13 days) to 6% (27 days). Monoadduct **2a** was also detected by ^1H NMR analysis, despite the excess HCl applied. Its proportion was 5% (1 day), 6% (3 days), 2% (7 days), and trace amounts after 13 and 27 days, each. In the ^1H NMR spectra of all reaction products, the intensities of the signals in the aromatic region were in excess over those expected for **2a** and **4a**. This excess amounted to 13, 27, 79, 89, and 94% in the products obtained after 1, 3, 7, 13, and 27 days, respectively. This was indicative of the enhanced formation of aromatic products at the expense of diadduct **4a** with increasing reaction times.

GLC analyses of the crude reaction products obtained after 13 and 27 days showed in each case **4a** as the minor component, whereas the major peaks had longer retention times. Chromatographic separation of these products afforded six compounds that corresponded to these peaks. The isolated compounds were assigned to the structures of **15a**–**20a**. From the crude products obtained after 13 days of reaction, the yields of the isolated, purified compounds were 7% for **15a**, 11% for **16a**, 8% for **17a**, 4% for **18a**, and ca. 1% for **19a** and **20a**, each. The actual yields were higher, but the purification resulted in considerable material losses. In addition to compounds **15a**–**20a**, ca. 46 wt % of a dark-brown solid material was isolated. Its ^1H NMR spectrum showed predominantly signals in the aromatic region (δ 6.3–8.0) and unstructured, broad signals in the aliphatic region (δ 0.6–2.8). GLC analysis showed no peaks, thus indicating that the material was probably oligomeric or polymeric.

Compounds **15a**–**17a** have been identified with the help of authentic samples: **15a** was prepared by the reaction of phosphorus pentachloride with 3-methyl-3-phenyl-1-

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[1] This paper has been presented by G. Leifker, V. V. Ramana Rao, K. Vittinghoff, and K. Griesbaum, at the 19th Hauptversammlug der Gesellschaft Deutscher Chemiker, held in Hamburg, 1981.

[2] For a summary, see, for example, P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian in "Vinyl Cations", Academic Press, New York, 1979.

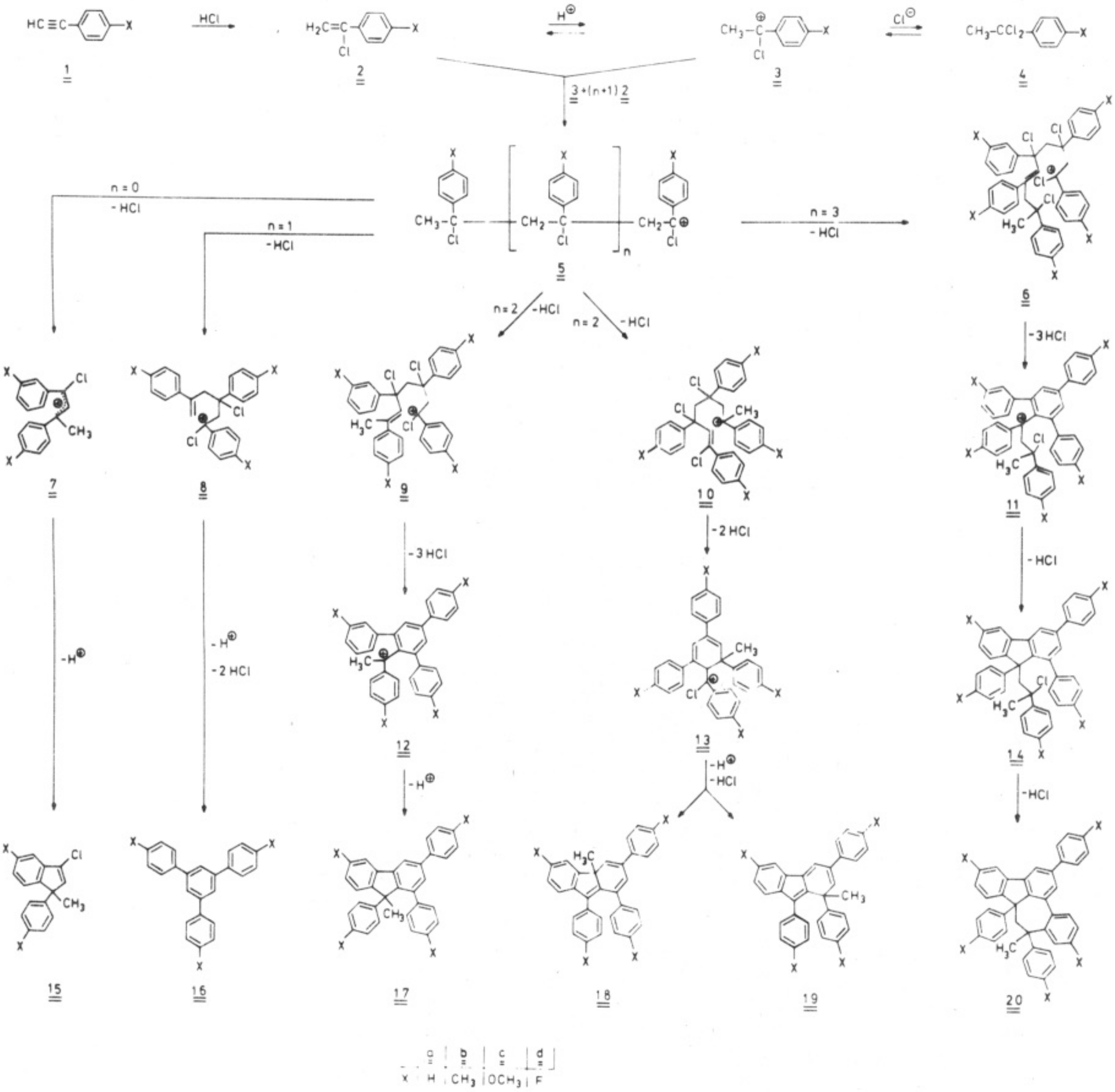
[3] G. Stammann and K. Griesbaum, *Chem. Ber.*, 113, 598 (1980), and references cited therein.

[4] Liquid-phase reactions of anhydrous HCl with the alkylaryl-substituted acetylene-1-phenylpropyne have been carried out in our laboratory. They afforded unusual products, having indene structures. Preliminary results about some reaction products have been reported,[1,5] and a full paper is in preparation.

[5] B. Deppisch and K. Vittinghoff, *Acta. Crystallogr.*, 36, 3191 (1980).

0022-3263/82/1947-4975$01.25/0

Scheme I



indanone; **16a** was commercially available, and **17a** was prepared by sequential reactions of 1,3,9-triphenyl-9-fluorenol with thionyl chloride and with methylmagnesium iodide. Compound **18a** was identified by comparison of its melting point[6] and its ^{1}H NMR data[7] with those published previously. The structure of **19a** was assigned based on the following data: The ^{1}H NMR spectrum showed a singlet signal in the aliphatic region for the CH_3 group, two doublet signals in the olefinic region for the two vinylic protons, and an unassigned group of signals for the 19 protons in the aromatic region. The ^{13}C NMR spectrum showed 1 quartet and 1 singlet signal in the aliphatic region, as well as 9 singlet and 13 doublet signals in the olefinic and aromatic region. The assignment of structure **20a** is only tentative. It is based on GC/MS data and on the fact that, as in the case of the reaction products of **1b–d**, it was the component with the longest GLC retention time. ^{1}H and ^{13}C NMR data are not conclusive, since, due to the low yield, isolation of a pure sample has not been possible.

***p*-Methylphenylacetylene (1b).** Reactions of **1b** with HCl in a molar ratio of 1:5 gave a mobile liquid after 1 h, a slightly viscous liquid after 6 h, a very viscous liquid after 40 h, and a solid product after 4 days. ^{1}H NMR analyses showed that in each case the starting material **1b** had been consumed. Diadduct **4b** was obtained in 61% after 1 h, in 53% after 6 h, in 25% after 40 h and in only trace amounts after 4 days. Monoadduct **2b** could be only detected in 5% after 1 h. The excess of aromatic protons over those expected for the mono- (**2b**) and/or diadduct (**4b**) was 34% after 1 h, 47% after 6 h, 75% after 40 h, and ca. 99% after 4 days.

GLC analysis of the crude reaction product obtained after 4 days of reaction showed three major peaks, along with several minor peaks having shorter retention times. Chromatographic separation of the crude product afforded compounds **16b** (12%), **17b** (28%), and **20b** (36%), which corresponded to the three major GLC peaks. In addition to compounds **16b**, **17b**, and **20b**, 9 wt % of a yellow solid material was isolated, which could not be identified.

***p*-Methoxyphenylacetylene (1c).** Reactions of **1c** with HCl were carried out in a molar ratio of 1:1, since preliminary experiments with a molar ratio of 1:5 had afforded complex reaction mixtures, containing a high

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(6) R. W. Roeske, D. B. Bright, R. I. Johnson, D. J. De Jarlais, R. W. Bush, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 3128 (1960).

(7) H. W. Moore and H. R. Snyder, *J. Org. Chem.*, **28**, 297 (1963).

percentage of intractable material. The reactions were very fast: Within 1 day the 1:1 reaction gave a pink solid material in which neither residual **1c** nor **2c** and, at the most, traces of **4c** could be detected by ^{1}H NMR analysis.

Chromatographic separation of the crude product afforded compounds **16c** (18%), **17c** (48%), and **20c** (4%), along with ca. 9% of a dark brown solid, which could not be identified. GLC analysis of the crude reaction product showed two major peaks, corresponding to **16c** and **17c**, along with the peak of **4c** and few additional minor peaks; a peak for **20c**, however, did not appear.

***p*-Fluorophenylacetylene (1d).** Reactions of **1d** with HCl in a molar ratio of 1:5 gave a mobile liquid after 7 days, a slightly viscous liquid after 14 days, and a very viscous liquid after 85 days. ^{1}H NMR analyses showed that in each case the starting material had been consumed. Diadduct **4d** was obtained in 84, 65, and 15% after 7, 14, and 85 days, respectively. Monoadduct **2d** was detected in 5 and 4% in the reaction mixtures obtained after 7 and 14 days, respectively. The excess of aromatic protons over those expected for **2d** and **4d** amounted to 11, 31, and 85% after 7, 14, and 85 days, respectively.

Reaction of **1d** with HCl in a molar ratio of 1:5 in the presence of 0.1 molar equiv (based on **1d**) of zinc chloride gave a solid product after 7 days. ^{1}H NMR analysis showed 2% of **4d** and 98% excess of aromatic protons. GLC analysis showed two major peaks, corresponding to **16d** and **17d** and several minor peaks, including that of **20d**.

Chromatographic separation of the crude reaction product gave pure **16d** (42%), **17d** (23%), and **20d** (7%), as well as 14% of a yellow solid material, which was not identified. Chromatographic separation of the viscous product obtained after 85 days of reaction in the absence of zinc chloride gave **16d**, **17d**, and **20d** in considerably lower yields of 9, 1, and 0.5%, respectively.

The structures of **16b–d** have been assigned based on their known melting points and on spectral data: The ^{13}C NMR spectra[8] showed in each case six different signals for the aromatic carbons in the expected multiplicities. The ^{1}H NMR spectra[8] showed singlet signals for the aromatic protons attached to the central benzene rings. The protons of the para-substituted benzene rings appeared as AA′BB′ systems in the spectra of **16b** and **16c**, and as AA′BB′X systems in the spectrum of **16d**, due to H–F couplings. The CH_3 signals in **16b** and **16c** appeared as singlets; the F signal in **16d** appeared as a triplet of a triplet. The mass spectra showed in each case the expected molecular ions as the major peaks.

Compounds **17b–d** and **20b–d** gave in each case correct elemental analyses, strong molecular ion peaks in the mass spectra, and the expected NMR spectra: The ^{13}C NMR spectra[8] of **17b** and of **17c** showed one singlet and five quartets in the aliphatic region, as well as 13 singlets and 10 doublets in the aromatic region. The ^{13}C NMR spectrum of **17d** showed 1 singlet and 1 quartet in the aliphatic region and 23 signals in the aromatic region. The observed C–F couplings provided additional proof for the assigned structure. The ^{1}H NMR spectra of **17b** and of **17c** showed 5 singlets, that of **17d** showed 1 singlet in the aliphatic region, and all spectra showed a total of 17 protons in the aromatic region. The latter could be conclusively assigned to the various structural units of the aromatic systems of compounds **17b–d**, as we have shown in a detalied analysis.[8] Compound **17d** was further characterized by its ^{19}F NMR spectrum and by the H–F couplings observed. The ^{13}C NMR spectra of **20b** and **20c** showed 6 quartets, 1 triplet, and 2 singlets in the aliphatic region, as well as 16 singlets and 14 doublets in the aromatic region. The ^{13}C NMR spectrum of **20d** showed 1 quartet, 1 triplet, and 2 singlets in the aliphatic region and 28 signals in the aromatic region, some of which exhibited typical C–F couplings. The ^{1}H NMR spectra of **20b** and **20c** showed 6 singlets, that of **20d** showed 1 singlet for the CH_3 groups, and all spectra showed a AB system for the CH_2 groups, along with the signals of 20 protons in the aromatic region. Compound **20d** exhibited, additionally, the typical ^{19}F NMR signals, viz., 3 as triplets of triplets and 2 as doublets of triplets.

Proposed Reaction Course. The formation of aromatic products, particularly of trimers during electrophilic additions to substituted acetylenes, is well known and it has been rationalized by invoking vinyl cations as crucial intermediates.[2] Similarly, the formation of indenes by the aluminum trichloride catalyzed reaction of benzylic chlorides with diphenylacetylene has been also formulated via vinyl cation intermediates.[9] By contrast, the dimer (**15**), as well as the trimers (**16**), tetramers (**17–19**), and pentamers (**20**), formed in the reactions of the corresponding arylacetylenes (**1**) with hydrogen chloride in the present investigation has to be rationalized by a different reaction course, since, as it was shown, the arylacetylenes were in each case totally consumed and sequentially converted into mono- (**2**) and diadducts (**4**), before any significant amounts of oligomers **15–20** were formed. Consequently, the diadducts **4** have to be considered as the starting materials for the formation of **15–20**. This assumption could be verified by the reaction of anhydrous hydrogen chloride with authentic **4b**. Under the conditions described in the foregoing for the reaction of HCl with **1b**, **4b** afforded **16b**, **17b**, and **20b**. Similarly, reaction of HCl with the monochloride **2b** gave also **16b**, **17b**, and **20b**.

We assume that, even in the presence of excess hydrogen chloride, there exists an equilibrium between monochlorides **2** and dichlorides **4** via the chlorinated cations **3**.[10] Cations **3**, in turn, can add to monoadducts **2** to give dimeric or oligomeric cations **5**. The latter may then serve as precursors for the cyclic end products as follows: (a) Dimeric **5** (n = 0) is dehydrochlorinated to form the allylic-type cation **7**, which in turn alkylates one of the benzene rings to produce **15**. (b) Trimeric **5** (n = 1) is dehydrochlorinated to cation **8**, which by intramolecular terminal alkylation and subsequent aromatization eventually gives **16**. (c) Tetrameric **5** (n = 2) obviously chooses two possible reaction paths, to give final products. The first one starts out by a 1,2-dehydrochlorination to give **9**. The latter then undergoes two sequential intramolecular alkylations to produce **17** via cation **12**. The second reaction path of tetrameric **5** starts out by loss of H^+ and Cl^- in more remote positions to give intermediate **10**, which in turn undergoes intramolecular alkylation to produce **13**. The latter cation can alkylate either of the neighboring aryl rings to afford **18** and **19**. (d) Pentameric **5** (n = 3), finally, undergoes dehydrochlorination to **6**, intramolecular alkylation and subsequent aromatization to form **11**, and two sequential intramolecular alkylations via **14** to give **20**. Some of the above reactions could also be formulated via dienic or trienic intermediates. However, since the reac-

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[8] A detailed analysis of the aromatic region of the ^{1}H NMR spectra and a partial analysis of the ^{13}C NMR spectra are reported elsewhere: V. V. Ramana Rao and K. Griesbaum, *Org. Magn. Reson.*, submitted for publication.

[9] R. Maroni and G. Melloni, *Tetrahedron Lett.*, 2869 (1972).

[10] This assumption is supported by the observation that even after prolonged reaction times in the presence of excess HCl, monoadducts 2 could be detected in the reaction mixtures.

tions occurred in the presence of excess hydrogen chloride, this appears less likely to us.

To our knowledge, aromatization reactions of geminal dichlorides with hydrogen chloride as they have been found here have not been reported before. Therefore, we have done some preliminary screening in order to test the scope of such reactions. It appears from these results that the reaction may be restricted to geminal dichlorides having the chlorine substituents in benzylic positions. It may be that the loss of chloride ion from dichlorides **4** to form cations **3** is assisted by protonation of the aryl rings of compounds **4**.

Experimental Section

General. ^{13}C NMR and 60-MHz ^{1}H NMR spectra were recorded on a Bruker WP 60, 300-MHz ^{1}H NMR spectra were recorded on a Bruker WH 300, GC/MS and mass spectra were recorded on a Hewlett-Packard 5985B, and IR spectra were recorded on a Beckman IR 4260 instrument. All GLC analyses were carried out on a Hewlett-Packard 5880A instrument, using the following column: 0.3 × 100 cm; 5% Poly S 176 on Chromosorb G. The individual analyses varied only in the column temperatures.

Most of the reactions of anhydrous hydrogen chloride with the substrates **1a–d** were carried out in thick-walled glass ampules by a standard procedure.[11] Some reactions were carried out in a cylindrical reaction vessel by passing gaseous HCl into the liquid substrate and also by a standard procedure.[12]

Reactions of HCl with Phenylacetylene (1a). In a 120-mL ampule, 9.0 g (0.25 mol) of HCl and 5.0 g (0.049 mol) of **1a** were reacted for 1 day. After evaporation of unreacted HCl, there remained 7.8 g of a greenish, transparent, mobile liquid. ^{1}H NMR analysis showed the presence of **4a** (CH$_3$ signal at δ 2.55) and **2a** [CH$_2$ signal at δ 6.09 and 6.33 (AB system with $J_{AB} = 1.6$ Hz)] in a molar ratio of 19:1. The intensity of the signals in the aromatic region (δ 7.25–7.87) was 13% in excess over that expected on the basis of the CH$_3$ and CH$_2$ signals of **4a** and of **2a**, respectively.

Reaction of the same mixture as above for 3 days afforded 8.0 g of a dark-green, nontransparent, mobile liquid, which contained **4a** and **2a** in a molar ratio of 14:1 and an excess of 27% of aromatic protons.

In a 350-mL ampule, 18.0 g (0.49 mol) of HCl and 10.0 g (0.098 mol) of **1a** were reacted for 7 days to yield 11.9 g of a dark-green, highly viscous product. ^{1}H NMR analysis showed the presence of **4a** and of **2a** in a molar ratio of 9:1 and an excess of 79% of aromatic protons.

Reaction of the same mixture as above for 13 days gave 11.9 g of a dark-green, semisolid product. ^{1}H NMR analysis showed **2a** (a trace), **4a** (11%), and an excess of 89% of aromatic protons. GLC analysis of the crude reaction product in acetone showed, in addition to that of **4a**, three major and several minor peaks. The major peaks could be assigned to **15a**, **16a**, and a mixture of **17a–19a**. One of the minor peaks having longer retention times corresponded to **20a** (conditions: 250–350 °C at 10 °C/min).

Reaction of the same mixture as above for 27 days gave 10.9 g of a dark-green solid product. ^{1}H NMR analysis showed 6% of **4a** and an excess of 94% of aromatic protons. GLC analysis (conditions as above) showed the peaks of **15a** (17%), **16a** (20%), **17a–19a** (together 50%), and **20a** (3%).

Isolation and Identification of 15a–20a. Of the crude product from the reaction after 13 days, 11.7 g was separated by column chromatography (column: 4 × 50 cm, 300 g of silica gel; solvent: pentane; pentane/CCl$_4$ in ratios of 40:1, 20:1, 10:1, 5:1, and 1:1; CCl$_4$; CCl$_4$/benzene in a ratio of 2:1; ether; methanol) to afford **15a–20a** and 5.4 g (46.2%) of a dark-brown solid material. In the ^{1}H NMR spectrum, the latter showed predominantly signals in the aromatic region, along with some unstructured, broad signals in the aliphatic region. The total material recovered, i.e. **15a–20a** and the dark-brown solid, amounted to ca. 90% of the crude product submitted to the chromatographic separation. However, further purification of **15a–20a** resulted in considerable losses.

1-Methyl-1-phenyl-3-chloroindene (15a): colorless, viscous liquid; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.73 (s, 3 H), 6.45 (s, 1 H), 7.03–7.44 (m, 9 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 22.66 (q, J = 129 Hz), 55.51 (s), 119.73 (d, J = 162 Hz), 122.68 (d, J = 159 Hz), 126.02 (d, J = 156 Hz), 126.80 (d, J = 156 Hz), 126.93 (d, J = 160 Hz), 127.14 (d, J = 159 Hz), 128.50 (d, J = 158 Hz), 130.77 (s), 140.03 (s), 140.47 (d, J = 177 Hz), 141.69 (s), 150.88 (s); IR (neat) 2964, 1565, 1495, 1029, 962, 758, 750, 697 cm^{-1}; MS, *m/e* (relative intensity) 242, 240 (8, 23, M$^+$), 205 [100 (M – Cl)$^+$]; GLC t_R = 1.4 min; yield 0.80 g (7%).

Independent Synthesis of 15a. A solution of 4.10 g (18.4 mmol) of 3-methyl-3-phenyl-1-indanone[13] in 10 mL of CCl$_4$ was added dropwise to a slurry of 5.00 g (24.0 mmol) of phosphorus pentachloride in 10 mL of CCl$_4$ at ambient temperatures. The mixture was stirred and refluxed for 1 h and cooled to 30 °C, and 100 mL of water was added dropwise. Then the mixture was kept at 60 °C for 1 h, subsequently cooled to room temperature, and 50 mL of CCl$_4$ was added. The organic layer was washed with 100 mL of a concentrated solution of aqueous potassium hydroxide and with water. After evaporation of the solvent, 4.40 g (78%) of crude **15a** remained as a yellowish viscous liquid. Pure **15a** was obtained by preparative GLC (column 0.8 × 350 cm, 5% OV-101 on Chromosorb G; 200 °C). Its spectral data were identical with those obtained from the sample of **15a** described above.

Anal. Calcd for C$_{16}$H$_{13}$Cl: C, 79.83; H, 5.44; Cl, 14.73. Found: C, 79.70; H, 5.55; Cl, 14.65.

1,3,5-Triphenylbenzene (16a): mp 175–176 °C (recrystallized from ethanol) (lit.[14] mp 176 °C); ^{1}H NMR, IR, and MS were identical with that of a commercial sample; GLC t_R = 9.7 min; yield 1.08 g (11%).

9-Methyl-1,3,9-triphenylfluorene (17a): mp 173–174 °C (recrystallized from acetone) (lit.[6] mp 171–172 °C); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.58 (s, 3 H), 6.64–8.04 (m, 21 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 22.58, 54,96, 117,71, 120.08, 123.91, 126.10, 126.83, 127.14, 127.38, 128.17, 128.90, 129.15, 129.51, 139.01, 140.47, 140.65, 141.08, 141.56, 145.46, 149.90, 155.87; IR (KBr) 3050, 3020, 1596, 1490, 1478, 1440, 1425, 1030, 1020, 878, 770, 760, 750, 700 cm^{-1}; MS, *m/e* (relative intensity) 408 (64, M$^+$), 393 [100, (M – CH$_3$)$^+$], 331 [20, (M – C$_6$H$_5$)$^+$], 315 [30, (M – C$_6$H$_5$ – CH$_4$)$^+$]; GLC t_R = 13.6 min; yield 0.84 g (8%).

Independent Synthesis of 17a. To a solution of 12.0 g (29.3 mmol) 1,3,9-triphenyl-9-fluorenol[15] in 20 mL of benzene was added 10 mL of thionyl chloride, and the mixture was kept stirring at 60 °C until the gas evolution had ceased. Then the mixture was refluxed for 1 h, and, subsequently, excess thionyl chloride and benzene was distilled off. The solid residue was recrystallized from ether to yield 12.1 g (97%) of 1,3,9-triphenyl-9-chlorofluorene: mp 203 °C; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 6.76–7.98 (m).

To a Grignard reagent, prepared from 1.50 g (61 mmol) of magnesium and 9.00 g (63 mmol) of iodomethane in 50 mL of ether was added under stirring a solution of 2.00 g (4.6 mmol) of 1,3,9-triphenyl-9-chlorofluorene in 50 mL of benzene at room temperature. Then the mixture was refluxed for 3 h, cooled, poured into 200 mL of ice–water, and neutralized with hydrochloric acid. The aqueous phase was extracted with ether, the extracts were combined with the organic layer and dried over sodium sulfate, and the solvent was removed. The yellowish solid residue was recrystallized from acetone and subsequently sublimated at 0.15 torr to afford 0.92 g (48%) of colorless, crystalline **17a**, mp (173–174 °C) as well as ^{1}H NMR, IR, and MS data were identical with those obtained from **17a** that had been formed from the HCl–phenylacetylene reaction.

Anal. Calcd for C$_{32}$H$_{24}$: C, 94.08; H, 5.92. Found: C, 93.84; H, 5.90.

4a-Methyl-1,3,9-triphenyl-4a*H*-fluorene (18a): yellow solid; mp 178–179 °C (recrystallized from chloroform) (lit.[6] mp 179–181 °C); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.71 (s, 3 H) (AB system with δ_A

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[11] H. Schneider and K. Griesbaum, *J. Org. Chem.*, **44**, 3316 (1979).

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[13] C. F. Koelsch, H. Hochmann, and C. D. Le Claire, *J. Am. Chem. Soc.*, **65**, 59 (1943).

[14] R. C. Weast, Ed., "Handbook of Chemistry and Physics", CRC Press, Cleveland, OH, 1980, p C-172.

[15] E. P. Kohler and L. W. Blanchard, Jr., *J. Am. Chem. Soc.*, **57**, 367 (1935).

6.67 (1 H), δ_B 6.63 (1 H), J_{AB} = 1.3 Hz), 6.97–7.54 (m, 19 H) [lit.[7] ^{1}H NMR δ 1.69 (s), 6.67 (center of AB system with J_{AB} = 1.5 Hz); IR (KBr) 3020, 2950, 1490, 1440, 765, 755, 732, 700 cm^{-1}; MS, m/e (relative intensity) 408 (81) (M)$^+$, 393 [100, (M − CH$_3$)$^+$], 331 [25, (M − C$_6$H$_5$)$^+$], 315 [52, (M − C$_6$H$_5$ − CH$_4$)$^+$], 77 [45, (C$_6$H$_5$)$^+$]; GLC t_R = 13.6 min; yield 0.41 g (4%).

1-Methyl-1,3,9-triphenyl-1*H*-fluorene (19a): yellow solid; mp 188 °C (recrystallized from chloroform); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.81 (s, 3 H), 6.43 (d, J = 1.37 Hz, 1 H), 6.79 (d, J = 1.37 Hz, 1 H), 7.10–7.58 (m, 19 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 12.72 (q, J = 119 Hz), 64.46 (s), 119.91 (d, J = 160 Hz), 123.02 (d, J = 160 Hz), 124.69 (d, J = 159 Hz), 125.87 (d, J = 158 Hz), 126.20 (d, J = 160 Hz), 126.71 (d, J = 161 Hz), 127.06 (d, J = 160 Hz), 127.37 (d, J = 161 Hz), 127.57 (d, J = 160 Hz), 127.83 (d, J = 160 Hz), 128.43 (d, J = 160 Hz), 128.52 (d, J = 160 Hz), 128.94 (d, J = 162 Hz), 129.13 (s), 131.17 (s), 137.59 (s), 139.26 (s), 140.20 (s), 142.68 (s), 145.64 (s), 146.03 (s), 150.83 (s); IR (CCl$_4$) 3080, 3060, 3025, 1600, 1492, 1447, 1385, 723, 697 cm^{-1}; MS, m/e (relative intensity) 409 [94, (M + H)$^+$], 394 [100, (M + 1 − CH$_3$)$^+$], 332 [22, (M + 1 − C$_6$H$_5$)$^+$], 316 [30, (M + 1 − C$_6$H$_5$ − CH$_4$)$^+$], GLC t_R = 12.9 min; yield 0.095 g (1%).

Anal. Calcd for C$_{32}$H$_{24}$: C, 94.08; H, 5.92. Found: C, 93.58; H, 6.11.

12-Methyl-6,12,13a-triphenylbenzo[6,7]cycloheptadieno-[1,2,3-*jk*]fluorene (20a): slightly yellow solid; GLC analysis showed one major peak (t_R = 35.3 min) and several peaks having shorter rentention times; MS data of the major peak, m/e (relative intensity) 510 (38, M$^+$), 495 [90, (M − CH$_3$)$^+$], 433 [15, (M − C$_6$H$_5$)$^+$], 395 [100, (M − C$_6$H$_5$ − C$_3$H$_5$)$^+$], 315 [70, (M − 2C$_6$H$_5$ − C$_3$H$_5$)$^+$]; the sample was not of analytical purity.

Reactions of HCl with *p*-Methylphenylacetylene (1b). In a 200-mL ampule were reacted 1.5 g (42 mmol) of HCl and 1.0 g (8.6 mmol) of **1b**[16] for 1 h. After evaporation of unreacted HCl there remained a dark-green mobile liquid. ^{1}H NMR analysis showed the presence of **4b** (CH$_3$CCl$_2$ signal at δ 2.53) and of **2b** (CH$_2$ signals at δ 5.43 and 5.67; AB system with J_{AB} = 2.0 Hz) in a molar ratio of 12:1. The intensity of the signals in the aromatic region (δ 7.0–7.8) was 35% in excess over that expected on the basis of the CH$_3$CCl$_2$ and CH$_2$ signals of **4b** and of **2b**, respectively.

Reaction of the same mixture as above for 6 h afforded a dark-green, slightly viscous liquid. It contained **4b** in 53% and an excess of 47% of aromatic protons.

Reaction of the same mixture as above for 40 h afforded a dark-green viscous liquid. It contained **4b** in 25% and an excess of 75% of aromatic protons.

In a 200-mL ampule were reacted 4.55 g (126 mmol) of HCl and 2.90 g (25 mmol) of **1b** for 4 days to yield 3.20 g of a dark blue solid. ^{1}H NMR analysis showed only traces of **4b** and mainly aromatic protons, along with broad signals for the *p*-methyl groups. GLC analysis (150–350 °C at 10 °C/min) of the crude reaction product in dichloromethane showed three major peaks, corresponding to **16b**, **17b**, and **20b**, along with several minor peaks having shorter retention times.

Isolation and Identification of 16b, 17b, and 20b. The crude product from the reaction after 4 days was separated by column chromatography (column 2.6 × 60 cm, 100 g of silica gel; solvent: 5% tetrachloromethane, 5% benzene, and 90% *n*-hexane) to afford pure **16b** (350 mg), **17b** (800 mg), and **20b** (1000 mg). Further elution with benzene afforded 300 mg of a yellow solid material. The ^{1}H NMR spectrum of the latter showed broad signals in the aromatic region (δ 6.53–7.97) and in the aliphatic region (δ 2.07–2.50 and 1.17–1.33). The total material recovered, i.e., **16b**, **17b**, **20b**, and the yellow solid amounted to 77% of the crude reaction product that was submitted to the chromatographic separation.

1,3,5-Tris(*p*-methylphenyl)benzene (16b): colorless crystals; mp 177–178 °C (recrystallized from methanol) (lit.[17] mp 178 °C); ^{1}H NMR (60 MHz, CDCl$_3$, Me$_4$Si) δ 2.41 (s, 9 H), 7.27 and 7.60 (AA′BB′ system, J = 8.4 Hz, 12 H), 7.73 (s, 3 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 21.09 (q, J = 126 Hz), 124.83 (d, J = 157 Hz), 127.45 (d, J = 158 Hz), 129.76 (d, J = 158 Hz), 137.40 (s), 138.89 (s), 142.54 (s); IR (KBr) 3020, 2910, 1900, 1592, 1510, 1430, 1390, 1310, 1180, 1110, 1020, 880, 820, 810, 760, 710, 705, 615 cm^{-1}; MS, m/e (relative intensity) 350, 349, 348 (5, 33, 100, M$^+$); GLC t_R = 21.7 min; yield 350 mg (12%).

7,9-Dimethyl-1,3,9-tris(*p*-methylphenyl)fluorene (17b): mp 183–184 °C (recrystallized from methanol); ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si) δ 1.54, 2.28, 2.29, 2.33, 2.39 (s, 3 H, each), 6.56 and 6.90 (J = 8.4 Hz), 6.79 and 6.93 (J = 8.2 Hz), 7.25 and 7.60 (J = 8.1 Hz), (AA′BB′ system, 4 H, each), 6.83, 7.24, 7.95 (d, $J \approx$ 1.6 Hz, 1 H, each), 7.11 (dd, J = 7.8 and 1.6 Hz, 1 H), 7.71 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 20.95, 21.05, 21.09, 21.58, 22.50 (q, J = 125 Hz, each), 127.83 (d, J = 158 Hz, three carbon intensity), 116.85, 119.62, 124.89, 128.57 (d, J = 158 Hz, one-carbon intensity, each), 126.65, 127.04, 128.69, 129.35, 129.44 (d, J = 158 Hz, two-carbon intensity, each), 54.53, 135.19, 136.03, 136.32, 136.84, 137.73, 137.79, 138.27, 140.31 (two-carbon intensity), 141.47, 142.82, 149.58, 156.01 (s, each); IR (KBr) 3020, 2960, 1615, 1610, 1510, 815, 790 cm^{-1}; MS, m/e (relative intensity) 466, 465, 464 (8, 41, 100, M$^+$), 450, 449 [34, 86, (M − CH$_3$)$^+$]; GLC t_R = 25.7 min; yield 800 mg (28%).

Anal. Calcd for C$_{36}$H$_{32}$: C, 93.06; H, 6.94. Found: C, 92.80; H, 7.04.

2,10,12-Trimethyl-6,12,13a-tris(*p*-methylphenyl)benzo-[6,7]cycloheptadieno[1,2,3-*jk*]fluorene (20b): mp 224 °C (recrystallized from methanol); ^{1}H NMR (300 MHz, CDCl$_3$, Me$_4$Si) δ 0.93, 1.87, 2.30, 2.32, 2.40, 2.48 (s, 3 H, each), 2.61 and 2.90 (AB system, J = 13.7 Hz, 2 H), 6.55 and 6.89, 7.08 and 7.11, 7.21 and 7.59 (AA′BB′ systems, J = 7.6 Hz, 4 H, each), 5.91, 7.10 (d, J = 1.3 Hz, 1 H, each), 7.25, 7.89 (d, J = 1.9 Hz, 1 H, each), 6.95, 6.99 (dd, J = 7.9 and 1.3 Hz, 1 H, each), 6.58, 7.59 (d, J = 7.9 Hz, 1 H, each); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 20.80, 21.04, 21.09, 21.23, 21.60, 30.61 (q, J = 125 Hz, each), 49.10 (t, J = 132 Hz), 116.72, 119.08, 124.50, 125.85, 126.83, 127.60, 128.72, 129.43 (d, J = 158 Hz, each), 127.27, 127.37, 128.38, 128.85, 129.67, 129.74 (d, J = 158 Hz, two-carbon intensity, each), 52.08, 62.41, 135.33, 135.96, 136.33, 136.51, 137.12, 137.64, 138.09, 138.55, 140.59, 140.77, 142.45, 147.22, 148.23, 148.90, 149.08, 155.05 (s, each); IR (KBr) 3020, 2940, 2920, 2860, 1610, 1490, 1440, 820 cm^{-1}; MS, m/e (relative intensity) 582, 581, 580 (2, 53, 100, M$^+$), 566, 565 [6, 10, (M − CH$_3$)$^+$], 475, 474, 473 (27, 43, 90, (M − C$_8$H$_{11}$)$^+$]; GLC t_R = 49.8 min; yield 1.0 g (36%).

Anal. Calcd for C$_{45}$H$_{40}$: C, 93.06; H, 6.94. Found: C, 92.82; H, 7.04.

Reactions of HCl with *p*-Methoxyphenylacetylene (1c). In a 320-mL ampule were reacted 1.8 g (0.05 mol) of HCl and 6.6 g (0.05 mol) of **1c**[16] for 1 day. After evaporation of unreacted HCl there remained 7.0 g of a pink solid. ^{1}H NMR analysis showed only traces of **4c** (CH$_3$CCl$_2$ signal at δ 2.54) and mainly aromatic protons in the region of δ 6.53–7.88, along with the CH$_3$ signals of the *p*-methoxy groups at 3.73–3.85. GLC analysis (350 °C, isothermal) of the crude reaction product in dichloromethane showed two major peaks, corresponding to **16c** and **17c**, along with several minor peaks having shorter retention times. The peak of **20c** did not appear.

Isolation and Identification of 16c, 17c, and 20c. The crude product of the above reaction was separated by column chromatography (column 2.2 × 140 cm, 230 g of silica gel; solvent: benzene, benzene/dichloromethane in ratios of 20:1, 10:1, 5:1, and 1:1, dichloromethane, acetone, and methanol) to afford pure **16c** (1.17 g), **17c** (3.18 g), and **20c** (0.21 g), as well as 0.60 g of a dark-brown solid material. The ^{1}H NMR spectrum of the latter showed broad signals in the aromatic region (δ 5.93–7.73) and in the aliphatic region (δ 3.33–3.90). The total material recovered, i.e., **16c**, **17c**, **20c**, and the brown solid amounted to 72% of the crude reaction product.

1,3,5-Tris(*p*-methoxyphenyl)benzene (16c): colorless crystals; mp 145 °C (recrystallized from methanol); (lit.[17] mp 143 °C); ^{1}H NMR (60 MHz, CDCl$_3$, Me$_4$Si) δ 3.86 (s, 9 H), 7.00 and 7.63 (AA′BB′ system, J = 8.4 Hz, 12 H), 7.66 (s, 3 H); ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 55.45 (q, J = 144 Hz), 114.48 (d, J = 160.4 Hz), 124.04 (d, J = 157 Hz), 128.54 (d, J = 159 Hz), 134.08 (s), 142.12 (s), 159.58 (s); IR (KBr) 1620, 1520, 1470, 1450, 1305, 1295, 1265, 1245, 1190, 1040, 1030, 840, 835 cm^{-1}; MS, m/e (relative intensity) 398, 397, 396 [5, 31, 100, M$^+$], 381 [25, (M − CH$_3$)$^+$], 198 [13, (M/2)$^+$]; GLC t_R = 40.5 min; yield 1.17 g (18%).

7-Methoxy-1,3,9-tris(*p*-methoxyphenyl)-9-methylfluorene (17c): mp 190–192 °C (recrystallized from dichloromethane); ^{1}H

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NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.54, 3.74, 3.77, 3.80, 3.85 (s, 3 H, each), 6.60 and 6.66 (J = 8.8 Hz), 6.67 and 6.80 (J = 9.2 Hz), 6.99 and 7.63 (J = 9.2 Hz), (AA′BB′ systems, 4 H, each), 6.54 (d, J = 2.4 Hz, 1 H), 6.87 (dd, J = 8.4 and 2.4 Hz, 1 H), 7.17, 7.86 (d, J = 1.7 Hz, 1 H, each), 7.73 (d, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 23.00 (q, J = 127 Hz), 55.19, 55.23, 55.31, 55.36 (q, J = 142 Hz, each), 109.08, 113.03, 116.24, 121.20, 127.79 (d, J = 160 Hz, each), 112.58, 113.43, 114.60, 127.79 (d, J = 160 Hz, two-carbon intensity, each), 130.46 (d, J = 160 Hz, four-carbon intensity), 54.33, 131.77, 133.07, 133.66, 137.70, 139.89, 139.95, 141.14, 149.17, 157.65, 157.87, 158.35, 159.14, 160.06 (s, each); IR (KBr) 1605, 1505, 1460, 1270, 1245, 1175, 1025, 830, 820 cm^{-1}; MS, *m/e* (relative intensity) 530, 529, 528 (12, 45, 100, M^+), 513 [84 $(M - CH_3)^+$], 264 [9, $(M/2)^+$]; GLC t_R = 77.8 min; yield 3.18 g (48%).

Anal. Calcd for $C_{36}H_{32}O_4$: C, 81.79; H, 6.10. Found: C, 81.66; H, 6.17.

2,10-Dimethoxy-6,12,13a-tris(*p*-methoxyphenyl)-12-methylbenzo[6,7]cycloheptadieno[1,2,3-*jk*]fluorene (20c): mp 247 °C (recrystallized from dichloromethane); ^1H NMR (300 MHz, CD_2Cl_2, Me_4Si) δ 0.95, 3.15, 3.73, 3.75, 3.84, 3.88, (s, 3 H, each), 2.64, 2.98 (d, J = 13.8 Hz, 1 H, each), 6.59 and 6.66, 6.80 and 7.18, 6.99 and 7.64 (AA′BB′ systems, $J \approx 8.5$ Hz, 4 H, each), 5.80 (d, J = 2.2 Hz, 1 H), 6.55 (d, J = 8.5 Hz, 1 H), 6.72 and 6.78 (dd, J = 8.5 and 2.2 Hz, 1 H, each), 6.82 (d, J = 2.6 Hz, 1 H), 7.16 and 7.83 (d, J = 1.8 Hz, 1 H, each), 7.62 (d, J = 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 31.04 (q, J = 125 Hz), 55.01, 55.23, 55.30, 55.37, 55.69 (q, J = 140 Hz, each), 53.15 (t, J = 132 Hz), 108.01, 110.98, 114.18, 115.08, 115,85, 120.15, 125.31, 128.42 (d, J = 156 Hz, one-carbon intensity, each), 113.07, 113.54, 114.18, 128.01, 128.20, 130.51 (d, J = 156 Hz, two-carbon intensity, each), 51.79, 62.29, 131.00, 133.24, 133.64, 140.04, 140.09, 141.94, 142.00, 143.95, 147.58, 149.93, 156.43, 157.54, 158.44, 159.16, 159.42, 159.86 (s, each); IR (KBr) 3420, 3000, 2980, 2965, 2815, 1610, 1580, 1510, 1490, 1410, 1300, 1250, 1180, 1040, 880, 830, 580, 530 cm^{-1}; MS, *m/e* (relative intensity) 662, 661, 660 [8, 31, 64, M^+], 645 [8, $(M - CH_3)^+$], 537 [60, $(M - C_8H_{11}O)^+$] 330 [29, $(M/2)^+$], 323 (47), 268 (41), 166 (23), 121 (51), 91 (28), 44 (100); GLC $t_R \approx 150$ min (broad peak); yield 0.21 g (4%).

Anal. Calcd for $C_{45}H_{40}O_5$: C, 81.79; H, 6.10. Found: C, 81.72; H, 6.08.

Reactions of HCl with *p*-Fluorophenylacetylene (1d). In a 100-mL ampule were reacted 1.5 g (40 mmol) of HCl and 1.0 g (8 mmol) of **1d**[16] for 7 days. After evaporation of unreacted HCl, there remained 1.7 g of a dark green liquid. ^1H NMR analysis showed the presence of **4d** (CH_3 signal at δ 2.55) and **2d** (CH_2 signal at δ 5.4–5.7, ABX system) in a molar ratio of 17:1. The intensity of the signals in the aromatic region (δ 6.8–7.9) was 11% in excess over that expected on the basis of the CH_3 and CH_2 signals of **4d** and **2d**, respectively. GLC analysis of the crude reaction product in dichloromethane showed one major peak, corresponding to **4d**, and two very small peaks, corresponding to **16d** and **17d**, respectively.

In a 200-mL ampule were reacted 3.0 g (83 mmol) of HCl and 2.0 g (17 mmol) of **1d** for 14 days. After evaporation of unreacted HCl, there remained 3.5 g of a dark green liquid. ^1H NMR analysis showed the presence of **4d** and of **2d** in a molar ratio of 16:1. The intensity of the signals in the aromatic region (δ 6.7–7.9) was 31% in excess over that expected on the basis of the CH_3 and CH_2 signals of **4d** and **2d**, respectively.

In a 320-mL ampule were reacted 6.7 g (180 mmol) of HCl and 4.5 g (38 mmol) of **1d** for 85 days. After evaporation of unreated HCl, there remained 5.4 g of a highly viscous dark brown liquid. ^1H NMR analysis showed the presence of **4d** in 15%. The intensity of the signals in the aromatic region was 85% in excess over that expected for **4d**.

In a 320-mL ampule was reacted a mixture of 4.5 g (125 mmol) of HCl, 3.0 g (25 mmol) of **1d**, and 0.33 g (2.5 mmol) of zinc chloride for 7 days. After evaporation of unreacted HCl, there remained 3.3 g of a dark brown solid. ^1H NMR analysis indicated only traces of **4d** and mainly aromatic protons. GLC analysis (150–350 °C at 10 °C/min) of the crude reaction product in dichloromethane showed two major peaks, corresponding to **16d** and **17d**, along with several minor peaks, including that of **20d**.

Isolation and Identification of 16d, 17d, and 20d. (a) The crude product (3.3 g) from the $ZnCl_2$-catalyzed reaction was separated by column chromatography (column 2.2 × 60 cm, 100 g of silica gel; solvent: 5% tetrachloromethane, 5% benzene, and 90% *n*-hexane) to afford mixtures of **16d** and **17d** and of **16d** and **20d**. Further elution with benzene afforded 450 mg of a yellow solid material. The ^1H NMR spectrum of the latter showed broad signals in the aromatic region. Pure **16d** (1260 mg), **17d** (700 mg), and **20d** (205 mg) were obtained by successive fractional crystallization of the above mixtures of **16d/17d** and **16d/20d** from chloroform and from methanol. The combined yields of pure **16d**, **17d**, and **20d**, as well as the yellow solid, amounted to 79% of the crude reaction product.

(b) Similar separation of the crude product (5.4 g) obtained from the noncatalyzed reaction after 85 days gave **16d** (400 mg), **17d** (40 mg), **20d** (20 mg), and a yellow solid (1500 mg). This amounted only to 36% of the crude reaction product.

1,3,5-Tris(*p*-fluorophenyl)benzene (16d): mp 238 °C (recrystallized from chloroform); (lit.[14] mp 238 °C); ^1H NMR (60 MHz, $CDCl_3$, Me_4Si) δ 7.16 and 7.65 (AA′BB′X system, J = 8.8, 8.2, and 5.4 Hz, 12 H), 7.66 (s, 3 H); ^{13}C NMR (DMF-d_7, Me_4Si, broad band decoupled) δ 116.42 (d, J = 21.6 Hz), 125.32, 130.16 (d, J = 8.3 Hz), 137.84 (d, J = 3.2 Hz), 142.00 (s), 163.57 (d, J = 245 Hz); ^{19}F NMR (DMF-d_7, $CFCl_3$) δ −115.79 (tt, J = 8.8 and 5.4 Hz); IR (KBr) 3440, 1605, 1500, 1450, 1390, 1225, 1160, 840, 820 cm^{-1}; MS, *m/e* (relative intensity) 361, 360 (30, 100, M^+), 338 (9); GLC t_R = 18.7 min; yield 1.26 g (42%).

7-Fluoro-1,3,9-tris(*p*-fluorophenyl)-9-methylfluorene (17d): mp 181 °C (recrystallized from methanol); ^1H NMR (300 MHz, CD_2Cl_2, Me_4Si) δ 1.56 (s, 3 H), 6.64 and 6.80 (partly overlapping AA′BB′X systems, 8 H),[18] 7.15 and 7.66 (AA′BB′X system, 4 H),[18] 6.70 (dd, J = 9.3 and 2.4 Hz, 1 H), 7.06 (ddd, J = 9.3, 8.4, and 2.4 Hz, 1 H), 7.21, 7.96 (d, J = 1.7 Hz, 1 H, each), 7.82 (dd, J = 8.4 and 5.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si, broad and decoupled) δ 22.92, 54.51, 117.47, 128.58, 139.49, 139.96, 140.49, 149.50 (s, each), 111.05, 114.05 (one-carbon intensity, each), 114.21, 115.00, 115.72 (d, $J \approx 22$ Hz, two-carbon intensity, each), 121.27, 157.49 (one-carbon intensity, each), 128.28 (two-carbon intensity), 130.87 (four-carbon intensity), (d, J = 7.4 Hz, each), 134.40, 135.77, 136.78, 140.08 (d, $J \approx 3$ Hz, each), 161.56, 161.95, 162.63, 163.19 (d, J = 246 Hz, each); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ −113.5 (dt, J = 8.9 and 5.1 Hz), −115.8 (tt, J = 8.8 and 5.1 Hz), −115.9 (tt, J = 8.8 and 5.1 Hz), −117.0 (tt, J = 6.8 and 6.8 Hz); IR (KBr) 3420, 2970, 2960, 1890, 1605, 1590, 1505, 1480, 1460, 1410, 1260, 1230, 1160, 1110, 920, 865, 830, 810, 790, 750, 550, 530 cm^{-1}; MS, *m/e* (relative intensity) 482, 481, 480 (7, 36, 100, M^+) 467, 466, 465 [5, 33, 97, $(M - CH_3)^+$], 385 [14, $(M - C_6H_4F)^+$], 370 [11, $(M - C_6H_4F - CH_3)^+$], 95 [30, $(C_6H_4F)^+$]; GLC t_R = 21.5 min; yield 0.7 g (23%).

Anal. Calcd for $C_{32}H_{20}F_4$: C, 79.99; H, 4.20; F, 15.81. Found: C, 80.14; H, 4.21; F, 15.66.

2,10-Difluoro-6,12,13a-tris(*p*-fluorophenyl)-12-methylbenzo[6,7]cycloheptadieno[1,2,3-*jk*]fluorene (20d): mp 252 °C (recrystallized from methanol); ^1H NMR (300 MHz, CD_2Cl_2, Me_4Si) δ 0.96 (s, 3 H), 2.96 and 3.00 (AB system, J = 14.0 Hz, 2 H), 6.69 and 6.87, 7.00 and 7.16, 7.17 and 7.67 (AA′BB′X systems, 4 H, each),[18] 5.83 (dd, J = 9.3 and 2.3 Hz, 1 H), 6.63 (dd, J = 7.5 and 5.2 Hz, 1 H), 6.94 (ddd, J = 9.0, 8.5, and 2.0 Hz, 2 H), 6.99 (dd, J = 8.8 and 1.6 Hz, 1 H), 7.23, 7.91 (d, J = 1.7 Hz, 1 H, each), 7.71 (dd, J = 8.5 and 5.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si, broad-band decoupled) δ 30.94, 51.86, 53.20, 62.18, 117.17, 129.46, 139.62, 140.18, 141.28, 147.68 (s, each), 111.87, 112.83, 114.44, 115.50 (one-carbon intensity, each), 114.68, 115.22, 115.78 (d, J = 20.4 Hz, two-carbon intensity, each), 120.54, 125.88, 150.57, 155.88 (one-carbon intensity, each), 128.80 (two-carbon intensity), 128.14 (four-carbon intensity) (d, J = 8.3 Hz, each), 134.05, 135.97, 136.69, 144.11, 146.13 (d, $J \approx 3.0$ Hz, each), 161.29, 162.01, 162.67, 162.92 (two-carbon intensity) (d, J = 246 Hz, each); ^{19}F NMR ($CDCl_3$, $CFCl_3$) δ −113.17 (dt, J = 9.2 and 5.1 Hz), −115.30 (dt, J = 8.8 and 5.4 Hz), −115.71 (tt, J = 8.5 and 5.6 Hz), −115.79 (tt, J = 8.3 and 5.5 Hz), −117.46 (tt, J = 8.0 and 5.5 Hz); IR (KBr) 3420, 2920, 1605, 1590, 1505, 1480, 1230, 1210, 1160, 830 cm^{-1}; MS, *m/e* (relative intensity) 602, 601, 600 (6, 26, 58, M^+), 585 [7, $(M - CH_3)^+$], 491, 490, 489 [26, 41, 100, $(M - C_7H_8F)^+$]; GLC t_R = 36.9 min; yield 0.2 g (6.8%).

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[18] Due to overlap of signals, the coupling constants could not be obtained.

Anal. Calcd for $C_{40}H_{25}F_5$: C, 79.99; H, 4.20; F, 15.81. Found: C, 79.95; H, 4.15; F, 15.96.

Reaction of HCl with 1,1-Dichloro-1-(*p*-methylphenyl)ethane (4b). In a 200-mL ampule were reacted 2.7 g (75 mmol) of HCl and 4.7 g (25 mmol) of **4b** for 4 days. After evaporation of the HCl, there remained 3.0 g of a dark blue solid. The crude product was separated by column chromatography (column and conditions as above) to yield **16b** (650 mg, 22%), **17b** (900 mg, 31%), and **20b** (1000 mg, 35%).

Reaction of HCl with 1-Chloro-1-(*p*-methylphenyl)ethylene (2b). In a 200-mL ampule were reacted 3.6 g (100 mmol) of HCl and 3.8 g (25 mmol) of **2b** for 4 days. After evaporation of the HCl, there remained 3.8 g of a dark blue solid. The crude product was separated by column chromatography (column 2.2 × 60 cm, 100 g of silica gel; solvent: 5% tetrachloromethane, 5% benzene, 90% *n*-hexane) to yield **16b** (350 mg, 12%), **17b** (400 mg, 14%), and **20b** (500 mg, 17%).

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Registry No. 1a, 536-74-3; **1b**, 766-97-2; **1c**, 768-60-5; **1d**, 766-98-3; **2a**, 618-34-8; **2b**, 42107-37-9; **2d**, 83313-74-0; **4a**, 3141-41-1; **4b**, 65114-80-9; **4c**, 69151-26-4; **4d**, 66228-21-5; **15a**, 83313-75-1; **16a**, 612-71-5; **16b**, 50446-43-0; **16c**, 7509-20-8; **16d**, 448-60-2; **17a**, 83313-76-2; **17b**, 83313-77-3; **17c**, 83313-78-4; **17d**, 83313-79-5; **18a**, 10229-33-1; **19a**, 83313-80-8; **20a**, 83313-81-9; **20b**, 83313-82-0; **20c**, 83313-83-1; **20d**, 83313-84-2; HCl, 7647-01-0; 3-methyl-3-phenyl-1-indanone, 26466-19-3; 1,3,9-triphenyl-9-fluorenol, 83313-85-3; 1,3,9-triphenyl-9-chlorofluorene, 83313-86-4.

Transmission of Substituent Effects through Unsaturated Systems. 5.[1] Brønsted and Lewis Basicities of β-Substituted α,β-Unsaturated Ketones

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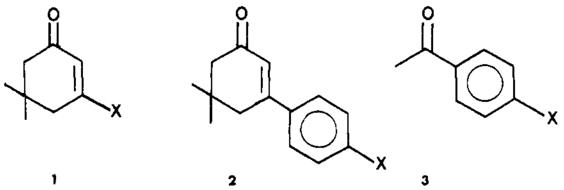
pK_{BH^+} values and enthalpies of complexation, $\Delta H°$, with boron trifluoride of a series of 16 3-substituted 5,5-dimethylcyclohex-2-en-1-ones are well correlated with σ_p^+ and σ_I,σ_R^+ constants. These compounds are therefore good models for the investigation of substituent effects on the reactivity of ethylenic systems directly substituted on the double bond. Comparisons with linear free energy relationships obtained from para-substituted 3-phenylcyclohexenones and para-substituted acetophenones allow us to evaluate the transmission factors of ethylene and phenylene groups. New σ_p^+ substituent constants are computed. Ab initio π-electron densities at the oxygen atom of the carbonyl group reproduce well the variations of Brønsted and Lewis basicities of 3-substituted cyclohexenones.

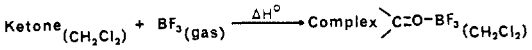
In the course of our study of substituent effects in nonaromatic systems,[2,3] we recently attempted to use the 5,5-dimethylcyclohex-2-en-1-one structure (1, Chart I) as a model compound to investigate the transmission of electronic substituent effects through a directly substituted ethylenic bond. We established the applicability of the classical substituent constants to describe some physical parameters of ground-state molecules such as ^1H and ^{13}C nuclear magnetic shielding constants[4] or infrared frequency ($\nu_{C=O}$).[5] However, some secondary effects peculiar to these spectral parameters (magnetic anisotropy effect, van der Waals steric effect, Fermi resonance and vibrational coupling effects, ...) led to only fair linear Hammett-type relationships. The next step, presented here, is to look for the applicability of Hammett-style equations to the energy differences linked to the basicity of the carbonyl function. Thus, we examine the substituent effects on pK_{BH^+} (Brønsted basicity) and the enthalpy of complex formation, $\Delta H°$ (Lewis basicity),[6] of these α-enones with boron trifluoride. This investigation may allow us (i) to test accurately the validity of mono- and multiparameter scales of substituent constants applied to this unsaturated framework, (ii) to compare the transmission factors of

Chart I



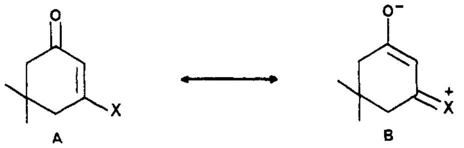
1 2 3

Scheme I



$$\text{Ketone}_{(CH_2Cl_2)} + BF_{3(gas)} \xrightarrow{\Delta H°} \text{Complex} \; {>}C{=}O{-}BF_{3(CH_2Cl_2)}$$

Scheme II



A B

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[5] Azzaro, M.; Gal, J. F.; Geribaldi, S.; Novo-Kremer, N. *Spectrochim. Acta, Part A* **1978**, *34A*, 225.

[6] Azzaro, M.; Gal, J. F.; Geribaldi, S.; Grec-Luciano, A.; Calleri, C. *J. Chem. Res., Synop.* **1979**, 134. For series 3 DSP analysis gives ρ_I = −1.26 and ρ_R^+ = −1.15 and gives ρ_I = 10.48 and ρ_R^+ = 10.49, respectively, from pK_{BH^+} and $\Delta H°$.

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