Friedel–Crafts Alkylations with Vinyl Halides.[1] Vinyl Cations and Spirobiindans

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Alkylation of toluene with 1-bromo-1-phenylethene (**1**, α-bromostyrene) in the presence of Al_2Br_6 produced 1-phenyl-1-*p*-tolylethene (**4a**) and minor amounts of phenylacetylene (**2**) and acetophenone (**3**). Reaction of **2** with toluene and Al_2Br_6 gave a low yield of 1-phenyl-1-*o*-tolylethene (**4b**) and a trace of **1**. Reaction of **2** with toluene and 100% H_3PO_4 gave **3** (mainly) and **4a** and **4b**. Reaction of **2** with anisole and 100% H_3PO_4 gave 1-phenyl-1-*p*-anisylethene (**4c**), 1-phenyl-1-*o*-anisylethene (**4d**), and **3**. Extended reactions of both **1** and **2** with toluene and anisole give polymeric products; **4c** was shown to polymerize faster than **4d**. The vinyl cation $C_6H_5C^+{=}CH_2$ is a presumed intermediate in these reactions. The major product from the reaction of benzene with 2-bromopropene in the presence of aluminum bromide is 2,2-diphenylpropane (**12a**). Minor products include 3,3,3′,3′-tetramethyl-1,1′-spirobiindan (**21a**), 1,1,3-trimethyl-3-phenylindan (**14a**), and 1,1,3-trimethylindene (**16a**). The corresponding products are formed from toluene. The key intermediates to all of these products are the 2-arylpropene (**10a**) and the 2-aryl-2-propyl cation (**11a**) produced from it by proton addition. Results of the earlier work in which the production of 1,1′-spirobiindans has been observed are correlated in terms of the mechanisms outlined.

1-Bromo-1-phenylethene. Depending on the catalyst and the conditions used, vinyl halides may react either at the double bond or at both the double bond and the halide sites.[2-4] Yuldashev and Tsukervanik[3] found that treatment of vinyl halides in benzene with BF_3–H_3PO_4 gave the corresponding phenylalkyl halides, whereas using $AlCl_3$ gave products resulting from reaction at both the double bond and the halide site. However, they reported that 1-bromo-1-phenylethene (**1**, α-bromostyrene) did not react with benzene in the presence of either $AlCl_3$ or BF_3–H_3PO_4 catalysts. They concluded that substitution of vinyl halides at the α position with alkyl or particularly aryl groups diminishes the reactivity of the double bond in alkylation reactions.

We investigated the reaction of 1-bromo-1-phenylethene (**1**) with toluene in the presence of Al_2Br_6 catalyst with the main interest of examining the possibility of a vinyl cation intermediate. Surprisingly, we found that **1** condensed rapidly with toluene in the presence of Al_2Br_6 to give mainly 1-phenyl-1-*p*-tolylethene (**4a**), besides small amounts of acetophenone (**3**) and phenylacetylene (**2**). The reaction was very fast and **4a** was detected by GLC as the main product after 3 min. At longer reaction times compound **4a** polymerized to higher boiling materials, as will be discussed later.

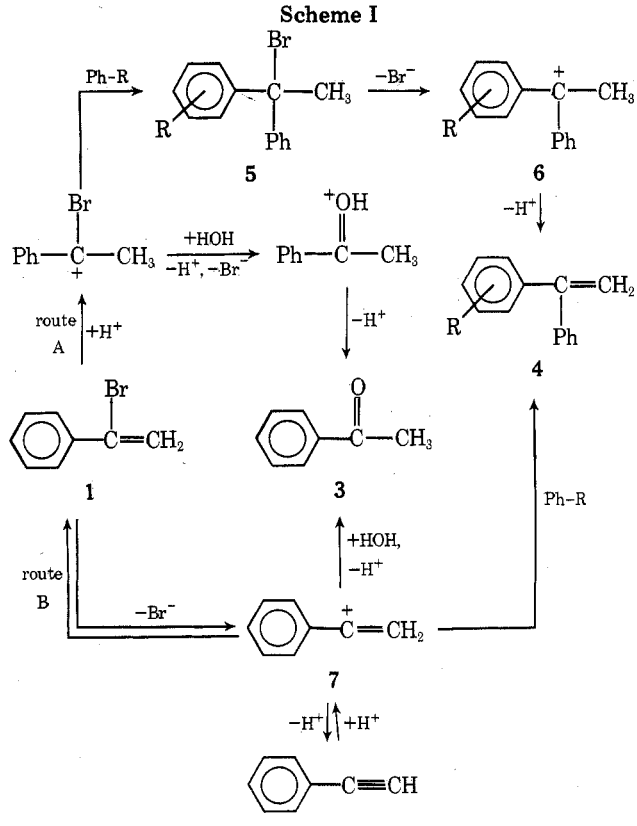
At least two mechanisms may account for these results. The first mechanism (route A of Scheme I) involves reaction at the double bond by addition of a proton or the Lewis acid catalyst to give a fairly stable cation, which either reacts with water to give acetophenone (**3**) or with toluene to give 1-phenyl-1-tolyl-1-bromoethane **5**. Compound **5** was not isolated, but it would be expected to react further in the presence of the catalyst to give a very stable cation (**6**) which then gives **4**. Further alkylation with **6** to give a triarylethane is unlikely owing to steric effects. Even if such alkylation took place, a dealkylation is likely to occur. This latter possibility was ruled out since no compound such as 1,1-ditolylethene was detected among the products.

The second mechanism (route B of Scheme I) involves direct ionization of **1** to a phenylvinyl cation **7** which either reacts with water to give acetophenone (**3**) or with the solvent to give 1-phenyl-1-tolylethene (**4**). Loss of a proton from **7** gives phenylacetylene (**2**).

To gain more insight on the possibility of vinyl cation intermediates in the course of Friedel–Crafts alkylation, the reaction of phenylacetylene with aromatic hydrocarbons in the presence of a protonic catalyst was studied. The catalyzed hydration of substituted phenylacetylenes in aqueous acidic solvents to give substituted acetophenones was shown to involve a rate-determining proton transfer to give arylvinyl cation intermediates.[5,6] This conclusion was supported by a large increase in the rate of the reaction produced by electron-releasing substituents on the benzene ring and a large negative ρ value. A large kinetic isotope effect, k H_2SO_4/k D_2SO_4, of 2.98 for phenylacetylene was obtained, consistent with a rate-determining proton transfer. Phenylacetylene was reported to condense with anisole in the presence of $AlCl_3$ to give (16%) 1-*p*-anisyl-1-phenylethene (**4c**) among other products.[7]

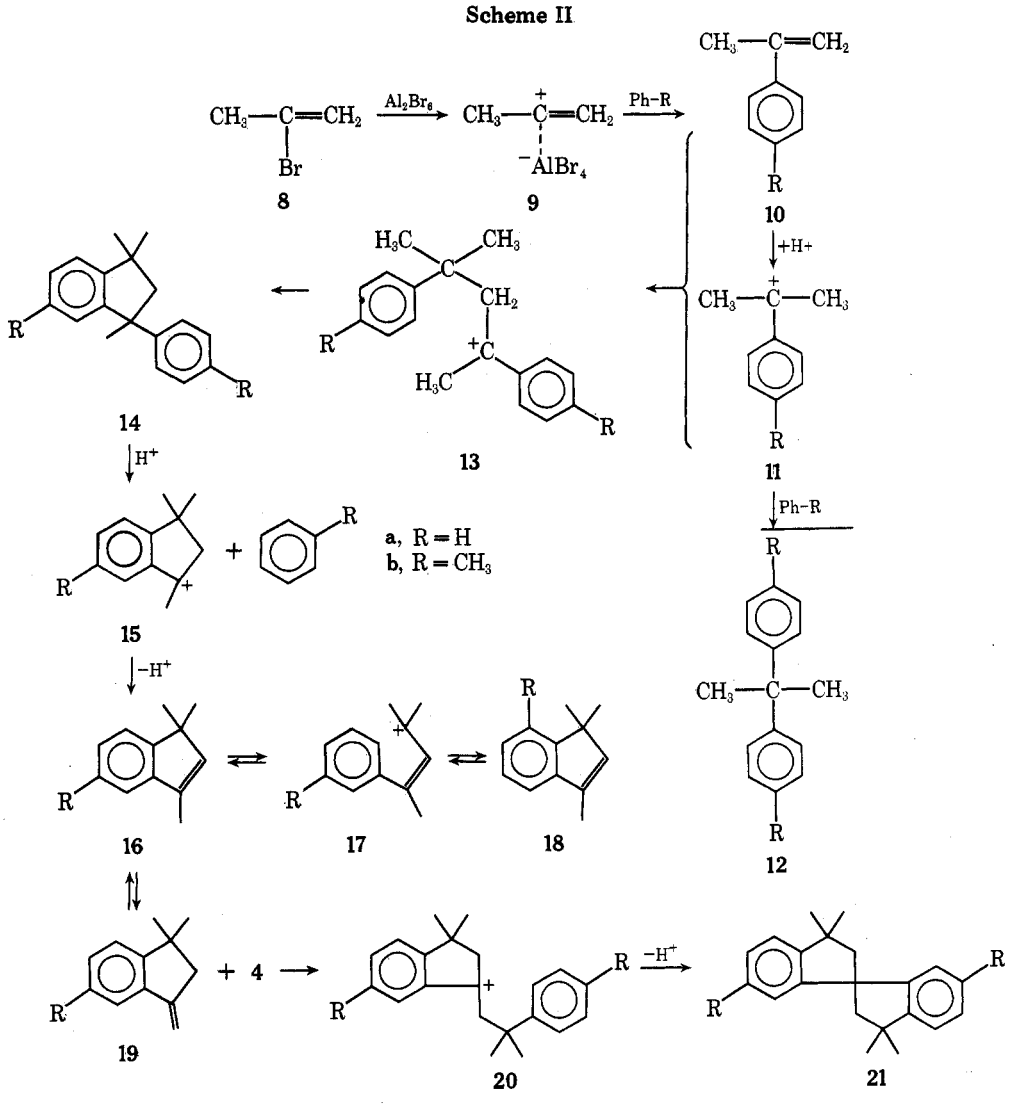
In the presence of BF_3–H_3PO_4, phenylacetylene was reported to condense with toluene to give 1-phenyl-1-tolyleth-

Scheme I



a, R = *p*-Me
b, R = *o*-Me
c, R = *p*-OMe
d, R = *o*-OMe

Scheme II



ene.[8] Phosphoric acid alone was used as catalyst in this investigation because the only way it could catalyze the reaction of phenylacetylene would be through proton addition to the triple bond to produce a vinyl cation. Phenylacetylene reacted with toluene in the presence of H_3PO_4 to produce 40% acetophenone (**3**), 7% 1-phenyl-1-*p*-tolylethene (**4a**), and 5% 1-phenyl-1-*o*-tolylethene (**4b**). Treatment of phenylacetylene with anisole and H_3PO_4 gave 25% acetophenone (**3**), 14% 1-*p*-anisyl-1-phenylethene (**4c**), and 12% 1-*o*-anisyl-1-phenylethene (**4d**). When Al_2Br_6 was used as catalyst in the presence of toluene, 1-bromo-1-phenylethene (**1**) was formed besides **4b**. The fact that **1** reacts with toluene and Al_2Br_6 to give **2** and **4** and that **2** reacts with toluene and Al_2Br_6 to give **1** and **4** suggests that the vinyl cation **7** is a reasonable common intermediate, but it does not necessarily rule out route A as an alternative pathway from **1** to **4**.

In the reaction of phenylacetylene with toluene, the ratio of alkylation to acetophenone formation was 12:40, whereas in the reaction with anisole it was 25:26. This probably reflects the higher reactivity of anisole toward electrophilic attack by the phenylvinyl cation, **7**.

It was surprising to find a high ratio of ortho-alkylation product. We suspected that the para isomers were formed initially in higher ratios, but they then polymerized at higher rates than the ortho isomers. The relative rates of formation and polymerization of both isomers (Table I) show that at the shortest reaction time the para isomer was formed more than twice as fast as the ortho isomer. At longer reaction times the percentage of the para isomer decreased, and after 30 min, almost equal amounts of both isomers were detected. Finally, after about 5 h, both isomers disappeared with the formation of polymeric materials.

The failure of Yuldashev and Tsukervanik[3] to obtain alkylation of benzene with 1-bromo-1-phenylethene may be attributed to two causes, the first of which is polymerization of the initial product, 1,1-diphenylethene. Secondly, the type of products they found from the other vinyl halides and arenes with $AlCl_3$ catalyst—those due to reaction at both the double bond and the halide site—were not formed because of the steric hindrance to introducing three aromatic rings on one carbon atom.

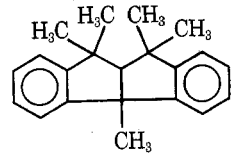
2-Bromopropene. The reactions of 2-bromopropene follow the general behavior of vinyl halides in that the major products are those resulting from reaction of both functional groups (double bond and halide).[3] However, the minor products of the reactions are very interesting and deserving of comment.

The major product of the reaction of 2-bromopropene (**8**) with benzene in the presence of Al_2Br_6 was 2,2-diphenylpropane (**12a**, Scheme II). Minor products were 1,1,3-trimethyl-3-phenylindan (**14a**), 1,1,3-trimethylindene (**16a**), and 3,3,3′,3′-tetramethyl-1,1′-spirobiindan (**21a**). Compound **21a** has a fascinating history. It was first reported by Hoffman[13] as a hydrocarbon of unknown structure from the reaction of 4-methyl-4-phenyl-2-pentanone with anhydrous $ZnCl_2$. The structure **22** was later assigned to the hydrocarbon by Barnes and Beitchman[14] on the basis of their investigations of similar reactions. This formula was accepted as correct for the product

Table I. Relative Concentrations of 1-*o*-Anisyl-1-phenylethene (4d) and 1-*p*-Anisyl-1-phenylethene (4c) Produced in the Presence of 100% H_3PO_4

Time, min	4d, wt %	4c, wt %
5	31	69
15	49	51
30	55	45
45	64	36
60	80	20
150	100	
300	Trace	

obtained from treatment of the "saturated dimer of α-methylstyrene" (1,1,3-trimethyl-3-phenylindan, **14a**) with $AlCl_3$ at 100 °C,[15] for the product obtained from methylacetylene and benzene in the presence of $AlCl_3$ and from treatment of α-methylstyrene (**10a**) with $AlCl_3$,[16] and for the product from reaction of cumene with nitrosonium hexafluorophosphate.[17]



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However, in 1962 Curtis and Lewis[18] demonstrated by NMR studies that the product obtained from all of these reactions was indeed the 1,1′-spirobiindan of structure **21a.** Barclay and Chapman[19] came to the same conclusion, and they proposed a mechanism for the formation of **21a** from 1,1,3-trimethylindene (**16a**) and the carbonium ion **11a** corresponding to the last three steps of Scheme II. The mechanism was supported by their demonstration of the production of **21a** from **16a** and α-methylstyrene (**10a**) in sulfuric acid and of two other new polyalkyl-1,1′-spirobiindans by analogous reactions.

Our contribution to the history of the 1,1′-spirobiindan **21a** consists of the first demonstration of its production from 2-bromopropene and benzene. Although it was not isolated in this experiment, 2-phenylpropene (α-methylstyrene, **10a**) is undoubtedly the initial product from these starting materials, and the rest of the steps in the formation of **21a** follow as outlined in Scheme II. 2-*p*-Tolylpropene (**10b**) was observed among the products from 2-bromopropene and toluene in the presence of aluminum chloride (vide infra). The other products (**12a, 14a,** and **16a**) also fit logically into this scheme. The formation of **21a** in each of the reactions reported in ref 15–17 is also reasonably explained in terms of Scheme II. (Methylacetylene and benzene give α-methylstyrene as one product.[16])

The 1,1′-spirobiindan (**21a**) was isolated in crystalline form only after separation from other products by vacuum distillation and preparative gas chromatography. However, in the work-up of the reaction mixture from 2-bromopropene, toluene, and Al_2Br_6, when the excess toluene was removed by distillation, the residue contained a mass of crystals. This was 3,3,6,3′,3′,6′-hexamethyl-1,1′-spirobiindan (**21b**). This compound had also been identified incorrectly earlier[14] as a homologue of **22,** but the correct structure was established at the same time as that of **21a.**[18] As in the reaction with benzene, the major product of the reaction of 2-bromopropene with toluene was the 2,2-diarylpropane, in this case 2,2-di-*p*-tolylpropane (**12b**), and the other corresponding minor products, 1,1,3,5-tetramethyl-3-*p*-tolylindan (**14b**) and 1,1,3,5-tetramethylindene (**16b**) were observed. An additional product was observed which gave a GLC peak very close to that of **16b** and had an NMR spectrum almost identical with that of **16b** except in the aromatic proton region. It is assumed to be 1,1,3,7-tetramethylindene (**18b**), which is formed from **16b** by a facile dealkylation–realkylation via the stable tertiary allylic cation **17b.**

One experiment was carried out using aluminum chloride as catalyst for the reaction of 2-bromopropene with toluene. The major product was 2,2-di-*p*-tolylpropane (**12b**), as with Al_2Br_6 catalyst, and the minor products **14b, 16b,** and **18b** were observed. An interesting difference in the results was the isolation of 2-*p*-tolylpropene, which was not identified among the products of the Al_2Br_6-catalyzed reaction, and the failure to isolate any 1,1′-spirobiindan (**21b**).

Barclay and Chapman[19] commented on the interesting NMR spectrum of **21a** and rationalized it in terms of the space relationships imposed by the rigid spirane structure. We found the NMR spectrum of **21b** also interesting, although it was highly perplexing at first. In CCl_4 solution the spectrum was surprisingly simple, consisting of five sharp singlets (Experimental Section). The two six-proton signals at 1.30 and 1.37 ppm could be assigned to two sets of equivalent methyl groups (at the 3,3′ positions), and the two singlets in the aromatic regions, two protons at 6.49 and four protons at 6.92 ppm, could be assigned in the same way as the corresponding ones in **21a** were assigned by Barclay and Chapman[19] (to the 7,7′ and 4,5,4′,5′ positions), but the ten-proton singlet at 2.24 ppm defied assignment. However, when the NMR spectrum was determined in pyridine solution, the signal at 2.24 ppm was separated into two singlets at 2.16 (6 H, 6,6′-$ArCH_3$'s) and 2.32 ppm (4 H, 2,2′-CH_2's). It was indeed surprising that the methylene hydrogens at the 2 and 2′ positions would give the same signal as the methyl groups at the 6 and 6′ positions in CCl_4 solution.

Experimental Section

Mass spectra were recorded on a Du Pont 21-491 spectrometer. ^1H NMR spectra were obtained using a Varian A-60 or HA-100 spectrometer, or a Perkin-Elmer R-12 spectrometer, in CCl_4 solution unless specified otherwise; results are expressed in parts per million downfield from internal Me_4Si (δ). Ir spectra were recorded on a Beckman IR-5A instrument.

Anhydrous aluminum bromide was prepared from aluminum, 30 mesh (50 g), and bromine (60 ml).[9]

1-Bromo-1-phenylethene (1) was prepared according to the procedure of Dufraisse[10] using phenylacetylene (0.147 mol) in glacial acetic acid (100 ml) and hydrogen bromide (0.118 mol) at 0 °C, bp 63 °C (2.5 mm).

Treatment of 1-Bromo-1-phenylethene (1) with Al_2Br_6 in Toluene. Freshly distilled Al_2Br_6 (3.0 g, 5.5 mmol) was dissolved in toluene (20 ml, 200 mmol). 1-Bromo-1-phenylethene (1, 3.0 g, 17 mmol) was added slowly during 5 min while stirring at room temperature for 30 min. Heat was evolved and the solution turned red. The usual workup with dilute HCl followed by vacuum distillation gave 1.2 g of an oil, bp 133–150 °C (2.5 mm), which was separated by preparative GLC (10-ft column, 10% SE-30 at 200 °C) and was found to be (4%) phenylacetylene (**2**), (8%) acetophenone (**3**), and (88%) 1-phenyl-1-*p*-tolylethene (**4a**):[11] mass spectrum *m/e* 194; NMR δ 2.28 (s, 3 H, $ArCH_3$), 5.31 (broad singlet, 2 H, C=CH_2, 7.04 (d, 4 H, ArH), and 7.2 ppm (s, 5 H, ArH). The yield of **4a** was 35% based on **1.**

Treatment of Phenylacetylene (2) with Al_2Br_6 in Toluene. Phenylacetylene (**2,** 4.2 g, 41 mmol) was dissolved in toluene (40 ml) and the solution was added dropwise into a cold solution (0 °C) of Al_2Br_6 (0.95 mmol) in toluene (50 ml). The mixture was stirred at 0 °C for 5 h. Regular workup with dilute HCl gave 4 g of a viscous oil. Vacuum distillation gave 0.2 g of an oil, bp 112–140 °C (0.05 mm). The overall yield was estimated to be about 5% of a mixture which was separated by preparative GLC and consisted of (10%) 1-bromo-1-phenylethene (1), mass spectrum *m/e* 182 (100%), 183 (13%), and 184 (99%), NMR δ 5.96 (d, 1 H, J = 1 Hz), 6.05 (d, 1 H, J = 1 Hz), and 7.1–8 ppm (m, 5 H), and (85%) 1-phenyl-1-*o*-tolylethene (**4b**), mass spectrum *m/e* 194, NMR (CS_2) δ 1.99 (s, 3 H, $ArCH_3$), 5.08 (d, 1 H, J = 2 Hz, C=CH), 5.65 (d, 1 H, J = 2 Hz, C=CH), 7.08 (s, 4 H, ArH), and 7.13 ppm (s, 5 H, ArH).

Treatment of Phenylacetylene (2) in Toluene with H_3PO_4. Anhydrous phosphoric acid was prepared[12] by dissolving 75% of P_2O_5 in 100 g of orthophosphoric acid. The reaction was carried out by

stirring phenylacetylene (**2**, 4.2 g, 41 mmol), toluene (50 ml), and anhydrous H_3PO_4 (10 ml) at 75–80 °C for 8 h. The mixture was worked up with water, extracted with ether, washed with water and 10% Na_2CO_3 solution, and then dried over anhydrous $MgSO_4$. Vacuum distillation gave two fractions: (1) bp 102–103 °C (12 mm), 2 g, and (2) bp 118–125 °C (0.05 mm), 0.4 g. The first fraction was mainly acetophenone (**3**) (40% yield) while the second fraction consisted of a mixture of (5%) 1-phenyl-1-*o*-tolylethene (**4b**) and (7%) 1-phenyl-1-*p*-tolylethene (**4a**).

Treatment of Phenylacetylene (2) in Anisole with H_3PO_4. Phenylacetylene (4.2 g, 41 mmol), anisole (50 ml), and 100% H_3PO_4 (5 ml) were heated at 75–80 °C with vigorous stirring for 9 h. Regular workup as before gave mostly polymeric material with traces of acetophenone (**3**) and 1-anisyl-1-phenylethene. The reaction was repeated, but with only a 30-min reaction period, to give (25%) acetophenone (**3**), (12%) 1-*o*-anisyl-1-phenylethene (**4d**), mass spectrum *m/e* 210, NMR δ 3.56 (s, 3 H, OCH_3), 5.20 (d, 1 H, J = 2 Hz, C=CH), 5.58 (d, 1 H, J = 2 Hz, CCH), and 6.8–7.16 ppm (singlet with multiplet at base, 9 H, ArH), and (14%) 1-*p*-anisyl-1-phenylethene (**4c**), mp 74–75 °C (ethanol) (lit.[7] 75–76 °C), mass spectrum *m/e* 210, NMR δ 3.70 (s, 3 H, OCH_3), 5.28 (q, AB system, 2 H, CCH_2), 6.6–7.2 (an AA'BB' system, 4 H, ArH), and 7.22 ppm (s, 5 H, ArH).

Relative Rates of Formation of 1-*o*-Anisyl-1-phenylethene (4d) and 1-*p*-Anisyl-1-phenylethene (4c). Phenylacetylene (**2**, 4.2 g, 41 mmol), anisole (50 ml), and 100% H_3PO_4 (5 ml) were heated at 75–80 °C with vigorous stirring; samples were withdrawn at different intervals and worked up as usual, then analyzed by GLC, and the relative concentrations of **4d** and **4c** were calculated from the corresponding peak areas. The GLC column was 5 ft × 0.125 in., 10% SE-30, used at 150 °C with nitrogen at 10 psi. The results are summarized in Table I.

Alkylation of Benzene with 2-Bromopropene. Anhydrous Al_2Br_6 (2 g, 3.8 mmol) was distilled into a 250-ml flask; 90 ml of benzene was added and the mixture was stirred at room temperature until all the Al_2Br_6 was dissolved. 2-Bromopropene (4.5 g, 37 mmol) was added dropwise during 5 min and stirring was continued for 3 h. The usual workup with ice and water followed by distillation under reduced pressure gave 4.2 g of crude product, bp 96 °C (10 mm)–133 °C (1 mm). This mixture was separated by preparative GLC using a Wilkens A-700 (Autoprep) instrument with 6 ft × 0.25 in. column containing 10% SE-30 on 60–80 mesh firebrick, He carrier gas. The approximate composition was 10% 1,1,3-trimethylindene (**16a**),[15] mass spectrum *m/e* 158, NMR (CCl_4) δ 1.25 [s, 6 H, $C_1(CH_3)_2$], 2.05 (broad d, 3 H, C_3CH_3), 5.90 (m, 1 H, $=C_2H$), and 7.10 ppm (s, 4 H, ArH); 78% 2,2-diphenylpropane (**12a**), mass spectrum *m/e* 196, NMR (CCl_4) δ 1.63 [s, 6 H, $C_2(CH_3)_2$] and 7.12 ppm (s, 10 H, ArH); 8% 1,1,3-trimethyl-3-phenylindan (**14a**),[15] mass spectrum *m/e* 236, NMR (CCl_4) δ 1.02 (s, 3 H, C_3CH_3), 1.32 (s, 3 H, C_3CH_3), 1.67 (s, 3 H, C_1CH_3), 2.30 (two d, AB, 2 H, J = 13 Hz, C_2H_2), and 7.10 ppm (two s, 9 H, ArH); and 4% 3,3,3',3'-tetramethyl-1,1'-spirobiindan (**21a**), mp 133–134 °C (from methanol, lit.[13–19] 132, 133–134 °C), mass spectrum *m/e* 276 and 261, NMR (CCl_4) δ 1.35 (s, 6 H, $C_{3,3'}CH_3$), 1.40 (s, 6 H, $C_{3,3'}CH_3$), 2.29 (s, 4 H, $C_{2,2'}H_2$) and 6.9–7.2 ppm (m, 8 H, ArH).

Alkylation of Toluene with 2-Bromopropene. The reaction was carried out as with benzene: Al_2Br_6 (2.1 g, 3.9 mmol), toluene (90 ml), and 2-bromopropene (5 g, 41 mmol) were stirred at room temperature for 4 h. After the usual workup with ice and water and removal of the excess toluene by distillation under reduced pressure, a mass of crystals appeared in the 4.5 g of residual yellow oil. Two recrystallizations of the solid gave 0.5 g of 3,3,6,3',3',6'-hexamethyl-1,1'-spirobiindan (**21b**): colorless needles, mp 130–132 °C; vacuum sublimation raised the melting point to 137–138° (lit.[18] 137–138 °C); mass spectrum *m/e* 304 and 289; NMR (CCl_4) δ 1.30 (s, 6 H, $C_{3,3'}CH_3$), 1.37 (s, 6 H, $C_{3,3'}CH_3$), 2.24 (s, 10 H, 6,6'-$ArCH_3$ and 2,2'-CH_2), 6.49 (s, 2 H, 7,7'-ArH), and 6.92 ppm (s, 4 H, 4,5,4',5'-ArH); (pyridine) δ 2.16 (s, 6 H, 6,6'-$ArCH_3$) and 2.32 ppm (s, 4 H, 2,2'-CH_2). The 0.5 g of pure **21b** corresponds to 12% of theory based on 2-bromopropene.

The liquid products, 3.3 g, bp 68–145 °C (0.1 mm), were separated by preparative GLC, using a 10 ft × 0.25 in. column of the same type described above and the components were identified by NMR: 18% 1,1,3,5-tetramethylindene (**16b**),[20] NMR (CCl_4) δ 1.24 [s, 6 H, $C_1(CH_3)_2$], 2.05 (d, 3 H, J = 2 Hz, C_3CH_3), 2.37 (s, 3 H, 5-CH_3), 5.85 (m, 1 H, $=C_2H$), and 6.9–7.1 ppm (m, 3 H, ArH); 4% 1,1,3,7-tetramethylindene (**18b**), NMR (CCl_4) δ 1.22 [s, 6 H, $C_1(CH_3)_2$], 2.25 (d, 3 H, J = 2 Hz, C_3CH_3), 2.51 (s, 3 H, 7-CH_3), 5.88 (m, 1 H, $=C_2H$), and 6.8–7.2 ppm (m, 3 H, ArH); 71% 2,2-di-*p*-tolylpropane (**12b**), NMR δ 1.6 [s, 6 H, $C_2(CH_3)_2$], 2.24 (s, 6 H, $ArCH_3$), and 6.97 ppm (s, 8 H, ArH); and 7% 1,3,3,6-tetramethyl-1-*p*-tolylindan (**14b**),[21] NMR (CCl_4) δ 1.02 (s, 3 H, C_3CH_3), 1.30 (s, 3 H, C_3CH_3), 1.62 (s, 3 H, C_1CH_3), 2.28–2.35 (two singlets with multiplet at base, 8 H, C_2H_2 and $ArCH_3$), and 6.95 ppm (m, 7 H, ArH).

Alkylation of Toluene with 2-Bromopropene in the Presence of Anhydrous Aluminum Chloride. 2-Bromopropene (1.95 g, 16 mmol), $AlCl_3$ (2.66 g, 20 mmol), and toluene (90 ml) were stirred together at room temperature for 2.5 h. After the usual workup with ice and water and removal of excess toluene by distillation under reduced pressure, the residue was 2.2 g of yellow oil, which did not yield any crystals. This oil was separated by GLC into the same components (**12b**, **14b**, **16b**, and **18b**) as in the Al_2Br_6-catalyzed reaction except that no 1,1'-spirobiindan (**21b**) was found, and 7% of 2-*p*-tolylpropene (**10b**) was isolated and identified by NMR (CCl_4): δ 2.11 (s with fine splitting, 3 H, $=C_2CH_3$), 2.34 (s, 3 H, $ArCH_3$), 4.98 (broad s, 1 H, C_1H), 5.24 (broad s, 1 H, C_1H), and 7.14 ppm (AB quartet, 4 H, ArH).

Registry No.—**1**, 98-81-7; **2**, 536-74-3; **3**, 98-86-2; **4a**, 948-55-0; **4b**, 947-77-3; **4c**, 4333-75-9; **4d**, 24892-80-6; **8**, 557-93-7; **10b**, 1195-32-0; **12a**, 778-22-3; **12b**, 1823-31-0; **14a**, 3910-35-8; **14b**, 1153-36-2; **16a**, 2177-45-9; **16b**, 14656-06-5; **18b**, 58343-28-5; **21a**, 58343-29-6; **21b**, 58343-30-9; Al_2Br_6, 18898-34-5; H_3PO_4, 7664-38-2; $AlCl_3$, 7446-70-0; toluene, 108-88-3; anisole, 100-66-3; benzene, 71-43-2.

References and Notes

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