Aluminum (III) chloride-catalyzed reaction of 1,1,1-trichloroethane with aromatic compounds: A facile synthesis of symmetrical 1,1-diphenylethenes

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1.1-Diarylethenes possessing the gem-diaryl arrangement are a unique group of olefins useful in organic synthesis and their high chemical reactivity enables them to undergo a wide range of reactions such as cycloadditions, dimerization, photodimerization, etc. The driving force for their reactivity is the ability of the aryl groups to stabilize an anionic, cationic or radical centre. Further, the steric interaction between the aryl groups prevents planarity of these molecules and inhibits polymerization. Hence, they have been extensively employed as models for investigating the initiation steps of cationic polymerization. Several methods of synthesis of 1,1-diarylethenes involving multisteps are reported and most of the traditional methods mainly rely upon the Grignard reaction and Wittig olefination besides other reactions such as organometallic carbenoids, α-aryl carbonions, α-trimethylstannyl carbanions, etc. wherein the reaction conditions are tedious. In this note, we describe in detail the results on the AlCl₃-catalyzed reaction of 1,1,1-trichloroethane with variety of aromatic substrates furnishing their corresponding 1,1-diphenylethenes in excellent yields (Scheme I).

Results and Discussion
Benzoylation under Friedel-Crafts reaction conditions acylations is an important unit process for the preparation of many industrially valuable chemicals. We have established, that an exceptionally stable phenylchlorocarbenium ion such as A could be readily generated even at ambient temperature under Friedel-Crafts reaction conditions. This study led to the development of a convenient method to obtain a variety of benzophenones upon reaction of A with aromatic compounds in excellent yields. Promoted by these findings, it was of interest to generate methylchlorocarbenium ion B from 1,1,1-trichloroethane and study its reactivity pattern towards aromatic substrates aiming at developing a method to obtain acetophenones (Scheme II).

However, in practice, the carbenium ion B, when reacted with different aromatic substrates, I, followed an unexpected course furnishing 1,1-diarylethenes 2 in high yields. The results are summarized in Table I. As can seen from the Table I, a variety of arenes have undergone the Friedel-Crafts reaction with CH₂Cl₂ furnishing their corresponding 1,1-diphenylethenes in good yields. For example, when benzene is stirred with CH₂Cl₂ in the presence of anhyd. AlCl₃ at 0-5°C, the reaction proceeds quantitatively producing 1,1-diphenylethylene. A sharp singlet at δ 5.3 in ²H NMR spectra of all the products confirms the formation of 1,1-diphenylethenes. A special feature of these results is that the aryl substituents have negligible effect on the efficiency of the process. In the case of mono-substituted arenes, para-selectivity for product formation has been observed. For
<table>
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<th>Entry</th>
<th>Substrate, 1</th>
<th>Temp (°C)</th>
<th>Period (hr)</th>
<th>Product, 2</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>&lt;i&gt;p/i&lt;/i&gt; ratio&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>10</td>
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</table>

<sup>a</sup> Isolated yield; <i>p/i</i> ratios were determined by GLC (Capillary Column HP-1).
example, when toluene was subjected to alkylation with CH₂CCL₃ under Friedel-Crafts conditions, a mixture of para- and ortho-1,1-diphenylethlenes in the ratio 81:19 was obtained as determined by GLC and their structures have been confirmed by GC-MS (Scheme III).

Although the separation of the para-isomer in a lowered isolated yield could be achieved by column chromatography (ethyl acetate : hexane), it is increasingly difficult to obtain the ortho-isomer in a pure state as it is always accompanied by a small amount of para-isomer (their TLC behaviour is homogeneous with hexane as eluant). It is interesting to note that in the case of acetanilide, the reaction proceeds in a moderate yield to give 1,1-bis(4-aminophenyl)ethylene. When the reaction was carried out with other Lewis acids such as TiCl₄, SnCl₄ and BF₃·OEt₂, it fails. However, solvents such as CH₂Cl₂, CHCl₃, CS₂ and CCl₄ could be used for the reaction successfully.

Mechanism
When anhydrous AlCl₃ is added to a solution of CH₂CCL₃ in 1,2-dichloroethane at 0.5°C, an instantaneous formation of red colour is observed indicating probably the generation of the incipient carbenium ion B. However, it is highly unstable (hence highly reactive) at room temperature as no signal corresponding to CH₂CCL₃⁺·AlCl₃ [B] could be detected in its ¹³C NMR (200 MHz) spectrum. Hence, it is possible that the two successive alkylations by carbenium ions B and C can lead to the tertiary chloride (I) which readily undergoes dehydrochlorination under the reaction conditions to yield 2 (Scheme IV).

In conclusion, we have described a new and efficient method for the synthesis of 1,1-diphenylethlenes 2 using a simple, inexpensive and safe alkylation agent 1,1,1-trichloroethane.

Experimental Section
All melting points reported are uncorrected. IR spectra were recorded as neat or nujol mulls (in case of solid samples) on Perkin-Elmer Infrared model 137-E. ¹H NMR spectra on a Varian FT200 MHz instruments; and ¹³C NMR spectra on a Bruker 50.3 MHz instrument. The chemical shifts were reported with TMS as the internal standard. The mass spectra (MS) were recorded on an automated Finnigan MAT 11020°C mass spectrometer using ionization energy of 70 eV.

Preparation of 1,1-diarylethlenes 2. General Procedure. To a cooled, stirred solution of aromatic substrate 1 (0.1 mole) and anhyd. AlCl₃ (0.15 mole) in 1,2-dichloroethane (50 mL), a solution of CH₂CCL₃ (0.06 mole) in 1,2-dichloroethane (10 mL) was added during 10 min. After the reaction was complete, the reaction mixture was decomposed with water/HCl mixture. The organic layer was separated and the aqueous layer extracted with 1,2-dichloroethane. The combined organic phase was washed with water, brine and dried over Na₂SO₄. Removal of the solvent afforded the 1,1-diarylethlenes 2 which were further analyzed by GLC and purified by column chromatography.

1,1-Diphenylethylene: Liquid, b.p.148°C/16 mm; IR (neat) : 1615, 1580, 1500, 1450, 1340, 1030, 910, 780 and 710 cm⁻¹; ¹H NMR (60 MHz, CCl₄) : δ 5.3 (2H, s, vinyllic), 7.1 (10H, s, ArH); MS (m/z % rel. intensity) : 180 (M⁺, 94), 179 (88), 178 (80), 165 (100), 152 (21), 139 (8), 126 (4), 115 (6), 102 (8), 89 (13), 77 (10) and 58 (39).

1,1-Bis(4-methylphenyl)ethylen: m.p. 60°C (lit. ¹b m.p.60°C); IR (nujol): 1615, 1520, 1450, 1340, 1200, 1120, 1040, 910, 840 and 740 cm⁻¹; ¹H NMR (60 MHz, CCl₄) : δ 2.26 (6H, brs, 2 × CH₃), 5.2 (2H, s, vinyllic), 6.6 - 7.2 (8H, m, ArH); MS (m/z % rel. intensity) : 208 (M⁺, 67), 193 (100), 180 (30), 170
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1.1-Bis(4-methoxyphenyl)ethylene: m.p. 143°C (lit. 143°C); IR (nujol); 1610, 1520, 1470, 1390, 1300, 1260, 1200, 1040, 910 and 855 cm⁻¹; ^1H NMR (60 MHz, CDCl₃): δ 3.7 (2H, s, vinyl), 5.3 (2H, s, vinyl), 6.65 (4H, d, J=8 Hz, Ar-H), 7.15 (4H, d, J=8 Hz, Ar-H); MS (m/z, % rel. intensity): 240 (M⁺, 100), 225 (88), 209 (44), 194 (11), 182 (16), 165 (32), 153 (23), 135 (9), 120 (8), 112 (8), 89 (9) and 77 (8).

1.1-Bis(4-chlorophenyl)ethylene: m.p. 94°C (lit. 94°C); IR (nujol); 1615, 1600, 1490, 1440, 1400, 1350, 1100, 1020, 920, 850, 760 and 690 cm⁻¹; ^1H NMR (80 MHz, CDCl₃): δ 5.5 (2H, s, vinyl), 6.9 - 7.1 (8H, brs, Ar-H); MS (m/z, % rel. intensity): 250 (M⁺, 22), 249 (M⁺, 14), 248 (M⁺, 76), 233 (8), 213 (60), 178 (100), 177 (50), 176 (46), 151 (13), 106 (12), 101 (15), 88 (30) and 75 (21).

1.1-Bis(4-bromophenyl)ethylene: m.p. 87°C (lit. 87°C); IR (nujol); 1620, 1600, 1490, 1400, 1130, 1100, 1020, 930, 850 and 760 cm⁻¹; ^1H NMR (80 MHz, CDCl₃): δ 5.3 (2H, s, vinyl), 7.0 (4H, d, J=8 Hz, Ar-H), 7.4 (4H, d, J=8 Hz, Ar-H); MS (m/z, % rel. intensity): 341(M+3,5) 340 (M⁺, 22), 339(M⁺, 110) 338 (M⁺, 44), 336 (25), 257 (5), 178 (100), 177 (20), 176 (23), 152 (11), 102 (13), 89 (16) and 76 (17).

1.1-Bis(4-fluorophenyl)ethylene: m.p. 47°C; IR (nujol); 1610, 1500, 1460, 1420, 1340, 1250, 1170, 1110, 1020, 910, 850 and 760 cm⁻¹; ^1H NMR (80 MHz, CDCl₃): δ 5.5 (2H, s, vinyl), 6.6 - 7.3 (8H, m, Ar-H); MS (m/z, % rel. intensity): 216 (M⁺, 100), 215 (38), 214 (38), 201 (90), 195 (25), 183 (10), 175 (8), 120 (15), 101 (12) and 77 (18).

1.1-Bis(4-iodophenyl)ethylene: Viscous liquid; IR (neat); 1610, 1450, 1380 and 910 cm⁻¹; ^1H NMR (200 MHz, CDCl₃): δ 5.5 (2H, s, vinyl), 7.1 (4H, d, J=8 Hz, Ar-H), 7.75 (4H, d, J=8 Hz, Ar-H); MS: (m/z, % rel. intensity): 432 (M⁺, 10), 306 (15), 298 (35), 283 (25), 279 (16), 266 (5), 254 (15), 242 (40), 204 (80), 180 (100), 156 (70), 145 (30), 141 (51), 127 (48), 115 (25), 109 (35), 85 (30), 74 (30) and 63 (20).

1.1-Bis(2,5-dimethylphenyl)ethylene: Liquid, b.p. 155°C/10 mm; IR (nujol); 1610,1500, 1450, 1390, 1320, 1050, 920 and 820 cm⁻¹; ^1H NMR (60 MHz, CDCl₃): δ 2.03 (6H, s, 2 × CH₃), 2.26(6H, s, 2 × CH₃). 5.3 (2H, s, vinyl).6.6 - 6.9 (6H, m, Ar-H); ^13C NMR (50.3 MHz, CDCl₃): δ 20.3 (Me), 21.0 (Me), 118.9 (C=β), 128.1, 130.5, 130.7, 132.6, 135.1, 142.3 (aromatic) and 150.5 (C-α); MS (m/z, % rel. intensity): 236 (M⁺, 57), 221 (89), 206 (100), 192 (28), 178 (13), 115 (17); Anal. C₉H₁₈O₂ require C, 91.53; H 8.47. Found C, 91.42; H, 8.45%.

1.1-Bis(3,4-dimethylphenyl)ethylene: Liquid: IR (neat); 1620, 1450, 1380, 1170, 1030, 890, 830 and 740 cm⁻¹; ^1H NMR (80 MHz, CDCl₃): δ 2.05 (6H, s, 2 × CH₃), 2.26(6H, s, 2 × CH₃), 5.3 (2H, s, vinyl), 6.6 - 6.9 (6H, m, Ar-H); MS (m/z, % rel. intensity): 236 (M⁺, 3), 221 (5), 206(5), 148 (22), 146 (47), 119 (25), 111 (20), 106 (58), 105 (30), 91 (100), 85 (19), 71 (22), 57 (63), 43 (48).

1.1-Bis(4-amino phenyl)ethylene: Viscous liquid: IR (neat); 3200, 610, 1450, 1240, 1050, 900 and 800 and 720 cm⁻¹; ^1H NMR (200 MHz, CDCl₃): δ 5.5 (2H, s, vinyl), 7.2 - 7.7 (12H, brs, ArH and NH₂); MS (m/z, % rel. intensity): 208 (10), 193 (15), 180 (100), 179 (76), 178 (81), 165 (95), 152 (16), 115 (12), 105 (23), 89 (11) and 77 (30).

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