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Electrophilic Substitution in Aromatic and Heteroaromatic Substrates by Trichlorocyclopropenylium Tetrachloroaluminate

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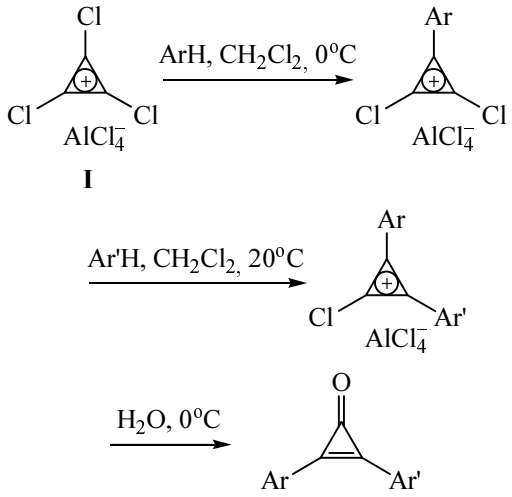
Abstract—Trichlorocyclopropenylium tetrachloroaluminate is an electrophilic reagent for the preparative introduction of a cyclopropenyl fragment into heteroaromatic and aromatic substrates.

Tetrachlorocyclopropene is among sufficiently available compounds of the cyclopropene series for it is prepared by a good preparative procedure from sodium trichloroacetate and trichloroethylene [1]. Its salt with the aluminum chloride, trichlorocyclopropenylium tetrachloroaluminate [2], is known to react with some aromatic substrates by the mechanism of electrophilic aromatic substitution. [3]. We demonstrated the general character of the reaction for not only substituted aranes but also aromatic heterocycles and their derivatives could be brought into the reaction.

Two different procedures were developed for dissimilar substrates. Compounds **II–VI** were obtained by adding the arene solution to salt **I** prepared *in situ.* The yield of reaction products were 65–85% (see table). For substrates capable of forming relatively stable complexes with the aluminum chloride, namely, in preparation of compounds **VII–X**, we used another method: The solution of tetrachlorocyclopropene was added to a mixture of the heterocyclic compound and excess anhydrous aluminum chloride in dichloromethane. The reaction



I

Conditions of reactions between trichlorocyclopropenylium tetrachloroaluminate (**I**) with various substrates

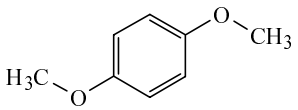
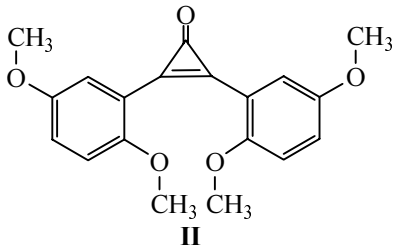
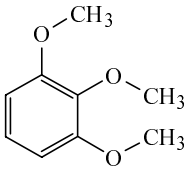
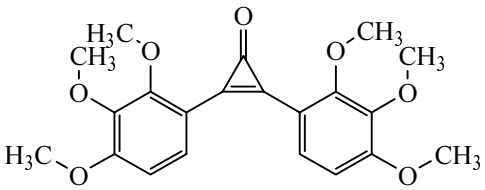
Substrate	Conditions	Reaction product	Yield, %
	–20–5°C, CH_2Cl_2, $AlCl_3$	 **II**	88
	–20–5°C, CH_2Cl_2, $AlCl_3$	 **III**	86

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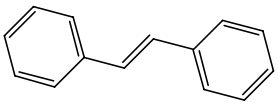
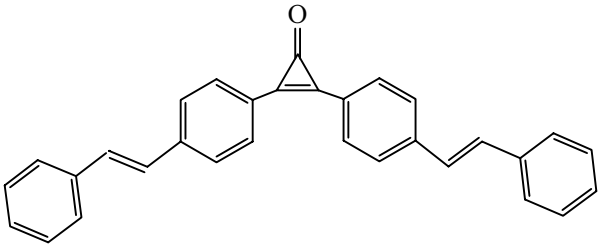
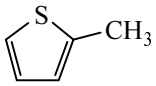
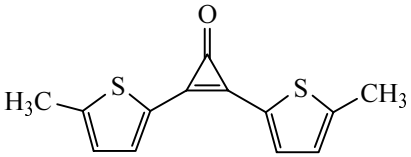
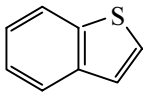
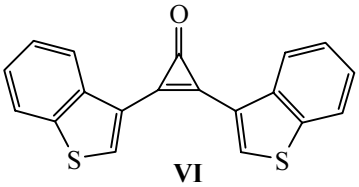
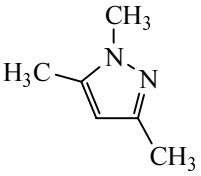
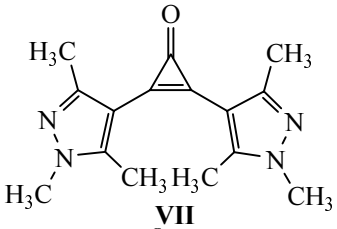
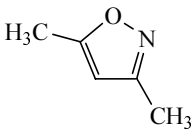
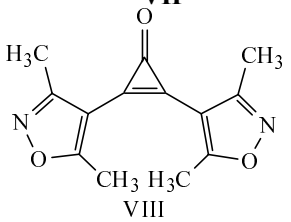
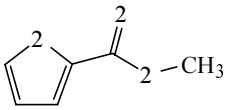
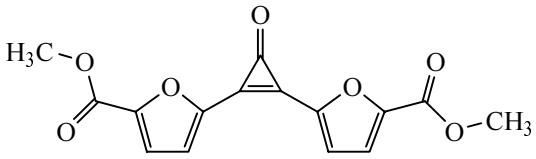
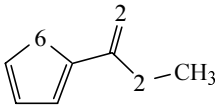
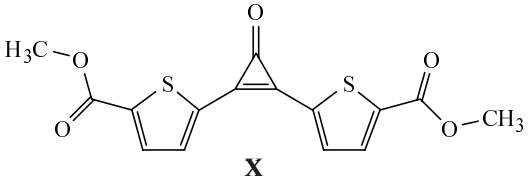
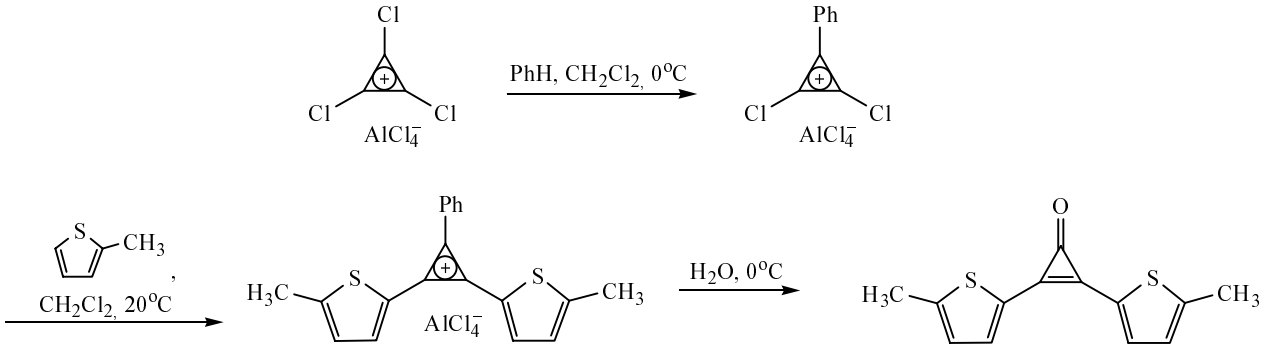
Table (Contd.)

Substrate	Conditions	Reaction product	Yield, %
	–20°C, CH_2Cl_2, $AlCl_3$	 **IV**	88
	–20°C, ethyl ether, $AlCl_3$	 **V**	85
	–20°C, CH_2Cl_2, $AlCl_3$	 **VI**	65
	–5–20°C, CH_2Cl_2, 4 equiv of $AlCl_3$	 **VII**	70
	–5–20°C, CH_2Cl_2, 4 equiv of $AlCl_3$	 VIII	55
	–5–20°C, CH_2Cl_2, 6 equiv of $AlCl_3$	 **IX**	68
	–5–20°C, CH_2Cl_2, 6 equiv of $AlCl_3$	 **X**	80



mixtures were kept at room temperature for 24 h and hydrolyzed with water to obtain in 55–80% yield previously unknown cyclopropenones **VII–X** (see table).

Under the above described conditions we carried out the reaction of salt **I** with an equimolar amount of benzene analogously to the process reported in [3]. According to TLC in 0.5 h the initial substances disappeared from the reaction mixture. Then at room temperature we added to the reaction mixture 2 equiv of 2-methylthiophene. As a result a disubstituted cyclopropenone was isolated completely identical to that previously obtained in reaction with 2-methylthiophene in the absence of benzene (cyclopropenone **V**).

These findings led to a conclusion that in the course of hydrolysis the aromatic fragment might be cleaved from the intermediately formed triarylcyclopropenylium salt. The following transformations at the use of substituted 1,1-2,3-diphenylcyclopropene (**XI**) confirm this suggestion. The reaction of 2-methylthiophene with 2,3-diphenyl-1-chlorocyclopropenylium tetrachloroaluminate gave rise on hydrolysis to unsymmetrical 2-phenyl-3-(5-methylthienyl-2)cyclopropenone-1 (**XII**). In the same way the reaction of salt **XI** with 1,2,3-trimethoxybenzene afforded after hydrolysis an unsymmetrical 2-phenyl-3-(2,3,4-trimethoxyphenyl)cyclopropenone-1 (**XIII**). These facts indicate that the hydrolysis of the cyclopropenylium triaryl-substituted salts results in a cyclopropenone retaining the most electron-donor substituents.

EXPERIMENTAL

IR spectra were registered on spectrophotometer Specord R-20 from mulls in mineral oil in a thin film. ^{1}H and ^{13}C NMR spectra were obtained on spectrometer Bruker AC-300 at operating frequency 300 MHz from solutions in $CDCl_3$ or DMSO-d_6. Mass spectra were measured on HP 5995 A instrument with a direct admission of the sample into the ion source, ionizing energy 70 eV, 60°C.

2,3-Di(2,5-dimethoxyphenyl)cyclopropen-1-one (II). To a solution of 250 mg (1.4 mmol) of tetrachlorocyclopropene in 5 ml of anhydrous dichloromethane was added while stirring at 20°C 180 mg of anhydrous aluminum chloride, and the mixture was stirred for 10 min. Then it was cooled to–20°C, and a solution of 380 mg (2.8 mmol) of 1,4-dimethoxybenzene in dichloromethane cooled to –5°C was added. The reaction mixture was warmed to 5°C; the solution turned yellow, and HCl liberation was observed. In 30 min the mixture was treated with 2 ml of ice water, the organic layer was immediately separated and dried with calcium chloride. On removing the solvent in a vacuum the yield of a mixture of mono- and disub-stituted product was 88% in a ratio 4:5 respectively. IR spectrum, ν, cm^{-1}: 1840 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.8–7.5 m, 3.75 s, 3.8 s, 3.9 s, 3.95 s (OCH_3).

Likewise were prepared compounds **III** and **IV.**

2,3-Di(2,3,4-trimethoxyphenyl)cyclopropen-1-one (III). Colorless needle-like crystals, mp 94°C (from cyclohexane). IR spectrum, ν, cm^{-1}: 1840 (C=O). Mass spectrum, *m/e*, (I_{rel}, %): 386 (0.5) $[M]^+$, 358 (100) $[M - C{=}O]^+$, 191 (12), 179 (18). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.95 s (6H), 4.0 s (6H), 4.05 s (6H), 6.9 d (2H), 8.15 d (2H). ^{13}C NMR spectrum, δ, ppm: 56.76, 61.47, 62.61, 108.27, 110.51, 130.87, 138.08, 142.20, 155.50, 156.04, 159.476. Found, %: C 65.76; H 5.54. $C_{27}H_{22}O_7$. Calculated, %: C 65.38; H 5.44.

2,3-Di (4-styrylphenyl)cyclopropen-1-one (IV). Viscous oily substance crystallized on standing into needle-like crystals, mp 51°C (from benzene). IR

spectrum, ν, cm^{-1}: 1840 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.9–7.3 m. Mass spectrum, *m/e*, (I_{rel}, %): 410–412 $[M]^+$ (none), 382 (6)–383 (20) $[M - C{=}O]^+$, 306 (16), 291 (20), 205 (26), 191 (100), 105 (50).

2,3-Di(5-methylthienyl-2)cyclopropen-1-one (V). To a solution of 1 g (5.6 mmol) of tetrachlorocyclopropene in 10 ml of dry dichloromethane was added a slight excess of $AlCl_3$ (0.8 g). The mixture was cooled to–20°C, and under an argon flow was added a double excess [1.1 g (11.2 mmol)] of 2-methylthiophene cooled to –5°C. The reaction started at once, the solution turned dark cherry-red. The reaction mixture was stirred for 1 h at –15°C under argon, then at stirring 5 ml of ice water was added. The organic layer was separated, dried with magnesium sulfate, and the solvent was removed in a vacuum. The reaction product (brown oily substance) was subjected to column chromatography on silica gel, eluent ethyl ether–dichloromethane, 3:1 (R_f 0.5). After purification we obtained a light-yellow chromatographically homogeneous oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.6 s (6H), 6.9 d (2H), 7.6 d (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 16 (CH_3), 119 (C=C), 127.5, 135.5 (CH tθΟτενα), 137, 140, 149 (C=O). Mass spectrum, *m/e* (I_{rel}, %): 246 (2) $[M]^+$, 218 (100) $[M - C{=}O]^+$, 203 (10). Found, %: C 63.77; H 3.97. $C_{13}H_{10}OS_2$. Calculated, %: C 63.38; H 4.09.

2,3-Di(benzothienyl-3)cyclopropen-1-one (VI) was prepared in the same way as compound **V**. The brown oily substance was subjected to column chromatography on silica gel, eluent ethyl ether–dichloromethane, 3:1 (R_f 0.55). On crystallization from benzene we obtained the product as colorless crystalline plates, mp 105–107°C (decomp.). IR spectrum, ν, cm^{-1}: 1855 (C=C), 1680. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.5–7.7 m (6H), 8.1–8.2 m (4H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 100.9, 119.0, 121.3, 124.2, 124.5, 133.0, 134.2, 135.3, 140.2, 150.0 (C=O).

2,3-Di(1,3,5-trimethylpyrazolyl-4)cyclopropen-1-one (VII). To a solution of 0.55 g (5 mmol) of 1,3,5-trimethylpyrazole in 20 ml of dry dichloromethane was added at stirring 20 mmol of anhydrous $AlCl_3$.The mixture was stirred for 1 h, cooled to –5°C, and 2.5 mmol of tetrachlorocyclopropene was added dropwise. The solution turned bright red, and hydrogen chloride evolution was observed. The reaction mixture was kept at room temperature for 24 h, then treated with 20 ml of water, the organic layer was separated, the water layer was extracted with dichloromethane (2×10 ml). The combined organic solutions were dried with sodium sulfate, and the solvent was distilled off in a vacuum. We obtained a yellow oily substance that crystallized on standing. It was subjected to column chromatography on silica gel, eluent dichloromethane–methanol, 20:1 (R_f 0.3), mp 80–85°C (from toluene). IR spectrum, ν, cm^{-1}: 1850, 1660. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.1 s (6H), 2.2 s (6H), 3.7 s (6H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.0, 11.1, 35.7, 116.0, 120.2, 139.7, 140.1, 153.0.

2,3-Di(3,5-dimethylisoxazolyl-4)cyclopropen-1-one (VIII) was similarly prepared. The reaction product was subjected to column chromatography on silica gel, eluent dichloromethane–methanol, 20:1 (R_f 0.4). Slightly colored oily substance, partially crystallizing at room temperature. IR spectrum, ν, cm^{-1}: 1845, 1665. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.23 s (6H), 2.4 s (6H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 9.8, 10.0, 112.7, 120.0, 149.5, 158.0, 167.2.

2,3-Di(5-carboxymethylfuryl-2)cyclopropen-1-one (IX) was obtained in the same fashion as compound **VII.** For 5 mmol of methyl pyromycate 30 mmol of aluminum chloride was used. The dark oily substance was purified by column chromatography on silica gel, eluent dichloromethane–methanol, 20:1 (R_f 0.35). Slightly colored oily substance, rapidly darkening at room temperature, quickly tarring at heating over 70°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.93 s (6H), 6.50 d (2H), 7.23 d (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 51.6, 110.1, 113.5, 118.0, 143.7, 151.8, 157.1, 160.2.

2,3-Di(5-carboxymethylthienyl-2)cyclopropen-1-one (X) was obtained in the same fashion as compound **VII.** The reaction product was purified by column chromatography on silica gel, eluent dichloromethane–methanol, 20:1 (R_f 0.35). Colorless crystals, mp 45–50°C (from benzene), stable at room temperature. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.93 s (6H), 6.50 d (2H), 7.23 d (2H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 53.0, 121.0, 125.3, 130.8, 135.1, 144.8, 156.2, 161.2.

2-Phenyl-3-(5-methylthienyl-2)cyclopropen-1-one (XII). In 20 ml of dry dichloromethane was dissolved 5 mmol of 2,3-diphenyl-1,1-dichlorocyclopropene, and 5.05 mmol of anhydrous aluminum chloride was added thereto. To the dispersion of the salt **XI** thus obtained was added at room temperature 10 mmol of 2-methylthiophene, and the reaction mixture was stirred for 12 h. After the end of hydrogen chloride liberation the reaction mixture was cooled to –5°C, and 10 ml of cold water was added. The organic layer was separated, dried over

anhydrous sodium sulfate, and the solvent was removed in a vacuum. Needle-like crystals, mp 65–67°C (from cyclohexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.51 s (3H), 6.84 d (1H), 6.99 d (1H), 7.25–7.85 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 15.1, 120.6, 123.0, 125.1, 125.5, 129.0, 130.0, 132.5, 138.1, 142.0, 152.8.

2-Phenyl-3-(2,3,4,-trimethoxyphenyl)cyclopropen-1-one (XIII) was prepared similarly. mp 99–100°C (from cyclohexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.90 s (3H), 4.0 s (3H), 4.03 s (3H), 6.8 d (1H), 7.30–8.00 m (6H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 56.8, 61.0, 61.7, 107.5, 119.0, 119.2, 129.3, 132.0, 132.5, 133.1, 145.0, 147.1, 148.0, 150.0, 154.2, 154.3.

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3. Musigmann, K. and Mayr, H., *Tetrahedron Lett*., 1987, vol. 28, p. 4517.