[$_{\pi}6_s + {}_{\pi}2_s$] Cycloadditions Catalysed by the $TiCl_4$–Et_2AlCl System

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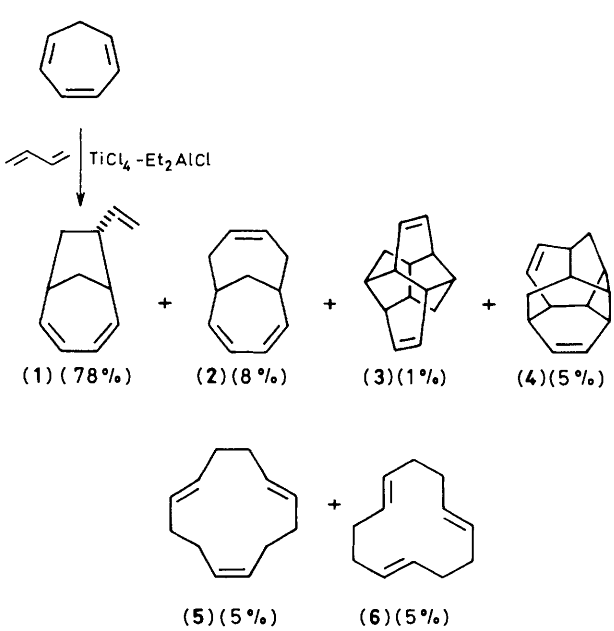
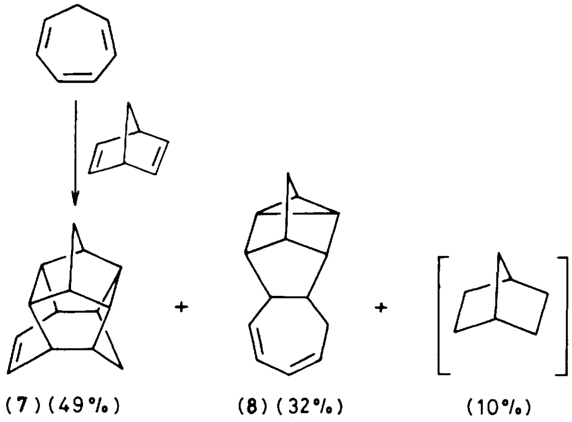
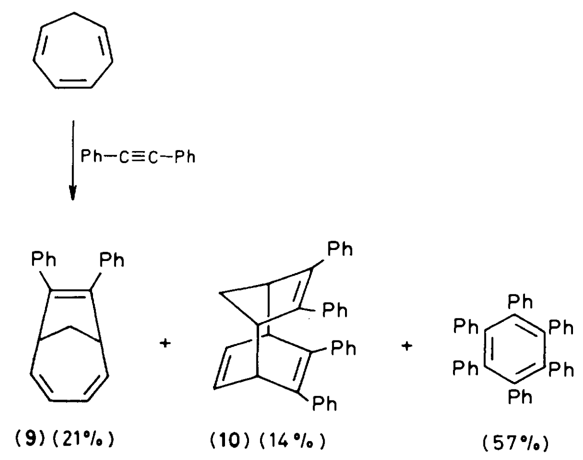
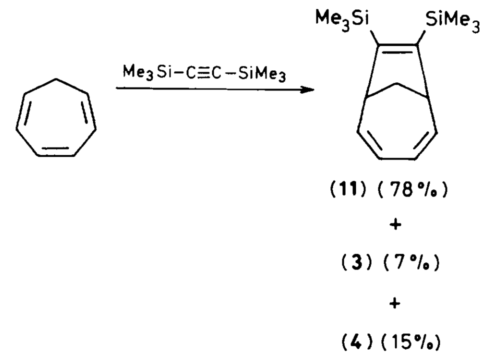
The catalyst system $TiCl_4$–Et_2AlCl induces [$_{\pi}6_s + {}_{\pi}2_s$] cycloadditions of cycloheptatriene to buta-1,3-diene, norbornadiene, and acetylenes.

There are only a few reported examples of [$_{\pi}6_s + {}_{\pi}2_s$] cycloadditions.[1–5] We have recently reported that low-valent titanium complexes, (η^6-C_6H_6)$Ti^{II}(AlCl_4)_2$ in combination with Et_2AlCl and the Ziegler catalyst $TiCl_4$–Et_2AlCl, induced a tandem [$_{\pi}6_s + {}_{\pi}2_s$]–[$_{\pi}4_s + {}_{\pi}2_s$] cyclodimerization of cycloheptatriene yielding two pentacyclic tetradecadienes.[6,7] We now report on the use of the $TiCl_4$–Et_2AlCl catalyst for cross-additions of cycloheptatriene to other trienophiles.









Buta-1,3-diene and cycloheptatriene (molar ratio C_4H_6:C_7H_8:Et_2AlCl:$TiCl_4$ = 100:100:20:1, for experimental details see ref. 7) afford mainly 7-*endo*-vinylbicyclo[4.2.1]nona-2,4-diene (**1**), a product of the [$_{\pi}6_{s} + {}_{\pi}2_{s}$] reaction, accompanied by bicyclo[4.4.1]undeca-2,4,8-triene (**2**), the cycloheptatriene dimers (**3**) and (**4**), and the butadiene cyclotrimers (**5**) and (**6**). Isoprene reacts similarly, giving a mixture of isomeric cycloaddition products, while (*E,E*)-hexa-2,4-diene and cyclo-octa-1,3-diene are unreactive.

Addition of cycloheptatriene to norbornadiene proceeds in two ways: the [$_{\pi}6_{s} + {}_{\pi}2_{s}$] cycloaddition, followed by an intramolecular Diels–Alder reaction, affords the hexacyclic compound (**7**) as the main product, while the minor adduct (**8**) arises *via* a [$_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{s}$] mechanism. The formation of (**7**) could alternatively be visualized as occurring by a [$_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{s}$] cycloaddition.

The catalysed addition of cycloheptatriene to acetylenes competes with cyclotrimerization of the latter compounds. But-2-yne and diphenylacetylene trimerize very rapidly, although in the latter case the [$_{\pi}6_{s} + {}_{\pi}2_{s}$] cycloaddition also takes place to give the bicyclononatriene (**9**).[4] This reacts further with diphenylacetylene to give the Diels–Alder adduct (**10**). Bis(trimethylsilyl)acetylene appeared to be the best alkyne $_{\pi}2_{s}$ component as it did not trimerize and added cleanly to cycloheptatriene, yielding the bicyclic compound (**11**).†

The choice of possible trienophiles for the [$_{\pi}6_{s} + {}_{\pi}2_{s}$] reaction is limited by two factors: first, the trienophile should not contain reducible groups (carbonyl, halogen, nitro, *etc.*) and, secondly, it should be able to complex weakly to the catalyst, preferentially through an auxiliary π-orbital.

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† All products were characterized by their i.r., ^{1}H and ^{13}C n.m.r., and mass spectra. Compounds (**1**), (**2**), (**8**), and (**11**) are liquids; m.p.s: (**7**), 168—169 °C; (**9**), 53—55 °C; (**10**), 175—177 °C; ^{13}C n.m.r. data (δ, p.p.m.): (**1**): 141.0 (d), 139.4 (d), 135.1 (d), 126.1 (d), 123.3 (d), 114.5 (t), 61.3 (d), 46.4 (d), 41.5 (t), 36.8 (d), and 33.5 (t); (**2**): 138.24 (d, 2C), 132.11 (d, 2C), 124.79 (d, 2C), 38.30 (d, 2C), 37.00 (t, 2C), and 32.15 (t, 1C); (**7**): 130.8 (d, 2C), 53.7 (d, 2C), 47.0 (d, 2C), 43.1 (d, 2C), 42.9 (d, 2C), 41.8 (d, 2C), 39.5 (t, 1C), and 35.4 (t, 1C); (**8**): 137.0 (d), 133.8 (d), 128.1 (d), 125.6 (d), 56.0 (d), 49.9 (d), 49.2 (d), 42.6 (d), 40.0 (d), 31.4 (t), 30.7 (t), 14.3 (d), 11.6 (d), and 10.8 (d); (**9**): 139.23 (d, 2C), 136.65 (s, 2C), 135.93 (s, 2C), 129.11 (d, 4C), 127.97 (d, 4C), 126.51 (d, 2C), 124.62 (d, 2C), 49.23 (d, 2C), and 30.50 (t, 1C); (**11**): 146.5 (s, 2C), 137.8 (d, 2C), 123.9 (d, 2C), 51.9 (d, 2C), 30.1 (t, 1C), and 1.79 (q, 6C).