The Reaction of Tetrachlorocyclopropene with Trimethylsiloxydienes: A 'One-pot' Diels–Alder Route to Trichloro-tropones and -tropolones

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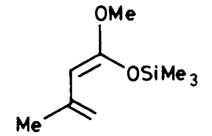
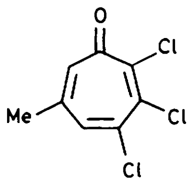
The trimethylsiloxydienes (**2**), (**7**), (**9**), and (**11**), react with tetrachlorocyclopropene (**3**) at room temperature to give the troponoids (**6**), (**8**), (**10a**), and (**12**), respectively; bromine oxidation of compound (**14**), derived from Diels–Alder reaction of diene (**13**) with dienophile (**3**), gives α-tropolone (**10a**) in 76% yield.

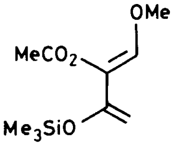
Tropones and tropolones serve as useful building blocks in organic synthesis.[1] In addition, many natural products contain the troponoid ring-system as a key structural element.[2] Consequently the development of flexible and efficient routes to these seven-membered conjugated carbocycles remains an important objective.[3] In a significant recent contribution, Boger and Brotherton have reported[4] that the Diels–Alder adducts derived from cyclopropenone acetal (**1**) and various dienes can be converted, over one or two steps, into tropones. We now describe a related process which provides a *direct* (one-pot) synthesis of tropones and tropolones. The method is experimentally simple, employs readily available starting materials, and provides the shortest route to troponoids so far devised.[5]

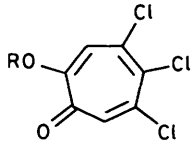
The well-documented ability of cyclopropenes[6] and siloxydienes[7] to function as 2π and 4π addends, respectively, in [$_\pi 4_s + {}_\pi 2_s$] cycloaddition reactions led to proposals of the type outlined in Scheme 1. Thus, cycloadduct (**4**) derived from Danishefsky's diene (**2**)[7] and tetrachlorocyclopropene (**3**),[8] should lose the elements of Me$_3$SiOMe to give the α,β-unsaturated ketone (**5**). Since we have demonstrated[9] that bicyclo[4.1.0]heptenones related to compound (**5**) undergo facile ring expansion to give troponoids, conversion (**5**) → (**6**) was expected to occur readily.

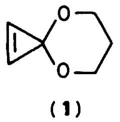
In accord with these expectations, reaction of equimolar quantities of (**2**) and (**3**) in CCl$_4$ at room temperature for four days gave trichlorotropone (**6**)[†] [56%;[‡] m.p. 90—91 °C; ^{1}H n.m.r. δ (CDCl$_3$) 6.76 (dd, *J* 12, 2 Hz, 1H, H-7), 7.30 (d, *J* 12 Hz, 1H, H-6), 7.34 (d, *J* 2 Hz, 1H, H-2); ν_{max} (KBr) 3018, 1643, 1618, 1598 cm^{-1}] directly. [By refluxing a benzene solution of the Diels–Alder components (**2**) and (**3**) a shorter

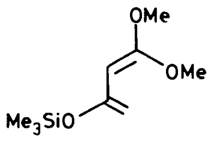

(**7**)

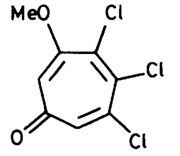

(**8**)

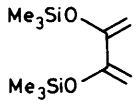

(**9**)

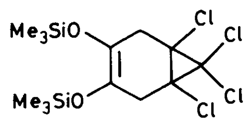

(**10**) a; R = H
b; R = MeCO

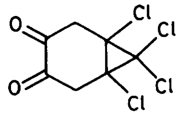

(**1**)

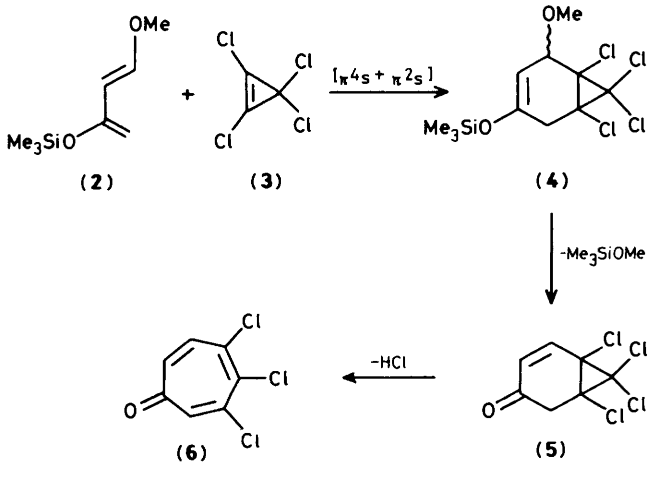

(**11**)


(**12**)


(**13**)


(**14**)


(**15**)



Scheme 1

[†] Satisfactory analytical and spectroscopic data have been obtained for all new compounds except bis(trimethylsilyloxy)alkene (**14**).

[‡] All yields quoted are of recrystallised materials.

reaction time (3.5 h) was achieved but lower yields (40%) of the tropone (**6**) were obtained.] Under similar conditions (CCl_4, 2 days) diene (**7**)[10] combined with (**3**) to produce methyl tropone (**8**) (30%, m.p. 132—133 °C). Reaction of dienophile (**3**) with the trioxygenated dienes (**9**)[11] (CCl_4, 4 days) and (**11**)[12] (CCl_4, 2 days) gave α-tropolone (**10a**) (40%, m.p. 152—153 °C) and β-tropolone methyl ether (**12**) (53%, m.p. 142—143 °C), respectively. Compound (**10a**) is probably formed as a result of hydrolysis (on work-up) of the initially produced tropolone acetate (**10b**). A higher yielding route to tropolone (**10a**) began with the Diels–Alder reaction (C_6H_6, 6 h, 80 °C) of compounds (**3**) and (**13**).[13] Oxidation (1 mol. equiv. Br_2, $-14\,°C \rightarrow$ room temperature, 4.5 h)[14] of the ensuing adduct (**14**) produced (**10a**) in 76% overall yield. Diketone (**15**) is presumably the key intermediate in the (**14**) → (**10a**) conversion but is not isolated because of spontaneous ring-expansion[9c] to product.

While the yields of product are only modest in most cases, this deficiency is more than offset by the ease with which relatively complex molecules can be assembled from simple starting materials. Given the wide range of siloxydienes now available[7] the methodology outlined above has considerable potential.

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