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New ‘substitution–recyclization’ reaction of a tetrachlorocyclopentadienone dimer with amines

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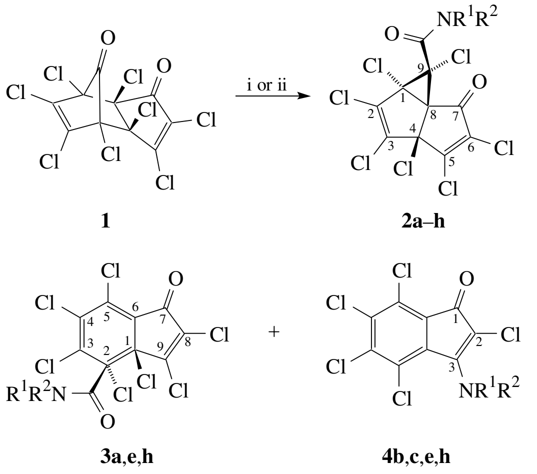
The interaction of a tetrachlorocyclopentadienone dimer with primary and secondary amines results in corresponding 9-carboxamidotricyclo[6.1.0.0^{4,8}]nona-2,5-dien-7-ones.

Although tetrachlorocyclopentadienone dimer **1** was described[1] as early as 1909, its reactions are studied insufficiently.[2–5] As the structure indicates, in the sterically crowded tricyclic skeleton of **1**, activated functional groups and double bonds are concentrated, and they are different in reactivity.



Scheme 1 *Reagents and conditions*: i, R^{1}R^{2}NH, C_6H_6, 20 °C; ii, R^{1}R^{2}NH·HCl, KOH (excess), C_6H_6, 20 °C.

The chemical behaviour of **1** and similar systems is difficult to predict because of their inclination to non-trivial transformations and the formation of untypical systems.[4,5] In this work, an unusual reaction of **1** with primary and secondary amines is discussed. The Ad$_N$E-type reaction of **1** with Et_2NH (the replacement of C^3–Cl by an amine residue in 2,3,5-trichlorocyclopentenones[6]) resulted in amide **2c** containing tricyclic cyclopropane of a new topology in 50% yield.

The structure of the latter was found by X-ray diffraction analysis[†] (Figure 1). 3-Substituted perchloroindenone **4c** is a by-product of this reaction (< 10%). The other primary and secondary amines similarly interact with **1** leading to corresponding tricycles **2a–h** and minor compounds **3a**,**e**,**h** and **4b**,**e**,**h**.

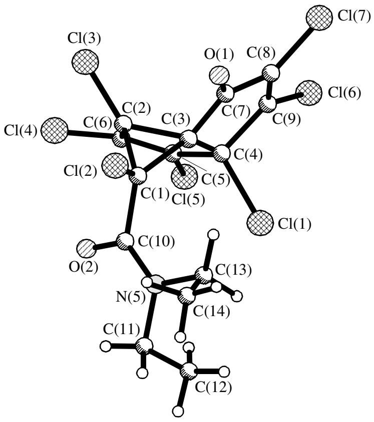
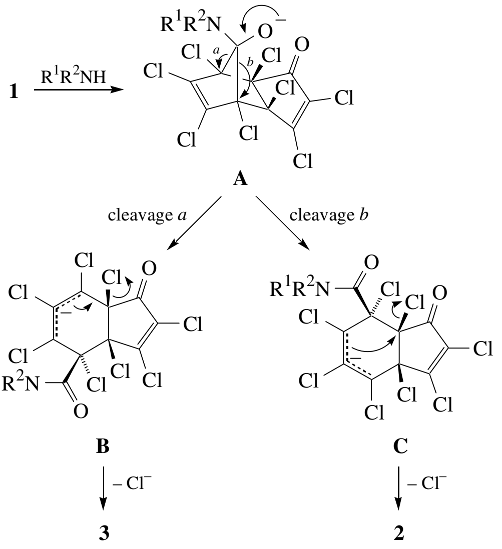


Figure 1 Molecular structure of compound **2c**.

The possible mechanism of the formation of tricycles (compounds **2a–h**) and dihydroindenones **3a**,**e**,**h** can be expressed as follows: firstly, the 1,2-addition of an amine to the sterically more available (and active) CO group of diketone **1** takes place. The opening of a bridge bond *a* in aminal **A** generates allylic carbanion **B**, which is stabilised by elimination of carbonyl activated *sp*^{3}-Cl thus producing **3**. Alternative opening *b* in **A** gives regioisomeric carbanion **C**. Its analogous stabilization by elimination of *sp*^{3}-Cl results in the formation of cyclopropanes



Scheme 2 Mechanism of product formation.

[†] *Crystallographic data for* **2c**: at 110 K, the crystals of **2c** ($C_{14}H_{10}Cl_7NO_2$) are monoclinic, space group $P2_1/c$, $a = 10.443(2)$ Å, $b = 11.847(2)$ Å, $c = 15.696(3)$ Å, $\beta = 109.25(3)°$, $V = 1837.56(6)$ Å^3, $M = 472.38$, $d_{calc} = 1.708$ g cm^{-3}, μ(MoKα) = 10.88 cm^{-1}, $F(000) = 944$; at 298 K. Intensities of 11007 (for **2c**) reflections were measured with a Siemens P3/PC diffractometer at 298, [λ(MoKα) = 0.71072 Å, $2\theta < 60°$], and 5373 independent reflections were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.0929$ and GOF = 0.996 for all independent reflections [$R_1 = 0.0348$ was calculated against F for 4156 observed reflections with $I > 2\sigma(I)$] for **2c**. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 204555. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2003.

2. Concerning the formation of perchloroindenones **4b**,**c**,**e**,**h**, the known aromatization of **1** may be mentioned.[5]

Table 1 Reactions of tetrachlorocyclopentadienone dimer **1** with amines.[‡]

Entry	Amine R^1, R^2	Method	Time/h	Yield of product (%)		
				2	**3**	**4**
a	H, Me	B	4	30	30	
b	Me, Me	B	3	40	—	20
c	Et, Et	A	2	50	—	10
d	Pr, Pr	A	4	40	—	—
e	H, c-C_6H_{11}	A	8	35	13	16
f	$(CH_2)_4$	A	3	54	—	—
g	$(CH_2CH_2)_2O$	A	3	42	—	—
h	$(CH_2CH_2)_2NMe$	A	8	35	22	< 3

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[‡] *General procedure A*. A solution (5 ml) of diketone **1** (1 mmol) and an amine (3–4 mmol) in benzene (8 ml) was stirred at 20 °C for an appropriate time (Table 1, TLC monitoring). The reaction mixture was diluted with chloroform, washed with brine, dried ($MgSO_4$), filtered and stripped of the solvent. The oily residue was separated by chromatography on silica gel (EtOAc–PE, 1:10).

General procedure B. An amine hydrochloride (3.45 mmol) was added to a stirred suspension of KOH (0.19 g, 3.45 mmol) in benzene (5 ml) at 20 °C. After stirring for 15 min, diketone **1** (0.5 g, 1.15 mmol) in benzene (3 ml) was added, and the mixture was stirred at room temperature for an appropriate time (Table 1, TLC monitoring) and treated as described in Procedure A.

The NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 (^{1}H) or 75.47 MHz (^{13}C) in $CDCl_3$ with TMS as a standard. Mass spectra were recorded on a Varian MAT CH-5 (70 eV) spectrometer. IR spectra were recorded on Specord M-80 and UR-20 (in Vaseline oil).

endo-*2,3,3a,4,5,6,7,7a-Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione* **1**. White crystals, mp 160–162.5 °C (light petroleum, lit.,[1] 157–163 °C). ^{13}C NMR ($CDCl_3$) δ: 72.87, 74.78 and 77.83 (3a-C, 4-C, 7-C, 7a-C), 130.93 and 131.39 (5-C, 6-C), 139.19 (2-C), 155.97 (3-C), 179.57 (1-C=O), 180.78 (8-C=O). IR (ν/cm^{-1}): 1588 (C=C), 1750, 1840 (C=O).

(1R*,4R*,8S*,9R*)-*1,2,3,4,5,6,9-Heptachloro-9-(diethylcarboxamido)-tricyclo[6.1.0.0^{4,8}]nona-2,5-dien-7-one* **2c**. Colourless crystals, mp 174–176 °C (EtOAc–light petroleum, 1:10). ^{1}H NMR, δ: 1.09 (t, 3H, Me, ^{3}J 7.1 Hz), 1.22 (t, 3H, Me, ^{3}J 7.0 Hz), 3.14 and 3.63 (each qd, 1H, CH_2N, ^{3}J 7.0 Hz, ^{2}J 14 Hz), 3.25 and 3.43 (each qd, 1H, CH_2N, ^{3}J 7.1 Hz, ^{2}J 14 Hz). ^{13}C NMR, δ: 11.68 and 12.89 (2Me), 40.39 and 44.68 ($2NCH_2$), 49.51 (8-C), 60.38 (9-C), 60.94 (1-C), 76.46 (4-C), 127.68 (6-C), 136.78 and 136.89 (2-C, 3-C), 157.37 (5-C), 159.27 (C=O amide), 179.58 (7-C). MS (EI), m/z: 477, 475, 473, 471, 469 $[M]^+$ (100%), 462, 460, 458, 456, 454 $[M - Me]^+$, 440, 438, 436, 434 $[M - Cl]^+$, 414, 412, 410, 408 $[M - Cl - C_2H_4]^+$, 100 $[Et_2N{-}C{\equiv}O]^+$, 72 $[Et_2N]^+$. IR (ν/cm^{-1}): 1590, 1610 (C=C), 1660 (C=O amide), 1740 (C=O). Found (%): C, 35.16; H, 2.10; Cl, 51.86; N, 2.80. Calc. for $C_{14}H_{10}Cl_7NO_2$ (%): C, 35.59; H, 2.13; Cl, 52.53; N, 2.96.

(1R*,4R*,8S*,9R*)-*1,2,3,4,5,6,9-Heptachloro-9-cyclohexylcarboxamido-tricyclo[6.1.0.0^{4,8}]nona-2,5-dien-7-one* **2e**. White needles, mp 188–190 °C (EtOAc–light petroleum, 1:5). ^{1}H NMR, δ: 1.15–1.36 (m, 5H), 1.58–1.68 (m, 3H) and 1.84–1.96 (m, 2H, $5CH_2$), 3.68–3.78 (m, 1H, CH), 6.24 (d, 1H, NH, J 7.5 Hz). ^{13}C NMR, δ: 24.53, 25.25, 31.93 and 32.42 ($5CH_2$), 49.22 (8-C), 49.89 (CH), 59.99 (1-C), 60.28 (9-C), 75.72 (4-C), 127.96 (6-C), 136.02, 136.79 (2-C, 3-C), 157.45 (5-C), 158.75 (C=O amide), 179.55 (7-C). IR (ν/cm^{-1}): 1580, 1608 (C=C), 1664 (C=O-amide), 1708 (C=O).

(1R*,4R*,8S*,9R*)-*1,2,3,4,5,6,9-Heptachloro-9-(pyrrolidincarboxamido)-tricyclo[6.1.0.0^{4,8}]nona-2,5-dien-7-one* **2f**. Colourless crystals, mp 180–182 °C (EtOAc–light petroleum, 1:10). ^{1}H NMR, δ: 1.60–2.05 (m, 4H, $2CH_2$), 3.25 (dt, 1H, J 7.7 Hz) and 3.50–3.75 (m, 3H, $2CH_2N$). ^{13}C NMR, δ: 23.54 and 25.88 ($2CH_2$), 47.09 and 48.38 ($2NCH_2$), 48.29 (8-C), 60.02 and 60.74 (1-C, 9-C), 76.13 (4-C), 127.43 (6-C), 136.62 and 136.89 (2-C, 3-C), 157.18 (5-C), 157.41 (C=O amide), 179.45 (7-C). IR (ν/cm^{-1}): 1580, 1608 (C=C), 1664 (C=O amide), 1708 (C=O). Found (%): C, 35.90; H, 1.52; Cl, 52.85; N, 2.66. Calc. for $C_{14}H_8Cl_7NO_2$ (%): C, 35.75; H, 1.71; Cl, 52.76; N, 2.98.

(1R*,2R*)-*1,2,3,4,5,8,9-Heptachloro-2-[(4-methylpiperazin)carboxamido]-bicyclo[4.3.0]nona-3,5,8-trien-7-one* **3h**. Red crystals, mp 202–204 °C (decomp.) (EtOAc–light petroleum, 1:5). ^{1}H NMR, δ: 2.31 (s, 3H, Me), 2.56 (m, 4H, $2NCH_2$), 3.58 (t, 4H, $2NCH_2$, J 4.8 Hz). ^{13}C NMR, δ: 46.02 (Me), 51.48 and 55.19 ($4NCH_2$), 53.85 (1-C), 77.20 (2-C), 124.95 (8-C), 127.93 (6-C), 128.01 (5-C), 135.53 (3-C), 136.19 (4-C), 137.78 (9-C), 159.19 (C=O-amide), 181.25 (7-C). IR (ν/cm^{-1}): 1460, 1584, 1612 (C=C), 1660 (C=O-amide), 1700 (C=O). MS (EI), m/z: 496, 498, 500, 502, 504 $[M]^+$. Found (%): C, 36.30; H, 2.20; Cl, 49.28; N, 5.30. Calc. for $C_{15}H_{11}Cl_7N_2O_2$ (%): C, 36.07; H, 2.22; Cl, 49.69; N, 5.61.

2,4,5,6,7-Pentachloro-3-diethylaminoinden-1-one **4c**. Dark-red needles, mp 189–190 °C (EtOAc–light petroleum, 1:10). ^{1}H NMR, δ: 1.22 (t, 6H, 2Me, J 7.1 Hz), 3.56 (q, 2H, CH_2, J 7.1 Hz). ^{13}C NMR, δ: 13.62 (Me), 46.85 (NCH_2), 113.55 (2-C), 124.98 (4-C), 127.83 (8-C, 9-C), 135.28 (7-C), 136.57 (6-C), 137.84 (5-C), 159.98 (3-C), 181.77 (1-C). IR (ν/cm^{-1}): 1460, 1580 (C=C), 1695 (C=O). Found (%): C, 42.10; H, 2.61; Cl, 47.93; N, 4.01. Calc. for $C_{13}H_{10}Cl_5NO$ (%): C, 41.81; H, 2.70; Cl, 47.46; N, 3.75.