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# Lewis acid-induced rearrangement of the Diels–Alder dimer of tetrachlorocyclopentadienone: structure reassignments

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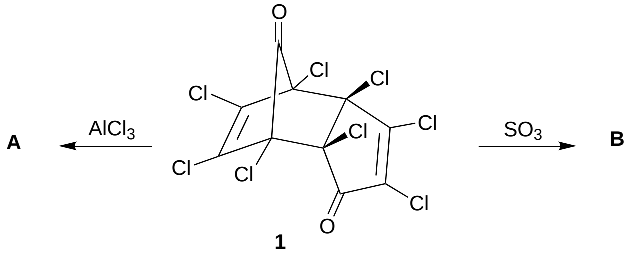
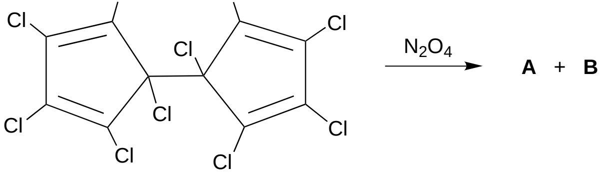
**Abstract**—The structures of various perhalodiones available by isomerization of the Diels–Alder dimers of tetrachloro- and tetrabromocyclopentadienone have finally been determined unambiguously. © 2001 Elsevier Science Ltd. All rights reserved.

The Diels–Alder dimer (*endo*-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione, **1**) of tetrachlorocyclopentadiene is rearranged on treatment with aluminum chloride to a single (∼95%) isomeric compound **A** (mp 190°C). Treatment of **1** with liquid sulfur trioxide gives **A** and another, but very similar, isomer **B** (mp 280°C, dec.), favoring the latter by about 3:1. Antimony pentafluoride rearranges **1** into a roughly equal mixture of **A** and **B**. Neither isomer under any of these reaction conditions is converted to the other.[1]



**1**

Optical spectroscopic analysis, all that was easily available at the time of the original work, made it clear that both **A** and **B** were without the strained bridged carbonyl group of the starting material and had instead only α,β-unsaturated ketone chromophores. Structures **2** and **3** were tentatively assigned to **A** and **B** (or vice versa) based entirely on a proposed mechanism for the Lewis acid-induced rearrangements, as shown in Scheme 1.[2] Structures **2** (to **A**) and **3** (to **B**) have also been assigned by Scribner (again tentatively, even with more evidence) to the products of reaction of **4**, decachlorobis(cyclopentadienyl), with dinitrogen tetraoxide.[3]



**4**

We have affirmed the gross 5-4-5 tricyclo[5.3.0.0$^{2,6}$]decane ring skeleton of **A** and **B** by $^{13}$C NMR spectroscopy;[4] each compound has only five pairs of magnetically different carbons. But no firm decision can be made from these data regarding the relative positions of the carbonyl groups (head-to-head versus head-to-tail) or of the *syn*/*anti* relation of the five-membered rings about the central cyclobutane.

Padwa et al. reported that isomer **A**, but not **B**,[5] can be photoisomerized to a new isomer. They assigned it structure **5** based primarily on $^{13}$C NMR and dipole moment data. As this isomerization is readily reversed thermally, **A** was assigned the *cis,syn,cis* and head-to-head geometry of structure **6**.[6] However, as we show here, these assignments are not correct.

We have now determined unambiguously, using single-crystal X-ray analysis, that **A** and **B** are both in the *cis,anti,cis* series, as originally assigned, and have structures **2** and **3**, respectively.[7]

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*Keywords*: tetrachloro- and tetrabromocyclopentadienone dimers; Lewis acid-induced and photochemical rearrangements; tricyclo-[5.3.0.0$^{2,6}$]- and tricyclo[4.2.1.1$^{2,5}$]decanes.

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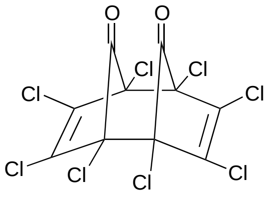
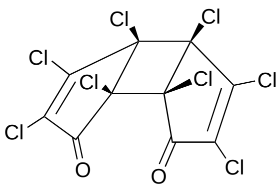
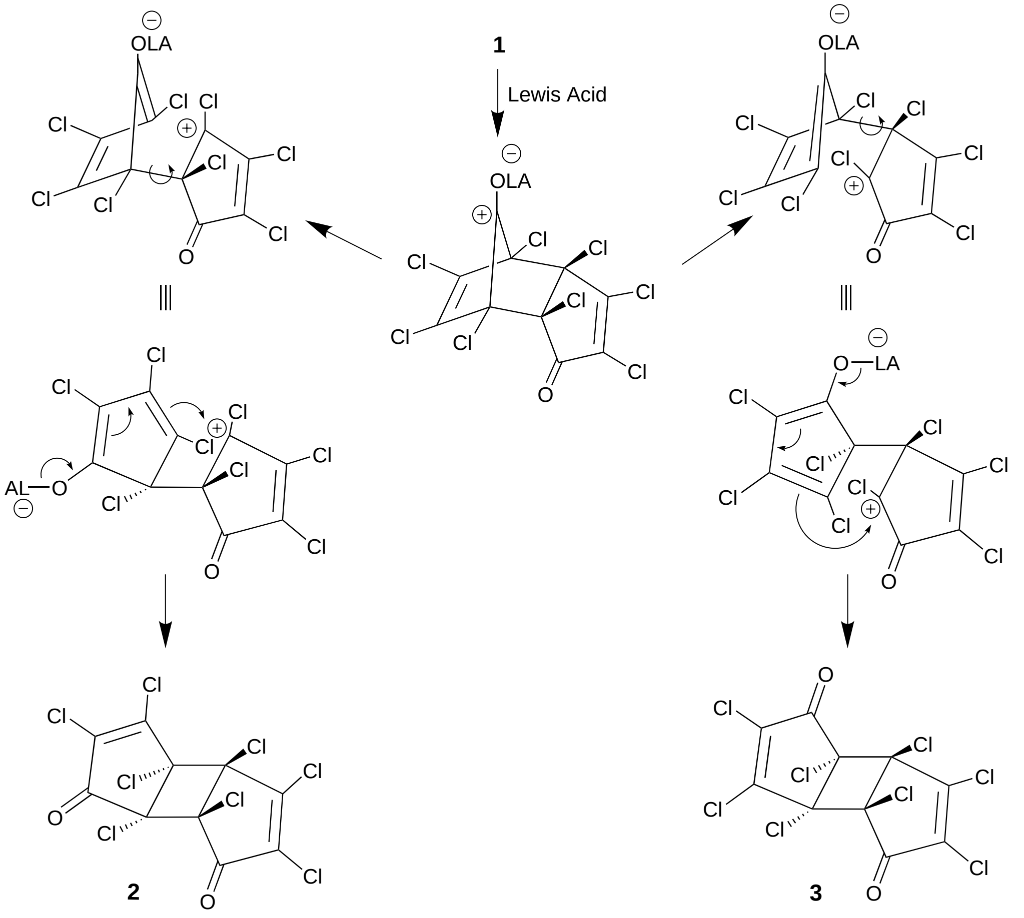


**5**

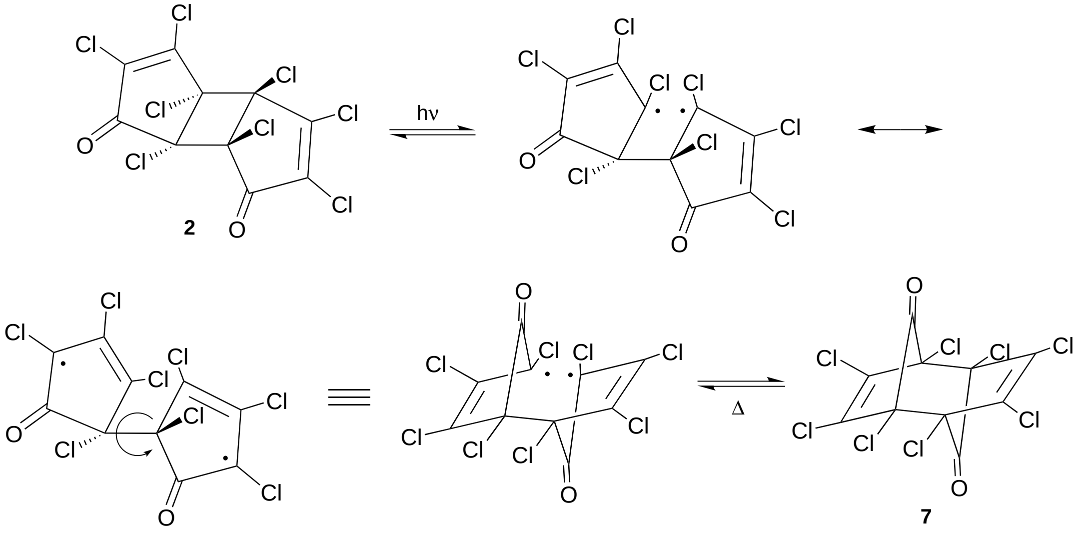


**6**

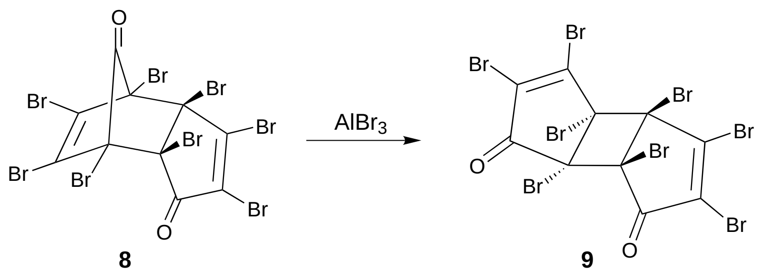
We have repeated the photoisomerization of **A** reported by Padwa et al. and have isolated the same product (mp and $^{13}$C NMR comparisons). Single-crystal X-ray analysis shows definitively that this product is the head-to-tail, centrosymmetric diketone **7**,[8] rather than the previously proposed head-to-head isomer **5**. The photochemical/thermal 'connection' between **2** and **7** is apparent in Scheme 2.



**Scheme 1.**



**Scheme 2.**



**8** **9**

We have found that octabromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione **8**, the Diels–Alder dimer of tetrabromocyclopentadienone, is also rearranged by treatment with Lewis acids. Both $AlBr_3$ and $SO_3$ give in good yield the *cis,anti,cis* diketone **9**;[9] its structure has been confirmed by single-crystal X-ray analysis.

## Acknowledgements

This work was supported by the US Army Research, Development and Engineering Center at Picatinny and the Office of Naval Research, Mechanics Division. We thank Drs. R. G. Pews and W. L. Dilling for generously providing a large sample of hexabromocyclopentadiene.

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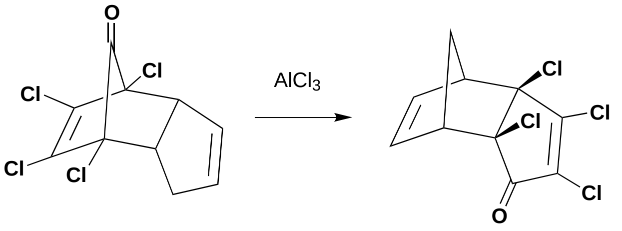
1. Eaton, P. E. Ph.D. Thesis, Harvard University, 1960.
2. Cf.: Yates, P.; Eaton, P. *Tetrahedron* **1961**, *12*, 13.



3. Scribner, R. M. *J. Org. Chem.* **1965**, *30*, 3657.
4. $^{13}C$ NMR (100 MHz, $CDCl_3$) **A**: $\delta$ 183.0, 159.7, 138.0, 76.5, 70.3 ppm; **B**: $^{13}C$ NMR $\delta$ 183.6, 160.3, 137.9, 73.6, 73.5 ppm.
5. The photochemical relationships between cyclopentadienone dimers are different in the hydrogen series. See: (a) Eaton, P. E.; Cole, T. W., Jr. *J. Chem. Soc., Chem. Commun.* **1970**, 1493; (b) Eaton, P. E.; Cerefice, S. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1494.
6. Padwa, A.; Masaracchia, J.; Mark, V. *Tetrahedron Lett.* **1971**, *34*, 3161.
7. Crystal data for **2**: Monoclinic space group $P2_1/c$, with $a=14.580(6)$, $b=13.504(5)$, $c=7.496(3)$ Å, $\beta=90.12(2)°$, $V=1476(1)$ Å$^3$, $Z=4$. $R=0.068$, $wR_2=0.121$ for all 2753 unique reflections. Crystal data for **3**: Orthorhombic space group *Cmca*, with $a=7.588(2)$, $b=13.624(3)$, $c=13.759(4)$ Å, $V=1422.5(6)$ Å$^3$, $Z=4$. $R=0.0440$ and $wR_2=0.0667$ for all 816 unique reflections.
8. $^{13}C$ NMR (100 MHz, $CDCl_3$) **7**: $\delta$ 180.4, 137.4, 77.4 ppm. Crystal data for **7**: triclinic space group $P$-1, with $a=8.3376(9)$, $b=9.318(1)$, $c=10.046(1)$ Å, $\alpha=90.182(2)$, $\beta=97.580(2)$, $\gamma=115.452(2)°$, $V=697.0(1)$ Å$^3$, $Z=2$. $R=0.0724$ and $wR_2=0.0980$ for all 2822 unique reflections.
9. $^{13}C$ NMR (100 MHz, $CDCl_3$) **9**: $\delta$ 184.8, 159.1, 132.0, 71.9, 61.9 ppm. Crystal data for **9**: Monoclinic space group $P2_1/c$, with $a=16.809(3)$, $b=13.626(3)$, $c=14.784(3)$ Å, $\beta=90.235(12)°$, $V=3386(1)$ Å$^3$, $Z=8$. $R=0.0621$ and $wR_2=0.1548$ for all 4621 unique reflections. Additional crystallographic data (excluding structure factors) for **2**, **3**, **7**, and **9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC172252-172255, respectively. Copies can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].