

Unexpected Formation of a 1,2-Dichloroacenaphthylene in a Friedel-Crafts Reaction with Chloral Hydrate

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An unprecedented rearrangement was encountered during an attempted alkylation of an electron-rich naphthalene with chloral hydrate. The reaction produced a dichlorinated acenaphthylene and presumably involves the intermediate formation of a chloronium ion which is opened to produce the five-membered ring of the final product.

Key words: Electrophile, Rearrangement,
X-Ray Crystallography, Cyclization

Introduction

Halonium ions have been proposed as reactive intermediates in electrophilic halogenation reactions of olefins and helped to explain the observed stereochemistry of these reactions. The first direct experimental evidence for their existence was the isolation of a sterically hindered bromonium salt by Olah [1] and later on an X-ray crystallographic analysis by Brown [2]. Due to the shorter bond lengths, the higher electronegativity and the lower polarizability of the lighter halogens, chloronium ions are higher in energy than bromonium ions [3] while fluoronium ions have never been seriously discussed as true reaction intermediates. In an attempt to react an electron-rich naphthalene with chloral hydrate under Brønsted acidic conditions [4], a

symmetrical product was isolated in appreciable yield which turned out to be a 1,2-dichloroacenaphthylene. Its formation suggests the intermediate formation of a chloronium ion in the elimination of water from the protonated α -(trichloromethyl)alcohol.

Results and Discussion

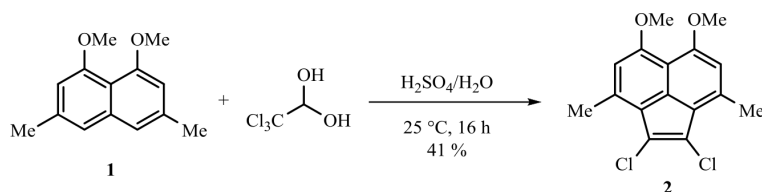
The reaction of 1,8-dimethoxy-3,6-dimethylnaphthalene [5] (**1**) with chloral hydrate in the presence of concentrated sulfuric acid leads to the formation of 1,2-dichloro-5,6-dimethoxy-3,8-dimethylacenaphthylene (**2**) in 41 % yield (Scheme 1).

The reaction mechanism presumably involves the formation of 1-aryl-2,2,2-trichloroethanol **3** which is subsequently protonated and eliminates water under formation of benzyl cation **4** which produces chloronium ion **5**. This is opened in a 1,2-migration of a chlorine atom, and under electrophilic substitution of the electron-rich peri-position of the naphthalene ring, the trichlorinated tricyclic **6** is formed. Acid-induced dehydrochlorination finally gives 1,2-dichloro-5,6-dimethoxy-3,8-dimethylacenaphthylene (**2**) (Scheme 2).

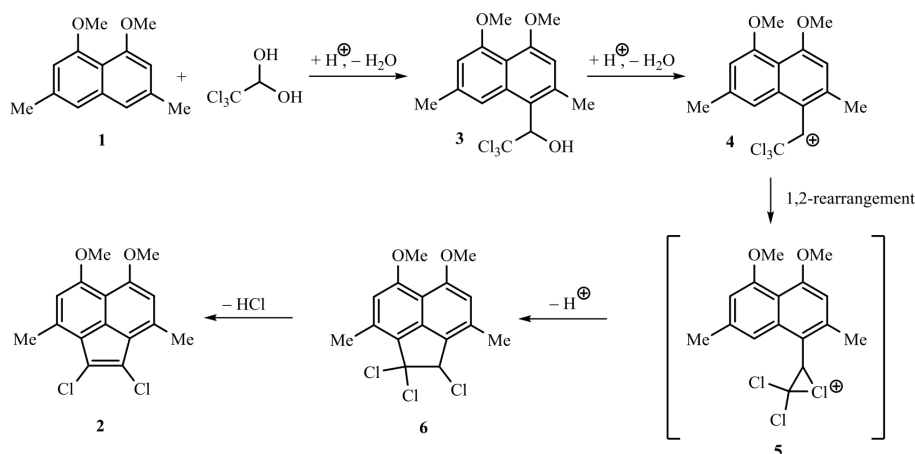
The product was characterized by elemental analysis, IR, MS, ^1H NMR, ^{13}C NMR and HMBC spectra and by X-ray crystallography (Fig. 1). Attempts to obtain similar dichloroacenaphthylenes from other aromatic systems such as 1,8-dihydroxy-3,6-dimethylnaphthalene (**7**), 5,8-dimethyl-2,2-di(propan-2-yl)naphtho[1,8-*de*][1,3,2]dioxasiline (**8**) or 1,8-bis(benzoyloxy)-3,6-dimethylnaphthylene (**9**) were unsuccessful (Scheme 3).

Experimental Section

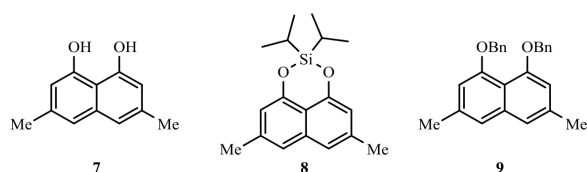
Flash chromatography was performed on silica gel 60 (0.035–0.070 mm, Acros). Chromatography solvents (cyclohexane, EtOAc) were distilled prior to use. For analytical TLC, Merck silica gel aluminum sheets (60 F₂₅₄) were used. Visualization was accomplished by illuminating with UV light (254 nm). ^1H and ^{13}C NMR spectra were recorded on Bruker AC 300 and AV 400 instruments in CDCl_3 , using the residual solvent peak as internal reference ($\delta_{\text{H}} = 7.26$,



Scheme 1. Reaction of 1,8-dimethoxy-3,6-dimethylnaphthalene (**1**) with chloral hydrate.



Scheme 2. Postulated mechanism of the acenaphthylene formation.



Scheme 3. Naphthalenes with which no formation of dichloroacenaphthylenes was observed.

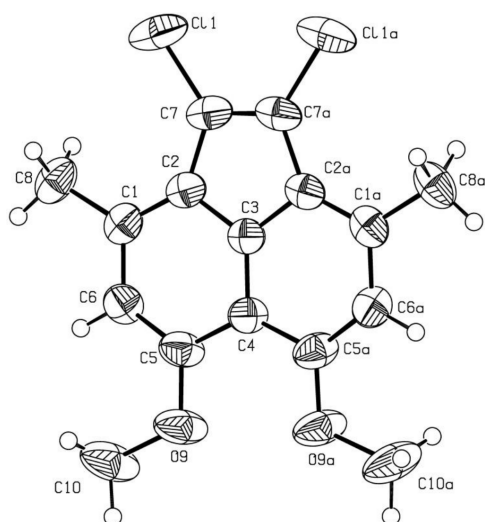


Fig. 1. ORTEP plot of 1,2-dichloro-5,6-dimethoxy-3,8-dimethylacenaphthylene (**2**) with crystallographic atom labeling adopted. Compound **2** exhibits crystallographic C_2 and nearly molecular C_{2v} symmetry. (Displacement ellipsoids at the 50% probability level for atoms refined anisotropically; hydrogen atoms with arbitrary radii; symmetry code (a) $y, x, -z$).

$\delta_C = 77.16$ ppm). An IR spectrum was recorded on a ThermoNicolet Avatar 370 FT-IR spectrometer. The

Table 1. Crystal structure data for compound **2**.

Formula	$C_{16}H_{14}Cl_2O_2$
M_r	309.2
Crystal size, mm^3	$0.22 \times 0.3 \times 0.5$ (yellow block)
Crystal system	trigonal
Space group	$P3_121$ (hexagonal setting)
$a = b$, Å	15.638(1)
c , Å	4.8780(5)
V , Å ³	1033.0(3)
Z	3
D_{calcd} , $g\ cm^{-3}$	1.49
$\mu(MoK\alpha)$, cm^{-1}	4.7
$F(000)$, e	480
hkl range	$\pm 20, \pm 20, \pm 6$
$((\sin \theta)/\lambda)_{max}$, Å ⁻¹	0.66
Refl. measured / unique / R_{int}	8304 / 1667 / 0.0418
Param. refined	94
$R(F) / wR(F^2)$ (all refl.) ^{a,b}	0.052 / 0.0932
GoF (F^2) ^c	1.080
x (Flack)	-0.01(9)
$\Delta\rho_{fin}$ (max / min), $e\ \text{\AA}^{-3}$	0.2 / -0.28

^a $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; ^b $wR = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{w}$, $w = [\sigma^2(F_o^2) + (0.0309P)^2 + 0.3825P]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.

FD mass spectrum was recorded on a Finnigan-MAT 95 spectrometer from ThermoElectron, Boston (USA).

1,2-Dichloro-5,6-dimethoxy-3,8-dimethylacenaphthylene (**2**)

1,8-Dimethoxy-3,6-dimethylnaphthalene (**1**) (70 mg, 0.32 mmol) and chloral hydrate (79 mg, 0.48 mmol, 1.5 eq.) were dissolved in a mixture of conc. sulfuric acid and water (57 : 3) [4]. After the mixture was stirred at r. t. for 16 h, ice (5 g) was added, and the mixture was extracted twice with dichloromethane (10 mL). The organic layer was dried over sodium sulfate, and all volatiles were evaporated under

reduced pressure. After purification by flash chromatography (silica gel, cyclohexane-ethylacetate, 5 : 1), compound **2** was obtained as yellow crystals. Yield: 41 mg, 0.13 mmol, 41 %. M. p.: 208.3–210.1 °C. – IR: $\nu = 2996, 2923, 2844, 1609, 1462, 1364, 1285, 1210, 1181, 1100, 838 \text{ cm}^{-1}$. – $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 6.66$ (s, 2H, H_{ar}), 4.02 (s, 6H, 2OCH₃), 2.78 (s, 6H, 2 CH₃). – $^{13}\text{C NMR}$, HMBC (75.5 MHz, CDCl_3): $\delta = 158.7$ (C-5, C-6), 137.9 (C-3, C-8), 127.6 (C-8b), 124.0 (C-1, C-2), 122.7 (C-2a, C-8a), 110.1 (C-5a), 109.6 (C-4, C-7), 56.4 (2 OCH₃), 19.3 (2 CH₃). – FD-MS (pos.): $m/z = 308.3$ [M]⁺. – C₁₆H₁₄Cl₂O₂ (309.19): calcd. C 62.15, H 4.56; found C 62.16, H 4.60.

X-Ray structure determination

The data set for compound **2** was collected with a Bruker Smart CCD diffractometer. Important crystallographic data

are summarized in Table 1. Programs used: Data collection: APEX2 [6]; cell refinement: SAINT [6]; structure solution: SIR97 [7]; refinement: SHELXL-97 [8]; molecular graphics and software used to prepare material for publication: PLATON [9].

CCDC 856602 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] G. A. Olah, P. Schilling, P. W. Westerman, H. C. Lin, *J. Am. Chem. Soc.* **1974**, *96*, 3581–3589.
- [2] H. Slebocka-Tilk, R. G. Ball, R. S. Brown, *J. Am. Chem. Soc.* **1985**, *107*, 4504–4508.
- [3] V. I. Teberekidis, M. P. Sigalas, *Tetrahedron* **2003**, *59*, 4749–4756.
- [4] E. H. Charlesworth, R. Robinson, *J. Chem. Soc.* **1934**, 1531–1533.
- [5] J. C. Overeem, G. J. M. van der Kerk, *Rec. Trav. Chim. Pays-Bas* **1964**, *83*, 1005–1022.
- [6] APEX2, SAINT, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2006**.
- [7] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. C. Moliterni, G. Polidori, R. Spagna, SIR97, A Program for the Automatic Solution of Crystal Structures by Direct Methods; see: *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
- [8] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.
- [9] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2010**. See also: A. L. Spek, *J. Appl. Crystallogr.* **2009**, *D65*, 148–155.