

Table 1. ¹H- and ¹³C-NMR data of the triquinacenyl cations at -70°C.

| | ¹ H-NMR (τ) in SO ₂ ClF | | | ¹³ C-NMR (δ) in SO ₂ ClF [a] | | |
|-----------------------------|--|---|---|---|--|--|
| | (7d) ≡ (2) | (8d) | (9d) | (7d) ≡ (2) | (8d) | (9d) |
| Pentadienyl unit | 0.95 (A-part; H ³ , H ⁸) | 1.02 (A-part; H ⁸) 1.43 (A-part; H ³) | 1.50 (A-part; H ³ , H ⁸) | 252.97 (C ¹) 195.15 (C ³ , C ⁸) | 243.68 (C ¹) 195.61 (C ⁸) | 237.03 (C ¹) |
| | 2.13 (B-part; H ² , H ⁹) of an AB system | 2.04 (B-part; H ²) 2.06 (B-part; H ⁹) of an AB system | 2.00 (B-part; H ² , H ⁹) | 137.86 (C ² , C ⁹) | 183.28 (C ³) 138.70 (C ⁹) 138.42 (C ²) | 183.92 (C ³ , C ⁸) 132.38 (C ² , C ⁹) |
| Olefinic positions | 4.17 (s, H ⁵ , H ⁶) | 3.99 (A-part; H ⁵) 4.19 (B-part; H ⁶) | 4.00 (s, H ⁵ , H ⁶) | 134.33 (C ⁵ , C ⁶) | 132.69 (C ⁵) 133.83 (C ⁶) | 132.28 (C ⁵ , C ⁶) |
| Central bridgehead position | 4.48 (m, H ¹⁰) | 4.38 (d, H ¹⁰) | 4.40 (s, H ¹⁰) | 77.67 (C ¹⁰) | 84.55 (C ¹⁰) | 91.69 (C ¹⁰) |
| Allylic positions | 5.46 (m, H ⁴ , H ⁷) | 5.22 (m, H ⁷) | | 56.48 (C ⁴ , C ⁷) | 56.46 (C ⁷) 73.61 (C ⁴) | 72.29 (C ⁴ , C ⁷) |

[a] Relative to tetramethylsilane.

(9e). A "dehydrotriquinacene"^[6] (tricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene and/or tricyclo[5.2.1.0^{4,10}]deca-1(2),3,5,8-tetraene) must occur as an intermediate; the chlorides (4), (5), (6), and especially the dimethylaminotriquinacene (7c), may be considered as potential precursors of this class of compounds.

For the generation and investigation of free carbocations of the triquinacene system all three chlorides (4), (5), and (6) were allowed to react with antimony pentafluoride in sulfuryl chloride fluoride at -78°C and the ¹H- and ¹³C-NMR spectra of the reaction mixture were recorded (see Table 1). According to these, only the monocations (7d) [≡(2)], (8d), and (9d), respectively, were present in each case. Their kinetic stability increases with increasing chlorine substitution; thus (7d) already decomposes at -40°C, whereas (9d) is still detectable spectroscopically even after 15 min at 25°C. Trapping experiments with sodium methoxide in methanol led to the methyl ethers (7b), (8b), and (9b), respectively, in good yields.

The ¹H- and ¹³C-NMR spectroscopic data of the free carbenium ions show that almost planar divinylcarbenium ion units are present in these species. Increasing chlorine substitution in (8d) and (9d) leads to a lowering of the electron deficit in the divinylcarbenium ion units and thus to high-field shifts of the ¹H- and ¹³C-NMR signals.

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(1), 6053-74-3; (2), 59983-40-3; (4), 59991-76-3; (5), 59991-77-4; (6), 59991-78-5; (8d), 59991-79-6; (9d), 59991-80-9; tert-butyl hypochlorite, 507-40-4

- [1] T. Jacobsen, Acta Chem. Scand. 21, 2235 (1967); C. Mercier, P. Soucy, W. Rosen, and P. Deslongchamps, Synth. Commun. 3, 161 (1973).
[2] E. D. Stevens, J. D. Kramer, and L. A. Paquette, J. Org. Chem. 41, 2266 (1976).
[3] P. Bischof, Angew. Chem. 88, 609 (1976); Angew. Chem. Int. Ed. Engl. 15, 556 (1976).
[4] The ¹H-NMR, ¹³C-NMR, and mass spectra as well as elemental analysis of all the new compounds are in agreement with the given structures.
[5] See also: K. B. Wiberg, R. K. Barnes, and I. Albin, J. Am. Chem. Soc. 79, 4994 (1957).
[6] A perchlorotriacyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene was detected by T. Jacobsen, Chem. Ser. 5, 174 (1974).

Cleavage of Allyl Ethers with Pd/C^[**]

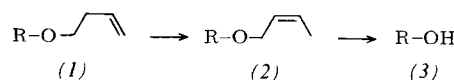
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Allyl ethers (1) are to a large extent stable under basic and acid conditions. Because of this property the allyl group

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is often used as protecting group for alcohols. Removal of the protecting group is usually effected by isomerization of the allyl ether to the corresponding enol ether (2) with subsequent H⁺ or Hg²⁺[¹] catalyzed hydrolysis or oxidative cleavage^[2].



Since the known methods^[3] for allyl ether cleavage did not lead to the alcohol (9a) in the case of the glycidonitrile allyl ether (9) we investigated the heterogeneously catalyzed isomerization of allyl ethers to *cis*-enol ethers. We found palladium/activated charcoal to be a particularly suitable catalyst for this purpose^[4].

If isomerization is carried out under conditions favoring hydrolysis of the *cis*-enol ethers the cleavage products alcohol and propionaldehyde are obtained directly. Since both the catalyst as well as the propionaldehyde (b.p. 49°C) can be separated very easily this allyl ether cleavage is very useful (cf. examples in Table 1). That the allyl protecting group can be selectively removed besides other protecting groups is illustrated by the examples glycerol 1-allyl 2,3-dibenzyl ether (7).

The allyl ether to be cleaved is heated for a few hours at 60° to 80°C in a mixed solvent (see Table 1) in the presence of a trace of *p*-toluenesulfonic acid or mineral acid (e.g. perchloric acid) and a catalytic amount of palladium on activated charcoal^[5]. In the case of sensitive substrates, e.g. the glycidonitrile (9), the cleavage can be carried out over a prolonged period of time (up to ca. 6 days) at room temperature.



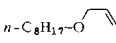



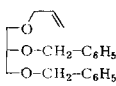
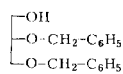
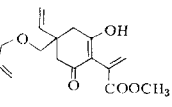
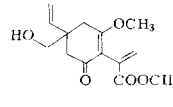
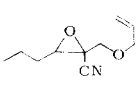
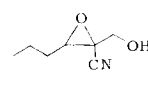
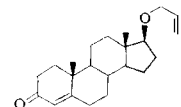
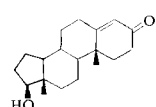
Using this method 2,5-dihydrofuran can be cleaved smoothly in methanol/water to 4-hydroxybutanol, while 3-methoxycyclohexene remains unchanged under comparable conditions. This finding would suggest that a *cisoid* conformation of the allyl ether partial structure is a prerequisite for the palladium-catalyzed isomerization^[3].

Experimental

Glycerol 1,2-dibenzyl ether (7a): A solution of (7) (1.00 g, 3.2 mmol) in methanol (10 ml) and water (2 ml) is treated with palladium/activated charcoal (0.1 g) and toluenesulfonic acid (0.1 g). The resulting suspension is boiled under reflux with stirring for 24 hours. After removal of catalyst by centrifugation the solution is extracted with ether, the solvent removed in a rotary evaporator, and the residue distilled. The yield of (7a) (b.p. 150°C/0.05 torr^[2]) is 0.85 g (97%).

Methyl 2-(4-hydroxymethyl-2-methoxy-6-oxo-4-vinyl-1-cyclohexenyl)acrylate (8a): To a solution of (8) (3.9 g, 13.3 mmol) in anhydrous methanol (170 ml) is added palladium/

Table 1. Converted allyl ethers.

| Allyl ether | Reaction conditions [a] | Product | Yield [%] [b] |
|--|---|--|---------------|
| (4)  | Pd/C methanol/H ₂ O/H ⁺ 6 h reflux | (4a)  | > 95 |
| (5)  | Pd/C methanol/H ₂ O/H ⁺ 6 h reflux | (5a)  | > 95 |
| (6)  | Pd/C H ₂ O/H ⁺ 6 h 80 °C | (6a)  | > 95 |
| (7)  | Pd/C methanol/H ₂ O/H ⁺ 24 h reflux | (7a)  | > 95 |
| (8)  | Pd/C anhydrous methanol/TsOH 20 h reflux | (8a)  | 84 |
| (9)  | Pd/C dioxane/H ₂ O/H ⁺ 6 days room temperature | (9a)  | 78 |
| (10)  | Pd/C ethanol/H ₂ O/H ⁺ 3 h reflux | (10a)  | 84 |

[a] Where not stated otherwise perchloric acid in concentrations of 1 to 5 mmol/ether was used as acid (H⁺).

[b] The yields refer to isolated material.

activated charcoal (0.6 g) and *p*-toluenesulfonic acid (0.3 g) and the stirred suspension boiled under reflux for 20 hours. After removal of the catalyst by filtration, the filtrate is concentrated to half its original volume in a rotary evaporator, treated with saturated NaCl solution and ice, and extracted five times with dichloromethane. After removal of solvent in a rotary evaporator there remains a pale yellow oil which crystallizes on drying in a high vacuum. Melting point after a single recrystallization from ether: 87 to 89 °C. Yield 3.0 g (84 %).

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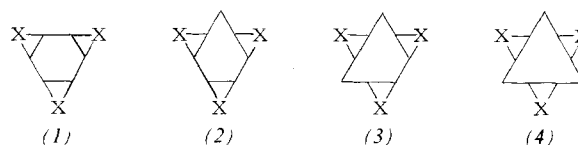
(4), 1746-13-0; (4a), 108-95-2; (5), 3295-97-4; (5a), 111-87-5; (6), 123-34-2; (6a), 56-87-5; (7), 59991-88-7; (7a), 59991-89-8; (8), 59991-90-1; (8a), 59991-91-2; (9), 59991-92-3; (9a), 59991-93-4; (10), 20860-14-4; (10a), 58-22-0; palladium 7440-05-3

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 [4] We used the hydrogenation catalyst 10 % palladium on activated charcoal obtainable from Fluka. Experiments with rhodium on activated charcoal also gave positive results; ruthenium and platinum on activated charcoal proved less useful. This is in agreement with the finding that palladium proves to have the greatest tendency for shifting double bonds in hydrogenations. Cf. also P. N. Rylander, *Adv. Chem. Ser.* 98, 150 (1971).
 [5] As is to be expected the allyl cleavage is blocked by traces of "catalyst poisons" such as thiophenol and potassium cyanide. It is therefore recommended that the reaction vessel be cleaned with chromic sulfuric acid, washed with potassium hydroxide solution, and finally rinsed with demineralized water.

Synthesis of *cis*-Trioxa-tris- σ -homotropilidene^[**]

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Preparative and mechanistic objectives stimulated extension of our work on the tris- σ -homobenzenes (1) (X=CR₂, O, NR, S)^[1] to investigation of the homologs (2)–(4). After having recently described the first valence isomeric σ/π -hexahomobenzenes (4)^[2], we now report the dioxa-bis- and trioxa-tris- σ -homotropilidenes (2) (X=O)^[3].



Mainly because of our particular interest in the stereoelectronic features of valence isomerization in the *cis*-trioxide (10), we have commenced our study program in this area with an investigation of the chances and stereoselectivity of a stepwise epoxidation of tropilidene. On reaction of excess peroxy acid (peroxyacetic acid, *m*-chloroperoxybenzoic acid) with the readily accessible oxide (5)^[4] in dichloromethane/Na₂CO₃ the four dioxides (6)–(9) are formed, whereby the dioxide (6) is, according to a capillary-GC/MS analysis, the least favored product (total yield of products up to 40 %, ratio in a typical experiment *ca.* 6:26:27:41). Preparative gas chromatography affords pure (7) and a mixture of (8)/(9)

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