This file is a part of the Rhodium site archive. This Aug 2004 static snapshot is hosted by Erowid as of May 2005 and is not being updated. >> Back to Rhodium Archive Index >>

REACTIONS OF BETA-ASARONE

RAO ET.AL., J. CHEM. SOC. 1338 (1937)

HTML by Rhodium

It was recorded (*Kelkar and Rao, J. Indian Inst. Sci., 1934, 17, A, 26*) that the main constituent of the oil from the roots of Acorus Calamus, Linn. was a liquid phenolic ether, which gave asaronic acid on oxidation with potassium permanganate and polymerised to par-asarone on treatment with arsenious acid. The ether, which differed from asarone, $C_6H_2(OMe)_3CH=CHMe$, in that it could not be obtained crystalline, was at first regarded as the allyl isomer (*Current Sci., 1935, 552*), but asarone and this liquid ether, β -asarone, are now shown to be *cis/trans*-isomerides.

This conclusion is based mainly upon the following considerations:

- **1.** Reduction of the two isomerides yields 2,4,5-trimethoxypropylbenzene, giving on nitration 4-nitro-2,5-dimethoxypropenylbenzene
- **2.** On bromination, asarone gives a crystalline dibromide, mp 82-83°C, whereas β-asarone yields a liquid dibromide with a trace of a crystalline dibromide, mp 82-83°C, identical with that prepared from asarone (*Széki, Ber., 1906, 39, 2420*); from both dibromides the same diasarone monobromide, mp 101°C, can be prepared.
- **3.** Oxidation of the two asarones with mercuric acetate in ethereal solution gives two glycols (compare *Balbiano*, *Gazzetta*, 1906, 36, [i], 283) which on distillation under diminished pressure yield 2,4,5-trimethoxy-β-ketopropylbenzene and a crystalline compound, C₂₄H₃₂O₈, mp 204-205°C; the latter substance is formed also if the glycols are digested with acetic anhydride.
- **4.** With nitrous acid both asarones give asarone-pseudonitrosite and 2,4,5-trimethoxynitrobenzene, the identity of the former being confirmed by the preparation from it of 2,4,5-trimethoxyphenylmethylglyoxime peroxide and β-nitroasarone (*Bruckner*, *J. Prakt. Chem.*, 1933, 136, 268).

PHYSICAL	PROPERTIES	ΟF	ASARONE	ISOMERS

Isomer	mp	bp _{12mm}	d30°/30°	n _D ^{20°}	[RL]D
Asarone	62-63°C	167-168°C	1.112	1.5683	62.7
β-Asarone		162-163°C	1.082	1.5552	62.2

β-Asarone can be converted into asarone by fusion with potassium hydroxide at 210-220°C or by heating in alcoholic solution with a small quantity of selenium dioxide for 30 min. If the heating is prolonged, a complex mixture of products is formed from which 2,5-dimethoxy- propenylbenzene has been isolated. Other reagents, which usually cause isomerisation, had no action.

No deduction as to configuration can safely be drawn from these figures, for Auwers (*Ber.*, 1935, 68, 1346) has shown that the Auwers-Skita rule does not hold for styrenes.

EXPERIMENTAL:

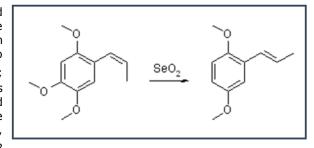
 β -Asarone, separated from calamus oil by repeated fractionation, was a pale yellow oil having the constants given above. The colour was not removed by evaporation in a Hickmann still at 70-80°. As with asarone, concentrated hydrochloric acid gave a blue colour and caused polymerisation. If β -asarone (10g) was added gradually to potassium hydroxide (100g) and water (10ml) at 200°C and the temperature was

1 of 3 2008-09-21 09:52

slowly (15 min) raised to 220°C, acidification of the melt gave asarone, mp 62-63°C.

ACTION OF SELENIUM DIOXIDE ORE B-ASARONE

- (a) A mixture of β -asarone (70g), alcohol (100ml), and selenium dioxide (10g) was heated on the water-bath for 30 min. The filtered solution was poured into water, the oil dissolved in ether, and the dried ethereal extract evaporated; the residue partly crystallised, and distillation gave asarone (60g).
- **(b)** A mixture of β-asarone (20g), alcohol (50 ml), and selenium dioxide (5g) was boiled for 5 hours. The product isolated by ether in the usual manner gave an oil, which on distillation under 8 mm. gave two fractions: **(i)** bp 140-145°C, d30° 1.052, nD^{30°} 1.5451; **(ii)** bp 145-150°C. From the former, a picrate was prepared, crystallising from alcohol in orange-red feathery leaflets, mp 87°C Decomposition of the picrate with alkali gave 2.5-dimethoxypropenylbenzene, bp128-129°C/4mmHg, d30°/30° 1.041, nD^{30°} 1.5548 The nitrosite, mp 118°C was a pale yellow powder.



Reduction of the ether with sodium and alcohol gave 2,5-dimethoxypropylbenzene, characterised by the preparation of the nitro-derivative, mp 64°C.

REDUCTION OF BETA-ASARONE

β-Asarone (10 g.) in alcohol (150 ml.) was reduced with sodium (10g), the recovered ether being treated twice more with sodium under similar conditions. 2,4,5-Trimethoxypropylbenzene, so obtained, had bp 128°C/6 mmHg, d30°/30° 1.024, n_D^{30} ° 1.5079, and a product having the same constants was obtained by the reduction of asarone. The identity of the two ethers was confirmed by nitration to 4-nitro-2,5-dimethoxypropylbenzene, mp 64°C.

BROMINATION OF B-ASARONE

To β-asarone (5g) in dry ether (20ml) cooled to -20°C, bromine (4g) in carbon disulphide (6ml) was added. Removal of the solvent gave a crystalline dibromide (0.4g), mp 82-83°C, the main product being an oil. Bromination of asarone under similar conditions gave a solid dibromide (7g), mp 82-83°C. To a solution of the solid or liquid dibromide (5 g.) in dry benzene (150 ml), cooled in ice, copper powder was added, and the mixture kept for 24 hours. The filtered solution was concentrated, whereupon diasarone monobromide (1.5 g.), mp 123°C, crystallised, the yield being the same from both dibromides. Reduction of the monobromide in alcoholic solution with zinc dust gave diasarone, mp 100-101°C (compare Széki, loc. cit., p. 2423).

ACTION OF NITROUS ACID ON B-ASARONE

To a cooled (ice-salt) solution of β -asarone (5 g.) in ether (50 ml.) containing sodium nitrite (20 g.) in suspension, sulphuric acid (20%; 30 ml.) was added during 5 hours. After standing overnight, the crystalline asarone pseudonitrosite (3g), decomp. 130°C, which had separated, was collected. Digestion of the pseudonitrosite with methyl alcohol gave 2,4,5-trimethoxyphenylmethylglyoxime peroxide, mp 155°C; and by the action of alcoholic potassium hydroxide β -nitroasarone, mp 101°C, was obtained. Evaporation of the ethereal solution from which the pseudonitrosite had separated gave a resin (1.2g), which crystallised from alcohol in needles, mp 130°C, identified as 2,4,5-trimethoxynitrobenzene. The same derivatives, in approximately similar yields, were prepared also from asarone.

ACTION OF MERCURIC ACETATE ON B-ASARONE

β-Asarone (25g) in ether (200 ml.) was mixed with a solution of mercuric acetate (100g) in water (400 ml). After 24 hours standing at room temperature with occasional shaking, 75 g. of mercurous acetate had separated, and 12g more separated after a further 12 hours, the ethereal layer, which was initially yellow, having then become colourless. The ether was separated, and the aqueous solution extracted twice with chloroform. The combined residue (26g), remaining after the evaporation of the solvents, contained some dissolved mercury salts. The mercury was removed with hydrogen sulphide, and β-2,4,5-trimethoxyphenyl-3-methylethylene glycol, a viscid oil, after remaining for some days in a vacuum, had d50°/4° 1.218, $n_{\rm D}^{50°}$ 1.5330. The diacetate was obtained when the glycol (5g), acetic anhydride (25ml), and phosphoric acid (0.3 ml) was kept below 40° for 2 h. After removal of the acetic anhydride and a small quantity of the bimolecular compound, mp 204-205°C (see below).

2 of 3

On distillation of the glycol under 4 mm., a red oil, bp 170-230°, was obtained, which solidified. Trituration with ether left undissolved a substance which crystallised from alcohol in rhombic prisms, mp 204-205°C. This substance was obtained in quantitative yield on digestion of the glycol with acetic annhydride. Evaporation of the ether from which the dimeride had been separated left an oil which partly crystallised. After purification through its semicarbazone, mp 157-158°C, 2,4,5-trimethoxy- β -ketopropylbenzene mp 47-48°C, was obtained. Treatment of asarone with mercuric acetate under similar conditions gave an isomeric glycol, d50°/4° 1.228, np $^{50°}$ 1.5415, which gave on distillation the dimeridc, mp 204-205°C, and 2,4,5-trimethoxy- β -ketopropylbenzene.

3 of 3 2008-09-21 09:52