

270.  $\beta$ -Asarone.

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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 parasarone on treatment with arsenious acid. The ether, which differed from asarone,  $C_6H_2(OMe)_3 \cdot CH:CHMe$ , 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,  $\beta$ -asarone, are now shown to be *cis-trans*-isomerides.

This conclusion is based mainly upon the following considerations : (i) Reduction of the two isomerides yields 2 : 4 : 5-trimethoxypropylbenzene, giving on nitration 4-nitro-2 : 5-dimethoxypropylbenzene. (ii) On bromination, asarone gives a crystalline dibromide, m. p. 82—83°, whereas  $\beta$ -asarone yields a liquid dibromide with a trace of a crystalline dibromide, m. p. 82—83°, identical with that prepared from asarone (Széki, *Ber.*, 1906, **39**, 2420) ; from both dibromides the same diasarone monobromide, m. p. 101°, can be prepared. (iii) 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- $\beta$ -ketopropylbenzene and a crystalline compound,  $C_{24}H_{32}O_8$ , m. p. 204—205° ; the latter substance is formed also if the glycols are digested with acetic anhydride. (iv) With nitrous acid both asarones give asarone- $\psi$ -nitrosite and 2 : 4 : 5-trimethoxynitrobenzene, the identity of the former being confirmed by the preparation from it of 2 : 4 : 5-trimethoxyphenylmethylglyoxime peroxide and  $\beta$ -nitroasarone (Bruckner, *J. pr. Chem.*, 1933, **136**, 268).

$\beta$ -Asarone can be converted into asarone by fusion with potassium hydroxide at 210—220° or by heating in alcoholic solution with a small quantity of selenium dioxide for  $\frac{1}{2}$  hour. If the heating is prolonged, a complex mixture of products is formed from which 2 : 5-dimethoxypropenylbenzene has been isolated. Other reagents, which usually cause isomerisation, had no action.

The isomerides have the following physical constants :

	M. p.	B. p.	$d_{30}^{30}$ .	$n_D^{20}$ .	$[R_L]_D$ .
Asarone .....	62—63°	167—168°/12 mm.	1.112	1.5683	62.7
$\beta$ -Asarone .....	—	162—163°/12 mm.	1.082	1.5552	62.2

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 in the styrene series.

#### EXPERIMENTAL.

$\beta$ -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  $\beta$ -asarone (10 g.) was added gradually to potassium hydroxide (100 g.) and water (10 c.c.) at 200° and the temperature was slowly (15 mins.) raised to 220°, acidification of the melt gave asarone, m. p. 62—63°.

*Action of Selenium Dioxide on  $\beta$ -Asarone.*—(a) A mixture of  $\beta$ -asarone (70 g.), alcohol (100 c.c.), and selenium dioxide (10 g.) was heated on the water-bath for  $\frac{1}{2}$  hour. 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 (60 g.).

(b) A mixture of  $\beta$ -asarone (20 g.), alcohol (50 c.c.), and selenium dioxide (5 g.) 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) b. p. 140—145°,  $d_{30}^{30}$  1.052,  $n_D^{30}$  1.5451; (ii) b. p. 145—150°. From the former, a *picrate* was prepared, crystallising from alcohol in orange-red feathery leaflets, m. p. 87° (Found: N, 10.1.  $C_{11}H_{14}O_2, C_6H_3O_7N_3$  requires N, 10.3%). Decomposition of the picrate with alkali gave 2 : 5-dimethoxypropenylbenzene, b. p. 128—129°/4 mm.,  $d_{30}^{30}$  1.041,  $n_D^{30}$  1.5548 (Found: C, 74.3; H, 7.8. Calc. for  $C_{11}H_{14}O_2$ : C, 74.1; H, 7.9%). The *nitrosite*, m. p. 118°, was a pale yellow powder (Found: N, 10.8.  $C_{11}H_{14}O_5N_2$  requires N, 11.0%). Reduction of the ether with sodium and alcohol gave 2 : 5-dimethoxypropylbenzene, characterised by the preparation of the nitro-derivative, m. p. 64°.

*Reduction of  $\beta$ -Asarone.*— $\beta$ -Asarone (10 g.) in alcohol (150 c.c.) was reduced with sodium (10 g.), the recovered ether being treated twice more with sodium under similar conditions. 2 : 4 : 5-Trimethoxypropylbenzene, so obtained, had b. p. 128—128°/6 mm.,  $d_{30}^{30}$  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, m. p. 64° (Found: N, 6.4. Calc. for  $C_{11}H_{15}O_4N$ : N, 6.2%).

*Bromination of  $\beta$ -Asarone.*—To  $\beta$ -asarone (5 g.) in dry ether (20 c.c.) cooled to  $-20^\circ$ , bromine (4 g.) in carbon disulphide (6 c.c.) was added. Removal of the solvent gave a crystalline dibromide (0.4 g.), m. p. 82—83°, the main product being an oil. Bromination of asarone under similar conditions gave a solid dibromide (7 g.), m. p. 82—83° (Found: Br, 43.1. Calc. for  $C_{12}H_{16}O_3Br_2$ : Br, 43.4%). To a solution of the solid or liquid dibromide (5 g.) in dry benzene (150 c.c.), 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.), m. p. 123°, crystallised, the yield being the same from both dibromides. Reduction of the monobromide in alcoholic solution with zinc dust gave diasarone, m. p. 100—101° (compare Széki, *loc. cit.*, p. 2423).

*Action of Nitrous Acid on  $\beta$ -Asarone.*—To a cooled (ice-salt) solution of  $\beta$ -asarone (5 g.) in ether (50 c.c.) containing sodium nitrite (20 g.) in suspension, sulphuric acid (20% ; 30 c.c.) was added during 5 hours. After standing overnight, the crystalline asarone- $\psi$ -nitrosite (3 g.), decomp. 130°, which had separated, was collected (Found: N, 10.1. Calc. for  $C_{12}H_{16}O_6N_2$ : N, 9.8%). Digestion of the  $\psi$ -nitrosite with methyl alcohol gave 2 : 4 : 5-trimethoxyphenylmethylglyoxime peroxide, m. p. 155° (Found: N, 10.2. Calc. for  $C_{12}H_{14}O_5N_2$ : N, 10.5%); and by the action of alcoholic potassium hydroxide  $\beta$ -nitroasarone, m. p. 101°, was obtained.

Evaporation of the ethereal solution from which the  $\psi$ -nitrosite had separated gave a resin (1.2 g.), which crystallised from alcohol in needles, m. p. 130°, identified as 2 : 4 : 5-trimethoxy-nitrobenzene. The same derivatives, in approximately similar yields, were prepared also from asarone.

*Action of Mercuric Acetate on  $\beta$ -Asarone.*— $\beta$ -Asarone (25 g.) in ether (200 c.c.) was mixed with a solution of mercuric acetate (100 g.) in water (400 c.c.). After 24 hours' standing at room temperature with occasional shaking, 75 g. of mercurous acetate had separated, and 12 g. more separated after a further 12 hours, the ethereal layer, which was initially yellow, having then be-

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come colourless. The ether was separated, and the aqueous solution extracted twice with chloroform. The combined residue (26 g.), remaining after the evaporation of the solvents, contained some dissolved mercury salts. The mercury was removed with hydrogen sulphide, and  $\alpha$ -2 : 4 : 5-trimethoxyphenyl- $\beta$ -methylethylene glycol, a viscid oil, after remaining for some days in a vacuum, had  $d_4^{20}$  1.218,  $n_D^{20}$  1.5330 (Found: C, 59.1; H, 7.6.  $C_{12}H_{18}O_5$  requires C, 59.5; H, 7.4%). The diacetate was obtained when a mixture of the glycol (5 g.), acetic anhydride (25 c.c.), and phosphoric acid (0.3 c.c.) was kept below 40° for 2 hours. After removal of the excess of acetic anhydride and a small quantity of the bimolecular compound, m. p. 204—205° (see below), the liquid diacetate was analysed [Found: OAc, 23.3.  $C_{14}H_{16}O_5(OAc)_2$  requires OAc, 23.9%].

On distillation of the glycol under 4 mm., a red oil, b. p. 170—230°, was obtained, which solidified. Trituration with ether left undissolved a substance which crystallised from alcohol in rhombic prisms, m. p. 204—205° [Found: C, 63.6; H, 7.6;  $M$  (in dioxan), 460.  $C_{24}H_{32}O_8$  requires C, 64.3; H, 7.1%;  $M$ , 448]. This substance was obtained in quantitative yield on digestion of the glycol with acetic anhydride. Evaporation of the ether from which the dimeride had been separated left an oil which partly crystallised. After purification through its semicarbazone, m. p. 157—158° (Found: N, 14.7. Calc. for  $C_{13}H_{19}O_4N_2$ : N, 14.9%), 2 : 4 : 5-trimethoxy- $\beta$ -ketopropylbenzene, m. p. 47—48°, was obtained.

Treatment of asarone with mercuric acetate under similar conditions gave an isomeric glycol,  $d_4^{20}$  1.228,  $n_D^{20}$  1.5415, which gave on distillation the dimeride, m. p. 204—205°, and 2 : 4 : 5-trimethoxy- $\beta$ -ketopropylbenzene.

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