

ASARYLALDEHYDE

BY

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Asarylaldehyde, 2 : 4 : 5-trimethoxybenzaldehyde, $C_6H_2 \cdot CHO \cdot (OCH_3)_3$ [1 : 2 : 4 : 5], was first prepared by Rizza and Butlerow¹⁾ by careful oxidation of asarone, 1-propenyl-2 : 4 : 5-trimethoxybenzaldehyde, $C_6H_2 \cdot CH : CH \cdot CH_3$ [1] $(OCH_3)_3$ [2 : 4 : 5], with potassium permanganate. Asarone can be obtained from calamus oil, the oil, which passes over when *Acorus Calamus* is distilled in steam.

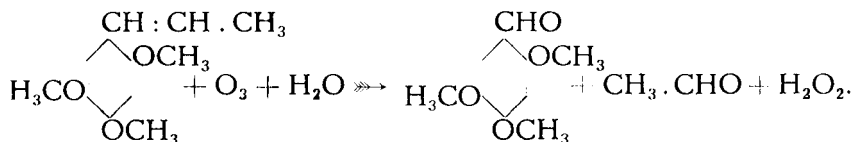
Since the aldehyde is easily oxidised further by the permanganate, to the corresponding acid the yield varies considerably and as a rule is not great. A repetition of the method, which according to Rizza gives the largest yield of aldehyde, gave bad results.

a. Preparation.

A mixture of 5 gr. powdered asarone and 7.5 gr. powdered potassium permanganate was slowly added to 750 cc. boiling water. Subsequently, the pale yellow liquid was filtered hot from the manganese peroxide and the latter washed with boiling water.

On cooling, the filtrate was extracted with ether, the ether distilled off and the residue recrystallised from water. In this way 0.6 gr. pale yellow coloured asarylaldehyde was obtained, m.p. 114° .

Asarylaldehyde was prepared in better yield by the ozonisation of asarone and subsequent fission of the ozonide formed with water.



For this purpose 5 gr. asarone were dissolved in 100 cc. dry chloroform and oxygen containing ozone (60 mgr. per litre) passed at a rate of 14 litres per hour, through the solution, which was cooled externally in ice. The ozone was completely absorbed and after 20 litres of gas (the theoretical quantity) had been passed through the solution, the gas issuing from the apparatus gave a strong blue colour with a moist starch-potassium iodide paper.

The chloroform solution of the ozonide was now shaken for four

¹⁾ J. Russ. Phys. Chem. Soc. **19**, 2 (1887); Ber. **20**, ref. 222 (1887); Gattermann, Ber. **32**, 289 (1899); Fabinyi and Szeki, Ber. **50**, 1339 (1917); Alessandri, Centr. 1915, 1, 1210.

hours with pieces of ice and calcium carbonate and the two layers separated.

The aqueous layer clearly smelt of acetaldehyde and after filtration, with an acetic acid solution of *p*-nitrophenylhydrazine it gave a yellow precipitate, m.p. $128^{\circ}.5$ ²⁾, which was not altered by mixing with acetaldehyde *p*-nitrophenylhydrazine.

By evaporation of the chloroform and recrystallisation of the residue from water, 3 gr. asarylaldehyde were obtained in fine white needles, melting at 114° alone or mixed with the aldehyde obtained by Rizza's method.

The ozonisation can be carried out also in dry ethyl acetate instead of chloroform, in which case the yield is somewhat larger. If relatively more asarone is taken the yield does not increase in the same ratio; thus 15 gr. asarone furnished only 5 gr. aldehyde.

b. Derivatives.

The oxime, m.p. 137° ³⁾, the azine, m.p. 263° ⁴⁾, the semicarbazone m.p. 205° — 206° ⁵⁾ and the phenylhydrazone, m.p. 120° — 121° ⁶⁾, of asarylaldehyde are known.

The two following derivatives have now been made;

a. Semioxamazone.

Solutions of asarylaldehyde (0.7 gr.) in 15 cc. alcohol and semioxamamide, $H_3N \cdot CO \cdot CO \cdot NH \cdot NH_2$ (0.4 gr.), in 30 cc. boiling water were mixed. The precipitate so formed weighed 1 gr., was insoluble in alcohol and dissolved with difficulty in boiling water, from which it was recrystallised. It was obtained in very pale yellow, felty needles m.p. 249° — 250° with decomposition.

Analysis: 0.1162 gr. gave 14.4 cc. N_2 at 13° and 768.6 mm.; N = 14.7%.
 $C_{12}H_{14}O_5N_3$ requires N = 14.9%.

b. *p*-Nitrophenylhydrazone.

p-Nitrophenylhydrazine (0.7 gr.) dissolved in 10 cc. 50% acetic acid was added to asarylaldehyde (0.5 gr.) dissolved in 10 cc. alcohol and the precipitate, which was insoluble in water, furnished red needles, melting at 234° , when recrystallised from alcohol.

Analysis: 0.1272 gr. gave 14.2 cc. N_2 at 13° and 742.4 mm.; N = 12.8%.
 $C_{17}H_{14}O_5N_3$ requires N = 12.7%.

Since the *p*-nitrophenylhydrazone is insoluble in water and crystallises well, it is exceptionally well suited for demonstrating asarylaldehyde and since asarone furnishes the aldehyde on ozonisation, this substance also can be identified by this means.

Freshly prepared calamus oil was investigated. This was prepared

²⁾ Hyde, Ber. **32**, 1813 (1899).

³⁾ Thoms and Beckstroem, ibid. **34**, 1023 (1901).

⁴⁾ Gattermann and Eggers, ibid. **22**, 290 (1899).

⁵⁾ Fabinyi and Szeki, ibid. **39**, 1212 (1906).

⁶⁾ Rizza and Butlerow, ibid. **20**, ref. 223 (1887).

by finely grinding the rhizomes of the common flag, *Acorus calamus*, which had been collected in January, mixing them with water and after standing overnight, submitting them to a distillation in steam. The distillate, in which drops of oil were suspended, was extracted with ether, the latter shaken with bisulphite solution, the bisulphite solution acidified with sulphuric acid and distilled in steam. No precipitate was produced on treating the distillate with *p*-nitrophenylhydrazine acetate. Thus freshly prepared calamus oil contains no asarylaldehyde⁷⁾.

The ethereal solution was dried with calcium chloride and evaporated. The calamus oil remaining behind contained asarone which was demonstrated as follows.

One gram of oil was introduced into 200 cc. boiling water and half a gram of powdered potassium permanganate added. The hot solution was filtered, the filtrate extracted with ether, the latter evaporated and the residue dissolved in a little alcohol. With *p*-nitrophenylhydrazine acetate a precipitate was produced, which melted at 234° when recrystallised from alcohol as did also a mixture with pure asarylaldehyde *p*-nitrophenylhydrazone.

The following method gave a better yield: 2 gr. oil were dissolved in 100 cc. dry chloroform and 5 litres ozonised oxygen (60 mgr. per litre) were passed through the solution. The ozone in the first four litres was completely absorbed. After working up the product as described for the ozonisation of asarone, when the odour of acetaldehyde was again clearly discernable, the asarylaldehyde was finally precipitated as its *p*-nitrophenylhydrazone (m.p. and mixed m.p. with pure asarylaldehyde *p*-nitrophenylhydrazone, 234°).

Asaronic acid is produced by oxidising asarylaldehyde⁸⁾. A mixture of 0.2 gr. aldehyde in 10 cc. water and 0.5 gr. potassium permanganate in 20 cc. water and 3 cc. 0.1 N-caustic soda was allowed to stand overnight. The solution was then decolourised with a little alcohol, filtered and the filtrate acidified, when asaronic acid, m.p. 144°⁹⁾ was precipitated after standing for one day.

c. Nitration of asarylaldehyde.

When half a gram asarylaldehyde was dissolved at 0° in 1 cc. absolute nitric acid, a brown colour and an evolution of gas were produced and no definite products could be isolated from the clear, yellow-brown, aqueous solution obtained on pouring the solution carefully on to ice.

The same result was obtained by dissolving the asarylaldehyde at -15° in a mixture of 0.5 cc. absolute nitric acid and 0.5 cc. strong sulphuric acid.

However, when 1 gr. aldehyde was dissolved in 8 cc. acetic anhydride at 0° and cooled to -10° the whole mass solidified. A

⁷⁾ Thoms and Beckström, loc. cit.

⁸⁾ Unlike benzaldehyde asarylaldehyde is stable in air.

⁹⁾ Rizza and Butlerow, loc. cit.

mixture of 4 cc. acetic anhydride and 0.5 cc. absolute nitric acid also cooled to -10° was then slowly added when a gas was evolved, which burned with the characteristic blue flame of carbon monoxide. Meanwhile the mass liquefied and solidified again while the temperature remained continually below -5° . On pouring on to 100 gr. ice there was produced a yellow precipitate, which was filtered off and recrystallised from alcohol, when it melted at 130° .

Analysis: 0.1872 gr. gave 9.8 cc. N_2 at 13° and 749.4 mm.; $N = 6.1\%$.
 $C_9H_{11}O_5N$ requires $N = 6.6\%$.

The compound is 1-nitro-2 : 4 : 5-trimethoxybenzene, the nitro group having displaced the aldehyde group ¹⁰⁾.



The same product was obtained by Fabinyi and Szeki ¹¹⁾ by nitrating asaronic acid in glacial acetic acid, the carboxyl group being displaced.

Attempts to prepare the corresponding benzoin derivative by warming 1 gr. asarylaldehyde in 5 cc. alcohol with 0.2 gr. potassium cyanide in 1 cc. water in a sealed tube in a boiling water bath for either one or five hours gave no result, unchanged aldehyde being recovered.

Summary of Results.

Oxidation of asarone with potassium permanganate gives only a small yield of asarylaldehyde. This aldehyde can be prepared in greater yields by making the ozonide of asarone and splitting the latter with water. Acetaldehyde is obtained as the second fission product. Like the oxidation of asarone the ozonisation furnishes a result, which shows that the side chain has the structure of the propenyl group, $-\text{CH} : \text{CH} \cdot \text{CH}_3$. However, while several examples of migration of the double bond are known in oxidation methods used for determining its position, this is seldom the case in ozonisations, where the temperature remains continuously in the neighbourhood of 0° ¹²⁾. Therefore, results obtained by the latter method are most reliable.

On nitrating asarylaldehyde in absolute nitric acid the substance

¹⁰⁾ For more examples of this displacement of the aldehyde group by the nitro group see: M. P. de Lange, *Verdringing van atomen en groepen uit de benzolkern*, Diss. Leiden 1922; this Journal **45**, 19 (1926); L. Elion, *Vorming van nevenproducten bij de diazoteering volgens de methode van Witt*, Diss. Leiden 1922; this Journal **42**, 145 (1923).

¹¹⁾ Ber. **39**, 3679 (1906); **43**, 2676 (1910); **44**, 1479 (1911).

¹²⁾ See: Miss. A. C. Noorduyn, "*Plaatsbepaling en verschuiving van den dubbelband*", Diss. Leiden 1918; this Journal **38**, 317 (1919).

is completely disintegrated. By careful nitration in acetic anhydride at -10° , however, the aldehyde group is displaced with the production of 1-nitro-2:4:5-trimethoxybenzene.

The semioxamzone and *p*-nitrophenylhydrazone of asarylaldehyde were prepared. By means of the latter substance it could be shown that while, according to Thoms¹³⁾, calamus oil, which has been standing exposed to air contains asarylaldehyde, this is not the case with fresh calamus oil, the aldehyde being produced by oxidation of the oil.

Attempts to prepare the corresponding benzoin derivative from asarylaldehyde were unsuccessful.

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¹³⁾ loc. cit.