stirrer. The separated solid was collected on a glass fritt, pressed to remove excess H_2O and oil, and washed thoroughly with ether (2 × 100 ml). The air dried solid weighed 409 g. We found that in large scale preparations of this type, varying amounts of $NaHSO_3$ (10–40% of the collected solid) separated with the bisulfite adduct. Thus the weight of the collected solid cannot be used to calculate the yield of the adduct.

The adduct was decomposed by heating with 10% aqueous H_2SO_4 (1200 ml) to a gentle reflux for 3 h. The (+)3-thujone was isolated by separating the oil from the aqueous phase and exhaustively extracting the aqueous phase with ether (7 × 200 ml). The ether extracts and the separated oil were combined, washed with 5% Na_2CO_3 solution, H_2O, dried with Na_2SO_4, and evaporated. The weight of crude (+)3-thujone was 111.2 g. Distillation of the crude ketone gave 91.1 g (22.9% based on **1** available in the isomerized oil) of pure (99.9%+) (+)3-thujone, b.p. 40.9° (0.5 mm) uncorrected; $[\alpha]_D^{25}$ +78.8° (neat).

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Preparation of β-Cyclocitral

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An improved method for the preparation of pure β-cyclocitral by cyclization of citral anil with 95% sulfuric acid is reported. By avoidance of steam distillation of the reaction product, the formation of the by-products *p*-cymene and 1-acetyl-4,4-dimethyl-1-cyclohexene was prevented. The formation of this ketone by treatment of α- or β-cyclocitral anil with dilute sulfuric acid followed by steam distillation supports the mechanism proposed by Henbest *et al.*

On rapporte une méthode améliorée de préparation de β-cyclocitral pur basée sur la cyclisation de l'anil de citral en présence d'acide sulfurique à 95%. En évitant de faire un entraînement à la vapeur des produits de la réaction, on élimine la formation des produits secondaires *p*-cymène et acétyl-1 diméthyl-4,4 cyclohexène-1. La formation de cette cétone lors du traitement de l'anil de l'α ou du β-cyclocitral par de l'acide sulfurique dilué suivi par un entraînement à la vapeur d'eau corrobore le mécanisme proposé par Henbest *et al.*

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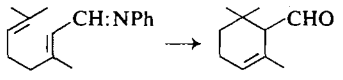
Introduction

β-Cyclocitral has been used as starting material in the synthesis of vitamin A and related compounds (1–4). The synthesis involves essentially the addition of two isoprene units to β-cyclocitral using two successive Reformatsky reactions with methyl 4-bromo-3-methylbut-2-enoate. One important disadvantage of this method is the lack of availability of pure β-cyclocitral.

β-Cyclocitral is most conveniently prepared by the cyclization of citral anil (**1**) with sulfuric acid at low temperatures (5–7). The accepted method consists of the reaction of citral anil (**1**) in ether with a large excess of 95% sulfuric acid at −20° followed by steam distillation of the product. Henbest *et al.* (6) have shown that under these conditions a mixture of three isomers is formed: α-cyclocitral (**2**), β-cyclocitral (**3**), and a ketone **4**



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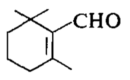

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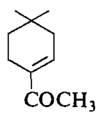


4

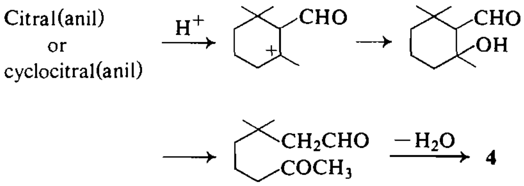
which was shown to be 1-acetyl-4,4-dimethyl-1-cyclohexene.

While α- and β-cyclocitral may be separated by fractional distillation, **3** and **4** have almost identical boiling points. The latter two compounds can be separated by conversion into semicarbazones followed by steam distillation in the presence of phthalic anhydride. Our investigations have indicated, however, that the recovery of pure β-cyclocitral by this method is only fair.

The present study has resulted in an improved method for the formation of pure β-cyclocitral from citral anil. According to Henbest *et al.* (6) the ketone **4** is probably formed during the steam distillation of the diluted product from the reaction of citral anil with sulfuric acid. By avoiding the use of steam distillation in the work-up procedure, we were able to obtain a mixture of α- and β-cyclocitral only from the cyclization in the ratio, 3 parts of α-cyclocitral to 1 part of the β-isomer. It was shown (using g.l.c.) that α-cyclocitral was rapidly converted to a mixture of approximately 8 parts of β-cyclocitral to 1 part of α-cyclocitral, when treated with methanolic KOH. It was also shown the formation of *p*-cymene, formed in about 10% yield, by the method of Henbest *et al.*, was avoided when steam distillation was not used.

It was observed that considerable quantities of black polymeric material were formed during the reaction of citral anil and sulfuric acid even at low temperature (−20°). The extent of polymer formation was reduced by conducting the reaction under nitrogen, with a resulting increase in the total yield of the α- and β-cyclocitrals from about 50% in air to 60% when nitrogen was used. It was also observed that, when conducted under nitrogen, the product was almost pure α-cyclocitral.

Henbest *et al.* (6) suggested the mechanism shown in Scheme 1 to explain the formation of the ketone **4** from citral anil, with hydration occurring at the steam distillation stage.



SCHEME 1

Our observation that the ketone was not formed when steam distillation was not used, would add support to this mechanism. Further support was offered by the observation that considerable amounts of ketone were formed when pure β-cyclocitral anil was refluxed with dilute sulfuric acid and then steam distilled. Under similar conditions α-cyclocitral anil also gave some ketone. A partial isomerization of α-cyclocitral to β-cyclocitral occurred during the steam distillation of the former in the presence of H_2SO_4. This is to be expected, since loss of a proton from the carbonium ion would result in the formation of a mixture of α- and β-cyclocitral.

Experimental

All melting points are uncorrected. The v.p.c. analysis was carried out using commercial (Varian Aerograph) 10 ft × 1/4 in. stainless steel columns containing the appropriate packing. Fractional distillations were carried out on an annular spinning band column, boiling points being uncorrected.

β-*Cyclocitral*

(*a*) Citral anil (from 76 g citral) in 75 ml ether was added dropwise to 95% sulfuric acid (500 g) at −20° during 30 min in a nitrogen atmosphere, and stirred for a further 45 min at −15°. The product was added to ice (1.5 kg) and extracted several times with ether. Distillation of the extracts gave a colorless liquid (43 g, 57%), b.p. 83–90°/13 mm. Gas chromatography on FFAP and Carbowax 20M showed only two peaks (area ratio 15:1) with relative retention times of 1 to 2 on FFAP and 1.7 to 3.0 on Carbowax 20M. Treatment of a sample with semicarbazide hydrochloride and sodium acetate in 50% aqueous ethanol gave α-cyclocitral semicarbazone, m.p. 202–203°; the other isomer formed in the cyclization was shown to be β-cyclocitral (when nitrogen was not used the cyclization yielded a mixture of 3 parts α- to 1 part β-cyclocitral in 48% yield, a larger amount of dark brown polymer being evident).

The crude α-cyclocitral (30 g) was treated with potassium hydroxide (10 g) in methanol (200 ml) at 0 °C for a few min. The mixture was diluted with water (500 ml), saturated with sodium chloride, and extracted with ether. Distillation of the extracts yielded a colorless liquid (21.6 g, 72%), b.p. 88–94°/12 mm which was shown by

TABLE 1. Physical data of fractions obtained from the cyclization of citral anil

Fraction	Boiling point (8 mm °C)	Weight (g)	n_D^{18}	λ_{max} (mμ)	Semicarbazone m.p. (°C)	% α	% β
1	60–62	1.5	1.4700	235	199–201	95	0
2	62–69	1.0	1.4831	—	—	40	45
3	69–73	1.0	1.4948	—	163–165	8	90
4	73–74	14.0	1.4944	275	165–167	0	99

gas chromatography to contain approximately 8 parts β-cyclocitral to 1 part of the α-isomer.

Fractional distillation of the product using the annular spinning band column gave the fractions listed in Table 1.

Gas chromatography on the FFAP column indicated the product ratios given in Table 1. No ketone semicarbazone was isolated from any of these fractions. The overall yield of pure β-cyclocitral was 25%.

(*b*) Citral anil was cyclized by the method of Henbest *et al.* (6). In agreement with the results of Henbest *et al.*, the products were *p*-cymene, α-cyclocitral, β-cyclocitral, and the ketone, 1-acetyl-4,4-dimethyl-1-cyclohexene, in the approximate ratio 2:6:10:1. The product of the steam distillation was analyzed using gas chromatography on the FFAP column. The ketone and β-cyclocitral were partially separated at 130° using FFAP. The identity of the products was confirmed by the melting points of their semicarbazones and their u.v. spectra.

Isomerization of α- *and* β-*Cyclocitral to 1-Acetyl-4,4-dimethyl-1-cyclohexene*

β-Cyclocitral (20 g) was refluxed with 50% sulfuric acid (200 ml) for 3 h and the product steam distilled. The distillate was extracted with ether and the ether evaporated. The residue was shown by gas chromatography on the FFAP column to consist of 60% ketone, 35% β-cyclocitral together with a small amount of α-cyclocitral and other unidentified products.

A similar reaction with α-cyclocitral and with α-cyclocitral anil was shown to give mainly β-cyclocitral together with smaller amounts of the ketone and some unchanged α-cyclocitral.

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Occurrence and Origin of the Tropylium Ion in the Mass Spectra of Arylboronic Acid Esters

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The mass spectra of a number of phenylboronic acid esters of 1,2- and 1,3-diols are examined and the presence and origin of the tropylium rearrangement ion is established.

On rapporte les spectres de masse d'un certain nombre d'esters dérivés de l'acide phénylboronique d'une part et de diols-1,2 et -1,3 d'autre part; on explique la présence et l'origine d'un ion tropylium.

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Increasing attention is being given to electron impact induced rearrangements involving the migration of atoms other than hydrogen (1, 2). Failure to recognize such skeletal rearrangements could lead to erroneous conclusions regarding the structures of unknown compounds. Conversely, a full understanding of the factors governing such rearrangements could provide useful stereochemical information.

The occurrence of the tropylium ($C_7H_7^+$, *m*/*e* 91) rearrangement ion is one of the most characteristic features of the mass spectra of aromatic