either a three-halves order or a second order formulation of this rearrangement, derivable from the donor-acceptor theory, will fit the facts better than the first-order formulation used by these authors.

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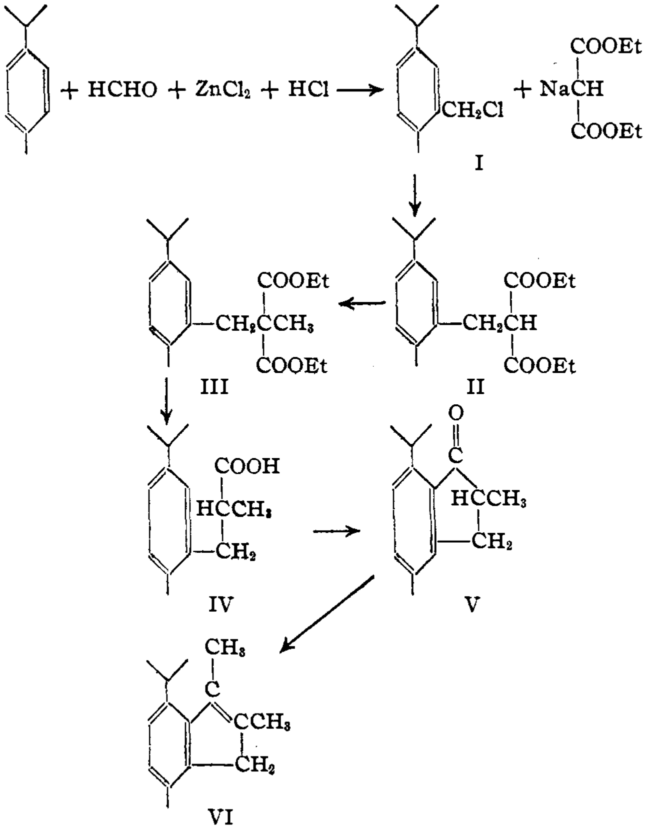
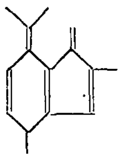
[CONTRIBUTION FROM THE NEW ZEALAND COÖPERATIVE RENNET CO., LTD.]

The Synthesis of 1,2,4-Trimethyl-7-isopropylindene

BY WALTER G. WHITTLESTON

The following equations represent the manner in which the synthesis of 1,2,4-trimethyl-7-isopropylindene was carried out



The synthesis was carried out with the object of producing a substance which on reduction and dehydrogenation would yield a compound of the structure 

Owing to shortage of materials and time, this was not completed.

The Introduction of the Chloromethyl Group into *p*-Cymene.—The first method attempted was that of Rapson and Short[1] in which *p*-cymene, anhydrous zinc chloride and paraformaldehyde were stirred into an emulsion and dry hydrogen chloride bubbled through the rapidly stirred mixture. This method was unsuccessful. It may be mentioned here that the yield obtained by the above authors, calculated on the basis of the amount of *p*-cymene taken at the start of the preparation, was 43%, and not the higher figure which they give.

The method due to Blanc[2] was finally employed, 40% aqueous formaldehyde being used in the place of paraformaldehyde. By employing apparatus in which the hydrogen chloride was distributed to the reaction mixture by a rapidly rotating hollow paddle stirrer, and keeping the temperature at 60° in a thermostatic bath, together with the use of nickel chloride as a catalyst, it was possible to get better yields than those of Blanc. The use of a small amount of nickel chloride reduced the production of tarry by-products in the reaction, and so made it much more efficient and convenient.

The preparation of diethyl methyl-(2-*p*-cymylmethyl)-malonate was carried out using the usual methods. This substance was saponified and decarboxylated. The acid chloride was prepared by the use of thionyl chloride, and after removal of the hydrogen chloride and sulfur dioxide by boiling, ring closure was effected by the addition of anhydrous aluminum chloride. The resultant ketone on treatment with methylmagnesium iodide gave 1,2,4,-trimethyl-7-isopropylindene.

Experimental

All temperatures are uncorrected. I. 2-*p*-Cymylmethyl Chloride.—Fifty grams of *p*-cymene, 20 g. of zinc chloride (anhyd.), 1 g. of nickel chloride and 40 g. of 40% formalde-

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[1] Rapson and Short, *J. Chem. Soc.*, 128 (1933).

[2] Blanc, *ibid.*, Ai, 549 (1923).

hyde were stirred together, and hydrogen chloride passed through, a temperature of 60° being maintained. After eight hours, the reaction mixture was steam distilled.

It was found better to use the small quantities mentioned, and to carry out many preparations, rather than to use larger quantities. Automatic apparatus requiring little attention facilitated the use of long reaction times; yield, 47 g. (69%) of a colorless liquid; b. p. 123–124° (20 mm.). A Stepanov chlorine determination gave 19.8% chlorine ($C_{11}H_{15}Cl$ requires 19.5%).

II. **Diethyl (2-*p*-Cymylmethyl)-malonate.**—Six grams of sodium was dissolved in a benzene solution of 40 g. of malonic ester, and 44 g. of 2-*p*-cymylmethyl chloride added. After boiling until the sodio derivative had disappeared, the reaction mixture was treated with water, and the benzene layer separated, dried and distilled. The required ester had a b. p. of 190–195° (9 mm.); yield 55 g. (60%).

III. **Diethyl Methyl-(2-*p*-cymylmethyl)-malonate.**—Four grams of sodium was dissolved in a benzene solution of 40 g. of *p*-cymylmethylmalonic ester. When the sodium had dissolved, 24 g. of methyl iodide was added. After boiling for two hours, the mixture was treated as in II; yield 32 g. of material (76%); b. p. 182–187° (8.5 mm.).

IV. **Methyl (2-*p*-Cymylmethyl)-malonic Acid.**—Twelve and eight-tenths grams of sodium was dissolved in 256 cc. of rectified spirits, and 48 g. of methyl (2-*p*-cymylmethyl)-malonic ester was added. After refluxing for four hours, the mixture was diluted with water and the excess alcohol distilled off. The aqueous solution of the sodium salt was extracted with ether and then acidified with hydrochloric acid. The organic acid was separated by filtration and dried in a vacuum desiccator, yield 95%.

The dibasic acid, after careful heating over a gauze followed by distillation at 12 mm., gave an oily liquid of b. p. 189–190° (12 mm.).

2-*p*-Cymylpropionic acid was prepared in the same way as the above, but omitting the introduction of a methyl group (step III). The corresponding dibasic acid in this case was a solid of m. p. 165°. On decarboxylation, a crystalline monobasic acid of b. p. 190–195° (20 mm.), and m. p. 76.5° was obtained. Equivalent weight by titration 210; by silver salt analysis 205.7 ($C_{13}H_{18}O_2$ requires 206.0).

The 3-*p*-cymylpropionic acid obtained by Cook, *et al.*,[3] has a m. p. of 61–62°. This indicates that the chloromethyl group definitely enters position 2 as has been supposed, in the initial synthesis.

V. **2,4 - Dimethyl - 7 - isopropylhydrindone.**—2 - *p* - Cymylisobutyryl chloride was prepared by treating 20 g. of the isobutyric derivative with 15 g. of thionyl chloride dissolved in petroleum ether free from aromatic hydrocarbons. After keeping at 60° for two to three hours, the temperature was raised, thus removing the sulfur dioxide and most of the hydrogen chloride formed.

The acid chloride was not isolated, but 12 g. of anhydrous aluminum chloride was added slowly. The product was heated on the water-bath for two to three hours, decomposed with dilute hydrochloric acid, and extracted with petroleum ether. Distillation yielded 15 g. of material, b. p. 147–150° (9 mm.). It was not found possible to crystallize the product which appeared to be contaminated with a highly colored impurity of similar boiling point.

VI. **1,2,4 - Trimethyl - 7 - isopropylindene.**—One and two-tenths grams of magnesium was dissolved in 6.0 g. of methyl iodide in anhydrous ether, and 8 g. of the ketone added. This reaction yielded 4 g. of a substance, which, on recrystallization from absolute ethanol, formed colorless, silky, acicular crystals with a high refractive index. The substance melted at 99.5°, and boiled with slight decomposition at 140–145° (10 mm.).

Analysis gave C, 89.7; H, 10.07. ($C_{15}H_{20}$ requires C, 90.0; H, 10.0.) This indicates that the elements of water have been lost, yielding the corresponding unsaturated indene derivative. The substance was found to absorb bromine readily, and to form a picrate consisting of fine, brick-red, acicular crystals, m. p. 88–89°.

Acknowledgments.—The author wishes to express his indebtedness to the late Dr. J. K. H. Inglis for his suggestions and kindly criticism. The work was carried out at Otago University during the tenure of a Sir George Grey Scholarship.

Summary

1. The use of formaldehyde, hydrochloric acid, and zinc chloride in the introduction of the chloromethyl group into *p*-cymene has been investigated.

2. It has been shown that with the use of nickel chloride as a catalyst, the yields in this reaction can be improved considerably.

3. The synthesis of 2-*p*-cymylisobutyric acid, 2-*p*-cymylpropionic acid, 2,4-dimethyl-7-isopropylhydrindone, and 1,2,4-trimethyl-7-isopropylindene has been carried out.

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(3) Cook, *et al.*, *J. Chem. Soc.*, 1727 (1934).