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DEHYDROABIETIC ACID

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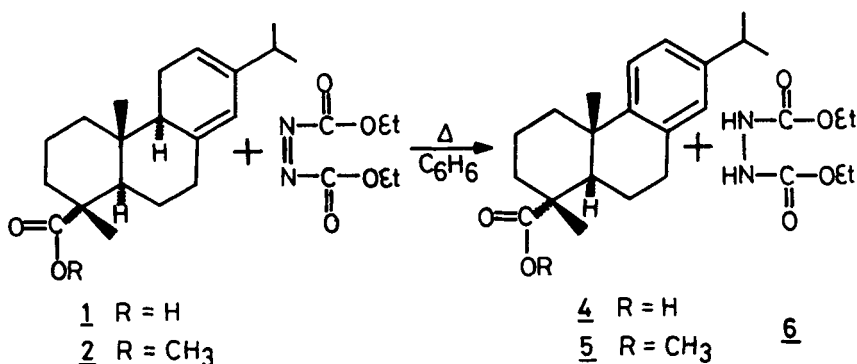
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DEHYDROABIETIC ACID

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Dehydroabietic acid 4 finds extensive use in a variety of diterpene transformations and stereochemical correlations.¹ The previous procedures for its preparation from abietic acid such as selenium dioxide oxidation,^{2a} dehydrogenation with Pd^{2bc} and chloranil,^{2d} bromination,^{2e} mercuric acetate



oxidation^{2f} and aromatisation with N-lithio ethylenediamine^{2g} are either multistep or cumbersome. As substantial amounts of 4 were required for a synthetic sequence, we developed an efficient and convenient preparation of 4 from levopimaric acid 1.³ The dehydrogenation^{4,5} of methyl levopimarate 2

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with diethyl azodicarboxylate 3 to methyl dehydroabietate 5 proceeds in 85% yield in a single step and is distinctly superior to previously reported procedures. The conversion of 5 to dehydroabietic acid 4 is already reported^{2b} in the literature.

EXPERIMENTAL

Methyl dehydroabietate 5.- Diethyl azodicarboxylate⁷ (3 g, 0.017 mole) in benzene (5 ml) was added with stirring to a solution of methyl levopimarate⁸ (4.6 g, 0.014 mole) in dry benzene (50 ml) at 25°. The reaction is exothermic and requires moderation⁹ in azoester addition with larger quantities. The reaction mixture was gently refluxed for 8 hr. and freed of solvent in vacuo to give a viscous semi-solid residue. This material was adsorbed on silica gel (60 g) and eluted with pentane-benzene (90:20) to give 4.3 g of colourless liquid. Distillation under reduced pressure, bp 180-85°/2 mm (bath) and crystallization from pentane yielded 4.0 g of pure methyl dehydroabietate 5 (85%), mp 60-61°C, lit.¹ 61-62°. Further elution of silica gel column with benzene-ethyl acetate (80:20) gave crystalline material 2.1 g mp 125-26°C identified⁶ as diethyl hydrazodicarboxylate 6 by comparison of its IR and NMR spectrum with an authentic specimen.

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8. Methyl levopimarate 2 is conveniently prepared by the reaction of 1 with ethereal diazomethane.
9. External cooling in ice bath is recommended when more than (0.1 mole) of diethylazocarboxylate is used.

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