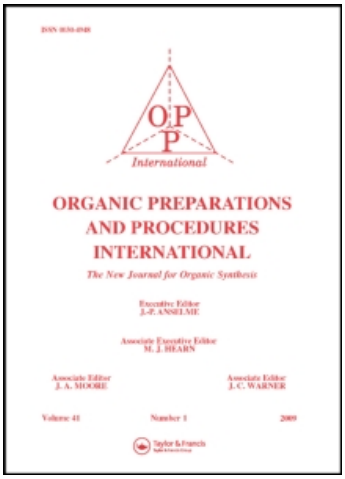

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DEHYDROABIETIC ACID

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DEHYDROABIETIC ACID

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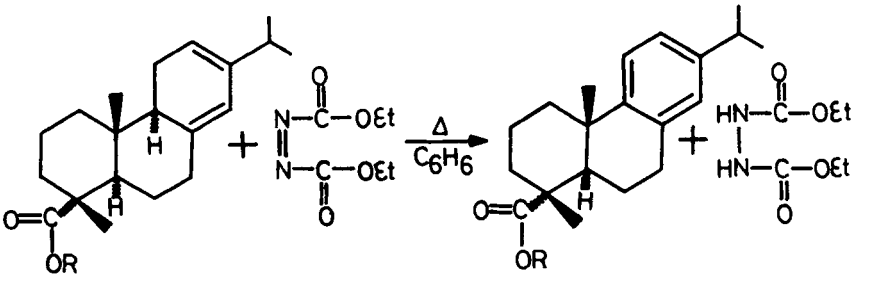
Dehydroabietic acid 4 finds extensive use in a variety of diterpene transformations and stereochemical correlations.[1] The previous procedures for its preparation from abietic acid such as selenium dioxide oxidation,[2a] dehydrogenation with Pd[2bc] and chloranil,[2d] bromination,[2e] mercuric acetate



1 R = H
2 R = CH_3

4 R = H
5 R = CH_3

6

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

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 azodicarboxylate[7] (3 g, 0.017 mole) in benzene (5 ml) was added with stirring to a solution of methyl levopimarate[8] (4.6 g, 0.014 mole) in dry benzene (50 ml) at 25°. The reaction is exothermic and requires moderation[9] 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 (80:20) 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 identified[6] as diethyl hydrazodicarboxylate 6 by comparison of its IR and NMR spectrum with an authentic specimen.

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3. W.D. Lloyd and G.W. Hedrick, Organic Syntheses, Vol. 45, 64 (1965).

4. F. Yoneda, K. Suzuki and Y. Nitta, J. Am. Chem. Soc., 88, 2328 (1966); F. Yoneda, K. Suzuki and Y. Nitta, J. Org. Chem., 32, 727 (1967).

5. This dehydrogenation was casually observed by us[6] during the addition of heterodienophiles to levopimaric acid.

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7. Supplied by Aldrich Chemical Co. U.S.A.

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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