# A New Reaction of an αβ-Unsaturated Nitro-compound

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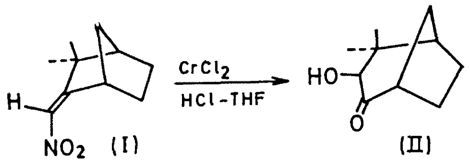
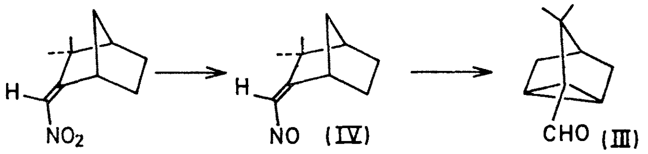
*Summary* ω-Nitrocamphene on treatment with chromous chloride undergoes a multi-stage rearrangement giving, in excellent yields, the ring-enlarged product 3-hydroxy-4,4-dimethylbicyclo[3,2,1]octan-2-one.

WE report the transformation of ω-nitrocamphene(I)[1] to the acyloin(II). Early investigations of Lipp[2] had shown that (I), on treatment with zinc–acetic acid, is transformed to the tricyclene aldehyde (III). We rationalized the formation of (III) on the basis of the αβ-unsaturated nitroso-compound (IV) as an intermediate. In attempts to study the transformation (I) → (III), employing reagents which are likely to produce (IV), a solution of (I) (6 g) in tetrahydrofuran (250 ml) was mixed with chromous chloride prepared from chromic chloride (60 g)[3] and the solution was heated under reflux for 3 hr.[4] Removal of tetrahydrofuran, followed by chloroform extraction, gave 78% of almost pure (II) (t.l.c.), which was distilled; b.p. 96—100°/5 mm, yield 61%.†‡ Apparently (IV), rather than undergoing bond migration





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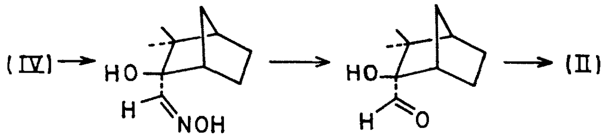
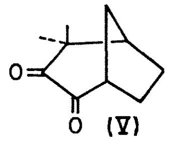
† Analysis in excellent accord with theory has been obtained for this compound.

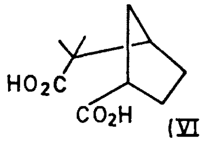
‡ Ir. $\lambda_{max}$ (film) 2·92(OH), 5·82(C=O) μm; n.m.r. δ ($CCl_4$) 0·75, 1·15(Me), 2·78(broad, ·CO·C*H*, bridgehead), 3·8(s, non-bridgehead *t*-proton).

that would have given (III), gave (II) by a sequence of addition of water, hydrolysis, and ring expansion. Compound (II) readily forms an acetate†§ and this compound is resistant to the action of zinc–acetic acid[5] and zinc–acetic anhydride,[6] thus indicating an equatorial disposition of the hydroxy-group in (II). The acyloin (II) was converted in 80% yield into the diketone (V), m.p. 48—50°, by treatment with copper(II) acetate.†¶ Potassium permanganate oxidation of camphene gives as the major product the dicarboxylic acid (VI), and there is some controversy about the mechanism of this reaction. De Mayo[7] has speculated the involvement of the then unknown acyloin (II) as an intermediate, and we have been able to support this view by converting (II) into (VI) under the conditions employed in the camphene oxidation.





(V)



(VI)

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§ I.r. $\lambda_{max}$ (film) 5·71 and 5·8(C=O) μm n.m.r. δ ($CCl_4$) 0·89, 1·06(Me), 2·08 (s, ·O·CO·Me) 2·7(broad, ·CO·C*H*, bridgehead), 4·9(non-bridgehead *t*-proton, s).

¶ I.r. $\lambda_{max}$ (KBr) 5·84(C=O) μm; n.m.r. δ ($CCl_4$) 1·1,1·14(Me), 2·98(broad, ·CO·C*H*, bridgehead proton).

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