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ON THE MECHANISM OF THE UNUSUAL TRANSFORMATION OF ω-NITROCAMPHENE TO 7,7-DIMETHYL TRICYCLO(2,2,1,$0^{2,6}$)HEPTANE -1-CARBOXYLIC ACID

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Camphene on treatment with excess of sodium nitrite and acetic acid gives ω-nitrocamphene(I)* in 30% yields(1)(2). The terminal location of the nitro group in I makes it readily susceptible for rearrangements and indeed the very early investigation of Lipp(3) meticulously documents a variety of such transformations. Perhaps the most striking amongst them is the conversion of I to the tricyclene acid V(CHART I) upon treatment with concentrated sulfuric acid. This transformation was postulated to proceed *via* a unique cyclic sulfate intermediate II**. After several trials we were able to isolate this compound by a modified procedure***. The crude cyclic sulfate is tremendously sensitive to moisture and decomposes around 110° giving off sulfurtrioxide ! The analytical, IR(λ_{max}(KBr) 3.03, 6, 6.9, 7.07μ) and NMR (δ ($CDCl_3$) 5.1(m), non-bridgehead tertiary proton) data are in agreement with structure II. Compound II on leaving overnight-taking no precautions to keep off moistrure- is transformed into dark syrupy hydroxamic acid III.

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* On principle two nitrocamphenes are possible. In the NMR one of the bridge head protons is two δ units lower in comparison with the other. This fact is accommodated by assigning a *syn* relationship as in I.

** No other system having structure similar to II is known to us. For related cases, D.S. Breslow and H. Skolnik, "Multi-Sulfur and Sulfur and Oxygen 5 and 6 membered Heterocycles", Part I, Interscience, New York (1966).

*** An ice-cold hexane solution of I(0.5 g in 30 ml) was added to ice-cold stirred concentrated sulfuric acid (3 ml). After 15 minutes the cherry-red lower layer is poured on to ice-ether, the ether extract dried and allowed to evaporate in a desiccator over phosphorous pentoxide; yield 34.8%.

Structure III is supported by IR(λ_{max}(film)3.05, 6.05μ) and through conversion to crystalline acetone adduct IIIa(32% from I); m.p. 204-205°. Structure IIIa is supported by analysis, IR(λ_{max}(KBr)2.9, 6.1μ), NMR (δ($CDCl_3$) 4.05(m), non-bridgehead tertiary proton) and by hydrolysis in 85% yields to the hydroxy acid IV(CHART I); further, IIIa gives positive ferric chloride test indicative of the presence of the free hydroxyl group(4). An aqueous solution of III-which is acidic due to hydrolysis of II-on heating for 24 hours on a steam bath gave hydroxy acid IV(22% from I)(2), m.p. 239-240°, IR(λ_{max}(KBr) 2.9, 5.92μ), NMR(δ($CDCl_3$) 4.12(m), non-bridgehead tertiary proton). A solution of IV in dilute sulfuric acid (1:1) when refluxed for 4 hours gave a 57% yield of the tricyclene acid V(2), m.p. 145-146°, IR(λ_{max}(KBr) 6.0μ), NMR(δ($CDCl_3$) 4 signals for 7 protons around 1.6, singlet for six protons at 1.08). A reasonable pathway for the formation of the cyclic sulfate II is presented in CHART I. The proposed mechanism is in agreement with the known conversion of camphene to isobornyl hydrogen sulfate(5) and is also in accord with the generally accepted pathways involved in the transformation of saturated nitro compounds to hydroxamic acids(6). In view of the known reluctance of hydroxamic acids to condense with carbonyl compounds(7), the ready formation of adduct IIIa is best explained as arising through a nitrone intermediate (CHART I). We are currently working on some of the other fascinating transformations of ω-nitrocamphene(3)(8), mainly with a view to further our understanding of the system.

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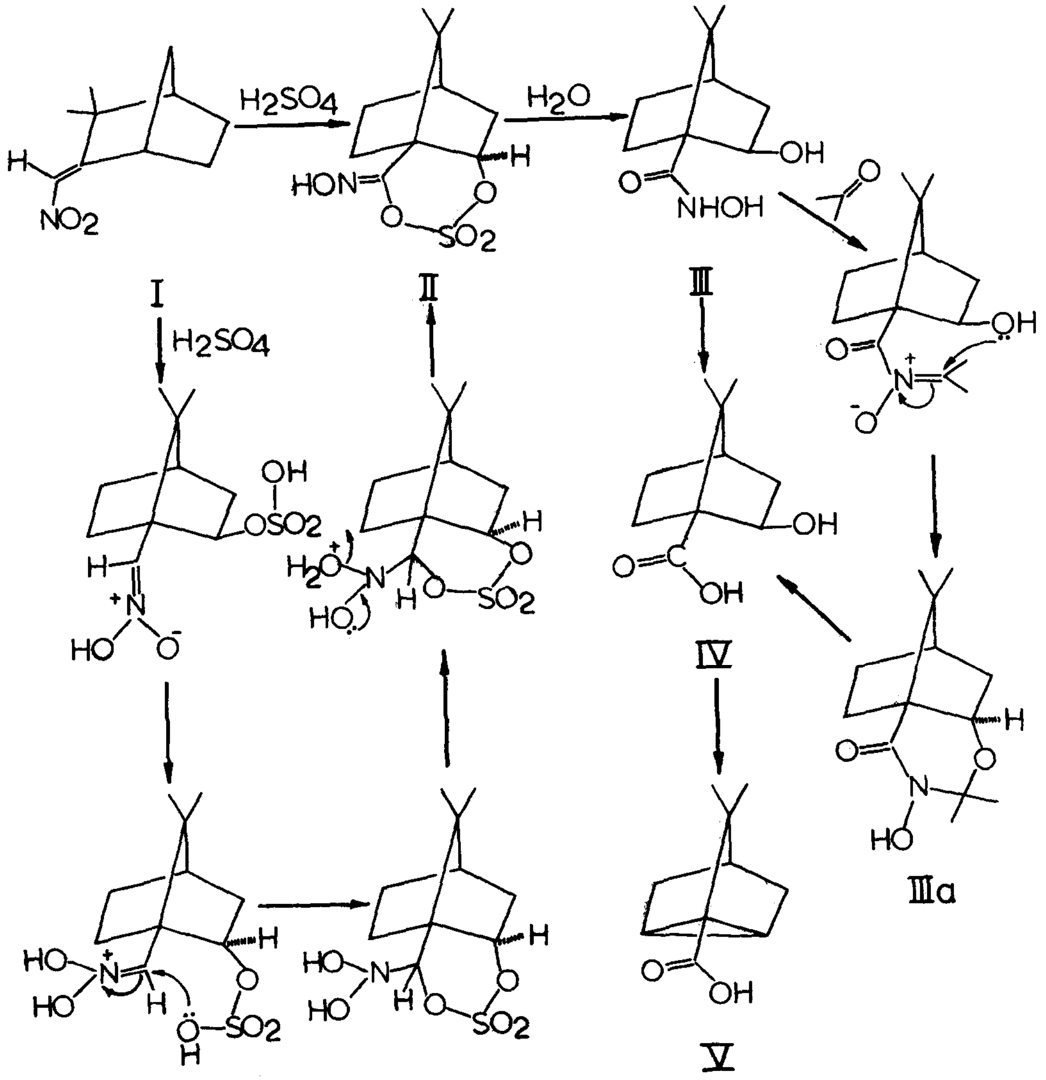
CHART I



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