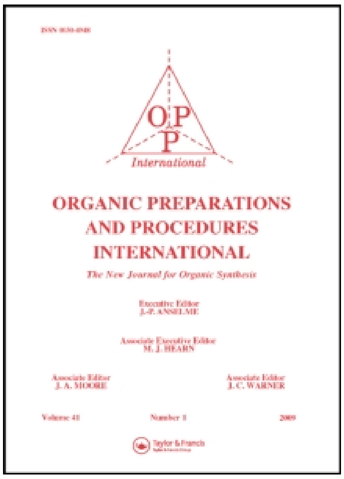


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

DICARBOXYLIC ACIDS FROM THE OXIDATIVE OZONOLYSIS OP HYDROXYMETHYLENE KETONES. AN IMPROVED PROCEDURE

D. T. C. Yang[a]
[a] Department of Chemistry, University of Arkansas at Little Rock, Little Rock, Arkansas

To cite this Article Yang, D. T. C.(1976) 'DICARBOXYLIC ACIDS FROM THE OXIDATIVE OZONOLYSIS OP HYDROXYMETHYLENE KETONES. AN IMPROVED PROCEDURE', Organic Preparations and Procedures International, 8: 5, 237 — 239

To link to this Article: DOI: 10.1080/00304947609355632

URL: http://dx.doi.org/10.1080/00304947609355632

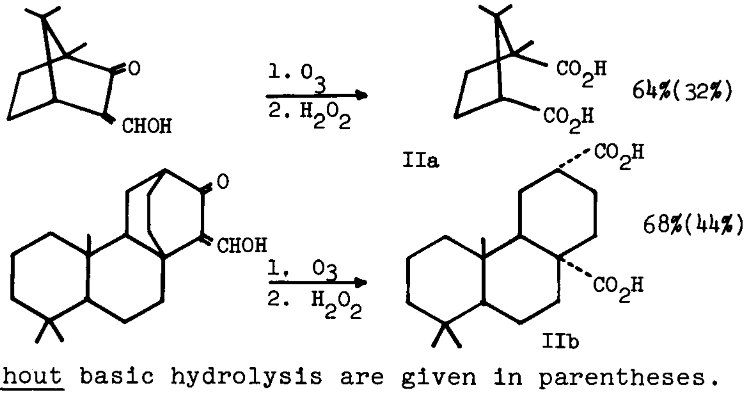
OPPI BRIEFS

(By James A. Moore, Associate Editor)

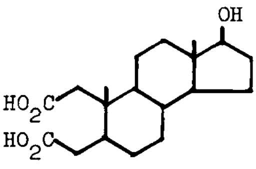
DICARBOXYLIC ACIDS FROM THE OXIDATIVE OZONOLYSIS OF HYDROXYMETHYLENE KETONES. AN IMPROVED PROCEDURE

Submitted by D. T. C. Yang
4/5/76
Department of Chemistry
University of Arkansas at Little Rock
Little Rock, Arkansas 72204

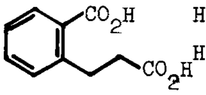
The formation of surprisingly large amounts of anhydrides[1] from the oxidative ozonolysis of hydroxymethylene ketones (I) by the procedure of Weisenborn and Applegate,[2] suggested the inclusion of a basic hydrolysis step during the workup. This step has resulted in improved yields of pure diacids IIa and IIb. New diacids IIc-e were similarly obtained although the yields were not improved over those obtained by the reported procedure.[2]



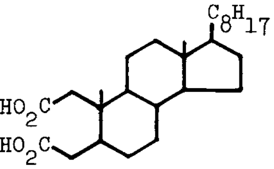
Yields without basic hydrolysis are given in parentheses.



IIc



IId



IIe

Camphoric Acid (Ia). General Procedure.- A solution 1.0 g (5.6 mmoles) of hydroxymethylene camphor in 30 ml of acetic acid was ozonized with 1.5 molar equivalent of ozone at room temperature. After the addition of 30 ml. of water, 2.3 ml. of 30% hydrogen peroxide was added dropwise over a period of 2 hrs to the stirred solution. The mixture was allowed to stand overnight. Ether extraction yielded, upon evaporation of the solvent, 1.23 g of a crude mixture of camphoric anhydride and camphoric acid which was dissolved in 1% sodium hydroxide solution (3 ml) by heating on a steam bath. After careful neutralization with 1 N hydrochloric acid, the mixture was extracted with ether. Removal of solvent *in vacuo*, gave a residue which was crystallized from methanol-hexane to give 750 mg (64%) of camphoric acid, mp. 188-189°, ν_{max} (Nujol) 1690 cm^{-1} (broad).

IIb, mp. 295-298°. Anal. Calcd for $C_{19}H_{30}O_4$: C, 70.77; H, 9.38. Found: C, 70.44; H, 9.32.

IIc, mp. 279-281°. Anal. Calcd for $C_{19}H_{30}O_5$: C, 67.43; H, 8.94. Found: C, 67.13; H, 8.91.

IId, mp. 165-167°. <u>Anal</u>. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.58; H, 5.42.

IIe, mp. 182-184°. <u>Anal</u>. Calcd for $C_{27}H_{46}O_4$: C, 74.61; H, 10.67. Found: C, 74.56; H, 10.67.

REFERENCES

1. This is presumably due to the stability of bicyclic anhydrides to hydrolysis in acetic acid at room temperature.
2. F. L. Weinsenborn and H. E. Applegate, J. Am. Chem. Soc., 81, 1960 (1959).

SIMPLE SYNTHESIS OF 3-t-BUTYLGLUTARIC ACID

Submitted 7/23/76

by M. Tichy

Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences
166 10 Prague 6
CZECHOSLOVAKIA

A recent synthesis of 3-t-butylglutaric acid (IIIa)[1] prompts us to report another route of IIIa which was obtained in 45% overall yield from the commercially available 4-t-butylcyclohexanone (I) in 3 steps. I was converted into its 2,6-dibenzylidene derivative II which was ozonized to give a mixture of benzoic acid and the desired acid IIIa, separated by fractionation of their esters.

EXPERIMENTAL

<u>2,6-Dibenzylidene-4-t-butylcyclohexanone (II)</u>.- A solution of sodium hydroxide (4 g) in water (10 ml) was added to a solu-