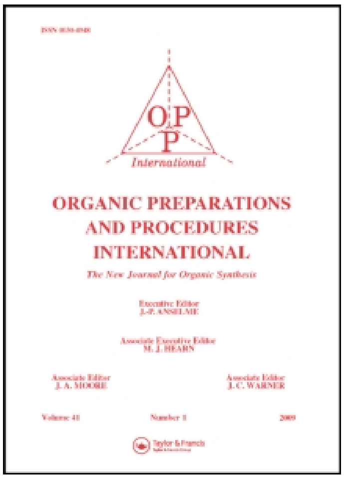


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

PREPARATION OF 3-PHENYL-1,2-CYCLOPROPANEDICARBOXYLIC ACIDS

S. Wawzonek[a]; A. R. Zigman[a]
[a] Department of Chemistry, University of Iowa, Iowa City, Iowa

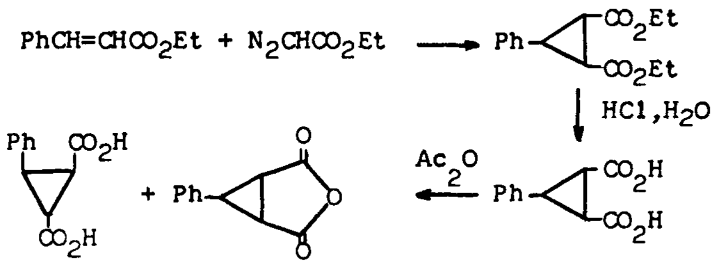
To cite this Article Wawzonek, S. and Zigman, A. R.(1969) 'PREPARATION OF 3-PHENYL-1,2-CYCLOPROPANEDICARBOXYLIC ACIDS', Organic Preparations and Procedures International, 1: 4, 243 — 248
To link to this Article: DOI: 10.1080/00304946909458391
URL: http://dx.doi.org/10.1080/00304946909458391

ORGANIC PREPARATIONS AND PROCEDURES 1(4), 243-248 (1969)

PREPARATION OF 3-PHENYL-1,2-CYCLOPROPANEDICARBOXYLIC ACIDS

S. Wawzonek and A. R. Zigman

Department of Chemistry
University of Iowa
Iowa City, Iowa 52240



3-Phenyl-1,2-cyclopropanedicarboxylic acid was needed as a possible starting compound for the synthesis of 3-phenyl-1-cyclopropene. Two methods are available for the preparation of this acid and involve the basic hydrolysis of the esters of 3-phenyl-1,1,2,2-cyclopropanetetracarboxylic acid[2] and 3-phenyl-1,2-cyclopropanedicarboxylic acid[3]. Since difficulties were encountered in the preparation of the former compound, more intensive studies were carried out using diethyl 3-phenyl-1,2-cyclopropanedicarboxylate as the source for the diacid.

The ester could be obtained in one step in a yield comparable to that in the literature[3] by the addition of ethyl diazoacetate to ethyl cinnamate at elevated temperatures.

Examination of the product by v.p.c. indicated the presence of two isomers. Saponification of this mixture gave, in agreement with the literature[4], a poor yield of the trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic acid. The reason for this poor yield became apparent when the saponification mixture was treated with acetic anhydride; a mixture of phenylglutaconic anhydride and trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic anhydride[4] was obtained indicating that the alkali was degrading the cyclopropane ring by a reverse Michael reaction.

In contrast, acid hydrolysis of the diester gave a mixture of isomeric 3-phenyl-1,2-cyclopropanedicarboxylic acids which was converted by treatment with acetic anhydride to a mixture of trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic anhydride and 3-phenyl-trans-1,2-cyclopropanedicarboxylic acid, separable by crystallization and column chromatography. The anhydride upon recrystallization from water gave the known trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic acid; the nmr spectrum was in agreement with this structure.

The acid isolated from the acetic anhydride treatment was 3-phenyl-trans-1,2-cyclopropanedicarboxylic acid based on the nmr spectrum. The melting point for this acid (172-3°) differed from that reported by Buchner[5] for the acid (121°) obtained by fusing trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic acid with alkali at 235-40° and formulated as 3-phenyl-trans-1,2-cyclopropanedicarboxylic acid. Repetition of this reaction gave benzoic acid as the only isolable compound.

Experimental[6]

Diethyl 3-Phenyl-1,2-cyclopropanedicarboxylate. This ester was prepared in a single step by a slight modification of the directions in the literature[3]. A mixture of ethyl diazoacetate (90g.) and ethyl cinnamate (126g.) was added dropwise with vigorous stirring to ethyl cinnamate (50 ml.) at 175-185°. After the addition was completed, the temperature of the reaction mixture was raised to 195° and maintained at this point for 12 hours. Distillation at reduced pressure gave the ester (90g.) boiling at 204-210° (25mm.)(lit.[4] b.p. 256-70°(120 mm)). Analysis by v.p.c. and nmr indicated the presence of a mixture of 40% cis- and 60% of trans- isomers; nmr (neat), δ7.50-7.10 (aromatic), two quartets centered at δ4.13 (CH_2), complex multiplet at δ3.93, δ2.25 (cyclopropyl hydrogens) and two triplets centered at δ1.2 (CH_3); infrared spectrum (neat), 3.32, 5.81, 6.12, 6.59, 7.32, 7.85, 8.55, 9.70, 11.70, 12.96, 13.25 and 14.40μ.

Analysis by v.p.c. was carried out on a 6ft by 0.25 in. W-98 silicon gum rubber column. Experimental conditions: oven temperature, 225°C; detector temperature 350°C; injector temperature 275°C; helium flow 30ml/min at 50 p.s.i.g.

Hydrolysis of Diethyl 3-Phenyl-1,2-cyclopropanedicarboxylate. The mixture of esters (40g.) was refluxed for 12 hours with 250 ml. of concentrated hydrochloric acid and 100 ml. of water. Removal of the solvent under reduced pressure gave a solid which was dried by azeotroping with benzene and treated with acetic anhydride (200 ml.) and heated at reflux for 2 hours. Removal of excess anhydride gave a dark red residue which was recrystallized from benzene. The *trans*-3-phenyl-*cis*-cyclopropanedicarboxylic 1,2-anhydride (6.0g.) melted at 131-4°. An additional recrystallization from ethyl acetate gave a compound with m.p. 134°. (Lit.[4] 134°).

The benzene filtrate was chromatographed on silica gel and gave upon elution with benzene more of the anhydride (3.6g.).

The remainder of the product, the *trans*-diacid was removed from the column with acetone; yield, 11.0g. Recrystallization from water after treatment with Norite gave 4.6g; m.p. 172-3°. Further recrystallization from a mixture of chloroform and acetone gave the same melting point.

Calcd. for $C_{11}H_{10}O_4$: C, 64.07; H, 4.88. *Found*: C, 64.21; H, 4.64. Infrared spectrum (nujol mull), 3.17, 3.40, 3.88, 5.90, 7.23, 7.75, 8.18, 10.32, 11.28, 12.61, 13.15, 13.30, 13.88 and 14.42μ; nmr (CF_3COOH), δ7.28 (aromatic), δ3.35 quartet (C_6H_5CH), δ3.35 quartet (CH) and δ2.84 (CH).

trans-3-Phenyl-cis-1,2-cyclopropanedicarboxylic Anhydride. Infrared spectrum (nujol mull), 3.35, 5.36, 5.61, 6.81, 7.22, 8.0, 9.02, 10.08, 10.95, 11.65, 11.82, 13.08, 13.92 and 14.32μ; nmr (acetone d6), δ7.30 singlet (aromatic), δ3.24 singlet (CH).

trans-3-Phenyl-cis-1,2-cyclopropanedicarboxylic acid. Infrared spectrum (nujol mull), 3.16, 3.40, 3.73, 3.85, 5.85, 6.20, 6.95, 7.23, 7.45, 7.65, 8.16, 9.12, 9.23, 9.45, 9.68, 10.07, 11.08, 11.77, 11.89, 12.12, 12.74, 13.23, 14.38 and 14.78μ; nmr (CF_3COOH), δ7.27 multiplet (aromatic), δ3.38 triplet (benzylic H), δ2.64 doublet (CH).

Saponification of Diethyl 3-Phenyl-1,2-cyclopropanedicarboxylate. The ester (10.0g.) was refluxed with sodium hydroxide (4.0g.) in 100 ml ethanol for 12 hours. The resulting solution was cooled, and the ethanol was removed by distillation under reduced pressure. The resulting solid was dissolved in water, and the solution was acidified with sulfuric acid. Extraction with ether gave 7.5g. of product which was refluxed with acetic anhydride (100 ml.) and benzene (25 ml.) for 1 hour. Removal of the solvents under reduced pressure gave a solid which was recrystallized from benzene; yield, 0.8g. Recrystallization from ethyl acetate gave β-phenylglutaconic anhydride, m.p. 206° (Lit.[6] m.p. 206°). Infrared spectrum (nujol), C=O, 5.59, 5.79, C-O-C, 8.89 and 10.17μ; nmr (CF COOH), δ7.64 multiplet (aromatic), δ6.82 triplet (=CH), δ4.19 doublet (CH_2).

The anhydride (0.3g.) upon recrystallization from water gave β-phenylglutaconic acid (0.120g.); m.p. 154-6°(Lit.[7] 154-5°). Infrared spectrum (nujol), 3.15, 3.70, 5.90, 6.15, 7.10, 7.54, 7.71, 8.18, 8.38, 10.80, 11.40, 12.93, 13.72 and 14.31, 14.65μ; nmr (CF_3COOH), δ8.01 singlet (=CH), δ7.20 singlet (aromatic), δ3.56 singlet (CH_2).

Concentration of the benzene filtrate gave a solid which after crystallization from a chloroform-pentane mixture and ethyl acetate melted at 127-134°; yield, 0.125g. (Lit.[4] m.p. for trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic anhydride, 134°). Recrystallization of this solid from water gave trans-3-phenyl-cis-1,2-cyclopropanedicarboxylic acid; m.p. 175°(Lit.[3] m.p. 175°).

References.

1. Abstracted in part from the Ph.D. thesis of A. R. Zigman, University of Iowa, Feb. 1969.
2. A. Kotz, J. Prakt. Chem., [2] 75, 490 (1907).
3. E. Buchner, Ber., 21, 2637 (1888).
4. E. Buchner and H. Dessauer, Ber., 25, 1147 (1892).
5. E. Buchner and L. Perkel, Ber., 36, 3774 (1903).
6. Melting points are not corrected. Analysis by v.p.c. was carried out on an F and M. 720 chromatograph with helium as the carrier gas.
7. J. C. Thorpe, J. Chem. Soc., 101, 856 (1912).

(Received May 15, 1969)