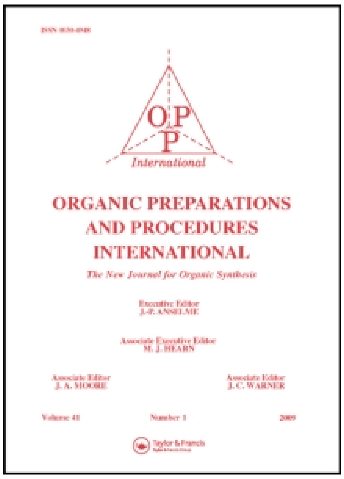

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PREPARATION OF ISOMERIC 1-METHYL-2-PHENYLCYCLOPROPANES

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PREPARATION OF ISOMERIC 1-METHYL-2-PHENYLCYCLOPROPANES.[1]

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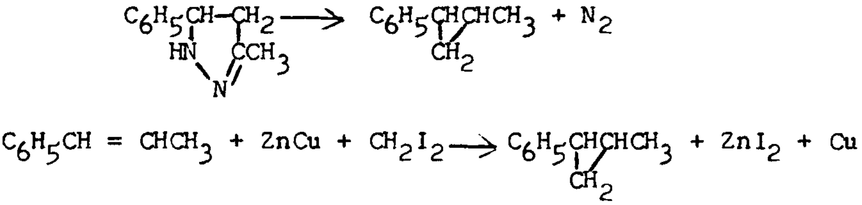

Pure samples of the isomeric 1-methyl-2-phenylcyclopropanes were required for another study. The pyrolysis of 3-methyl-5-phenyl-2-pyrazoline[2,3], and the Simmons-Smith reaction of methylene iodide in the presence of a zinc-copper couple with the isomeric 1-phenylpropenes[4] were investigated as sources of these compounds.

The first of these reactions gave a mixture containing 35.5 percent cis-1-methyl-2-phenylcyclopropane and 64.5 percent of the trans-isomer.

The Simmons-Smith reaction of cis-1-phenylpropene prepared by the catalytic hydrogenation of 1-phenylpropyne gave a mixture of 80.5 percent cis-1-methyl-2-phenylcyclopropane and 19.5 percent of the trans-isomer. These results suggest that this olefin does not react stereospecifically as reported for cis-and trans-3-hexene[4]. The possibility of isomerization of cis cyclopropane in the work up of the reaction mixture, (which involved removal of unreacted olefin by oxidation with potassium permanganate in acetone) was eliminated by the stability of the cis-isomer towards such treatment. Since the unreacted olefin was not recovered in this reaction it is not known whether the olefin was isomerized prior to the addition reaction or whether the addition reaction is non-stereospecific with this example.

trans-1-Phenylpropene prepared by the alkaline isomerization of allylbenzene was not pure but consisted of a mixture of the trans-isomer (90.1%) and the cis-isomer (9.9%). This mixture when treated with methylene iodide and zinc-copper couple gave a mixture consisting of 93.7 percent trans-1-methyl-2-phenylcyclopropane and 6.3 percent of the cis-isomer. The results indicate that the trans olefin reacts stereospecifically and that the cis isomer again does not.

Pure samples of each of the cyclopropanes were obtained by preparative v.p.c. of the products from the Simmons-Smith reaction and their structures were confirmed by nmr and ir spectra.

Experimental[6]

Pyrolysis of 3-Methyl-5-phenyl-2-pyrazoline. The reaction was carried out using the directions in the literature[2,3] and gave an 84.4 percent yield of cis and trans-1-methyl-2-phenylcyclopropane, b.p. 176-8° at 746 mm., (lit.[3] b.p. 187-9°).

Analysis by v.p.c. on a 50 ft by 1/4 in. column (A) packed with XF-1150 (16.0.g.)(Nitrile silicon polymer liquid) on Chromosorb P (15.0 g.)(35/80 mesh) showed that the relative distribution of the two products was 35.5% cis and 64.5% trans-1-methyl-2-phenylcyclopropane. Retention times were 83.0 and 100 minutes respectively. Experimental conditions: detector temperature 305°, injector port temperature 290°; sensitivity 4; column temperature, 105°; flow rate, 66 ml./min.

The ratio of isomers was not changed after refluxing with potassium permanganate in acetone for five days.

cis-1-Phenylpropene. This olefin was prepared from 1-phenylpropyne using 5 percent palladium on barium sulfate as the catalyst[7,8].

V.p.c. analysis with a 10 ft by 1/4 in. column (B) packed with phenyl diethanolamine succinate polyester (45.0 g.) on Chromosorb P (80/100 mesh)(125g.) showed a product distribution of 37.6% 1-phenylpropane, 60.6% cis-1-phenylpropene and 1.8% trans-1-phenylpropene. Retention times were 8.3, 12.7 and 16.5 minutes respectively. Experimental conditions: detector temperature, 200°; injection port temperature, 210°; column temperature, 175°; flow rate 90 ml./min.

Preparative v.p.c. on the same column gave a pure sample of cis-1-phenylpropene, n_D^{20}, 1.5423, (lit.[7] n_D^{25}, 1.5400); nmr (neat), δ1.75 multiplet (CH_3), δ5.64 multiplet (2-CH), δ6.40 multiplet (1-CH), δ7.17 singlet (aromatic). The relative ratios were 3:1:1:5 respectively.

trans-1-Phenylpropene[5]. Allylbenzene (66.3g.) was isomerized with 20 percent potassium hydroxide in butanol[5].

The product (40.0g.) distilled at 170-175° at 750 mm. with the major fraction distilling at 175° (lit.[5] b.p. 174-5°).

Analysis by v.p.c. on an 8 ft. by 1/4 in. column (C) packed with Carbowax 20 M (0.2g.) on Gas Chrom P (19.8g.) showed a mixture of 9.9 percent <u>cis</u>-1-phenylpropene and 90.1 percent <u>trans</u>-1-phenylpropene with retention times of 12.5 and 22.9 minutes respectively. Experimental conditions: block temp. 200°; column temperature; 60°, gas pressure, 20 p.s.i; flow rate, 50 ml./min.

Preparative v.p.c. at 170° on a 10 ft by 3/8 in. column (D) packed with Carbowax 20M$_1$(14.6g.) on Chromosorb P(80/100 mesh)(131.4g.) gave a pure sample of <u>trans</u>-1-phenylpropene; n_D^{20}, 1.5495 (lit.[9] n_D^{25}, 1.5461) nmr ($CDCl_3$), δ1.74 multiplet (CH), δ6.14 multiplet (CH=CH) δ7.17 multiplet (Aromatic).

<u>trans-1-Methyl-2-phenylcyclopropane.</u> Methylene iodide (68.5g.) and iodine (0.15g.) were added to a mixture of zinc-copper couple[10] (20.9g.) and anhydrous ether (320 ml.). The gray colored mixture was refluxed with stirring for four hrs. and treated with a mixture of <u>cis</u>- and <u>trans</u>-1-phenylpropene (30.0g., 9.9% cis and 90.1% trans) in 30 ml of anhydrous ether dropwise over a period of 0.5 hours. The resulting mixture was refluxed with stirring for 60 hours and allowed to stand for four days. The reaction mixture was filtered and the ether solution was washed with 5 percent hydrochloric acid, aqueous sodium bicarbonate and water. Removal of the solvent was followed by oxidation in acetone (500 ml.) with excess potassium permanganate (400g.) for six days. The hydrocarbon

residue obtained after filtration and removal of the solvent was taken up in pentane and chromatographed through an alumina column. Analysis by v.p.c. using column C showed the product to consist of 93.7% trans-1-methyl-2-phenylcyclopropane and 6.3% cis-1-methyl-2-phenylcyclopropane. Preparative v.p.c. on column B at 175° gave pure trans-1-methyl-2-phenylcyclopropane; infrared spectrum (film), medium to strong bands at 3.32, 3.38, 6.22, 6.67, 6.87, 7.26, 8.18, 9.23, 9.47, 9.68, 9.73, 10.77, 11.64, 12.72, 13.47 and 14.38µ; nmr (neat) δ0.40-1.60 broad multiplet with major peaksat δ1.07 (aliphatic hydrogens); broad multiplet centered at δ7.00 (aromatic hydrogens).

cis-1-Methyl-2-phenylcyclopropane. Pure cis-1-phenylpropene was treated in a similar manner to that described for the trans-isomer. Analysis by v.p.c. on column B showed that the product consisted of 80.5% cis-1-methyl-2-phenylcyclopropane and 19.5% trans-1-methyl-2-phenylcyclopropane. Preparative v.p.c. on the same column at 150° gave a pure sample of the cis isomer: infrared spectrum (film), medium to strong bands at 3.32, 3.38, 6.23, 6.67, 6.89, 7.20, 7.40, 8.55, 9.20, 9.35, 9.51, 9.74, 11.01, 11.56, 11.89, 12.86, 13.20, 13.77 and 14.34µ; nmr (CCl_4) δ0.48-1.17 broad multiplet with a major peak at δ0.82 (aliphatic hydrogens), δ2.03 multiplet (2-CH), δ7.09 singlet (aromatic).

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