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THE ABSOLUTE CONFIGURATION OF cis-2-PHENYLCYCLOPROPANECARBOXYLIC ACID

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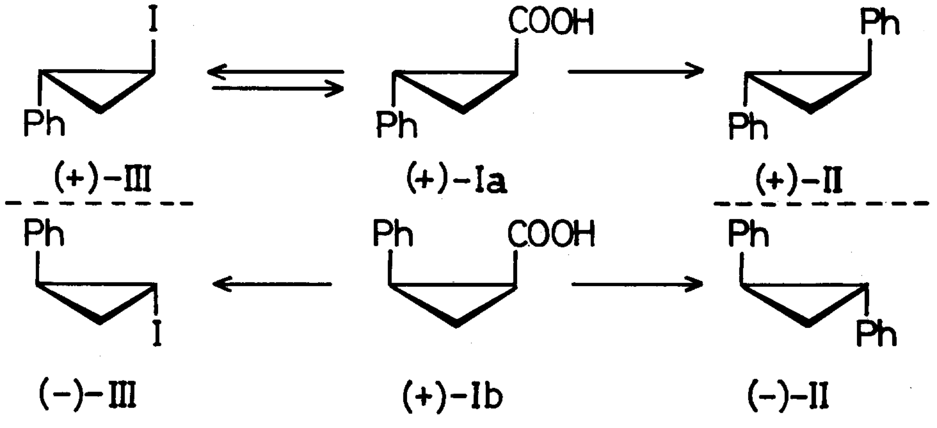
The reaction of alkanecarboxylic acids with lead tetraacetate gives alkyl radicals (1). We have subjected cyclopropanecarboxylic acids to this reaction, and established the absolute configuration of the titled acid.

Both trans and cis isomers of 2-phenylcyclopropanecarboxylic acid (Ia,b) were decarboxylated with lead tetraacetate in benzene at 80° in the presence of a catalytic amount of pyridine and cupric acetate. The solely detectable phenylated product of intermediary 2-phenylcyclopropyl radical was found to be trans-1,2-diphenylcyclopropane (II) (18 and 22% yield from Ia and Ib, respectively). The fact that each of Ia and Ib gives the same single isomer of II may be explained on the basis of mobile configuration of the radical carbon (2). On the other hand, the retention of configuration at the phenyl-substituted carbon of Ia was shown as follows. Thus (+)-(1S:2S)-Ia, $[\alpha]_D^{20}$ +376° (c 0.88, $CHCl_3$) (optical purity 99%) (3), gave (+)-(1S:2S)-II, $[\alpha]_D^{20}$ +418°(c 0.96, $CHCl_3$) (4).

The laevorotatory isomer (1R:2R) of II, $[\alpha]_D^{20}$ -266°(c 1.94, $CHCl_3$), was obtained upon similar treatment of partially resolved cis-acid (+)-Ib, $[\alpha]_D^{20}$ +20°(c 1.40, $CHCl_3$).



Assuming the retention of configuration at the phenyl-substituted carbon of Ib, we may conclude that (+)-Ib should have the absolute configuration of 1S:2R.

Following experiments warranted such a conclusion. The Barton reaction of Ia and Ib was effected by means of lead tetraacetate and iodine under irradiation (5) to afford only trans isomer of 2-phenylcyclopropyl iodide (III) (b.p. 77-78°/2 mm, 43 and 42% yield from Ia and Ib, respectively). (+)-(1S:2S)-Ia (optical purity 95%) gave (+)-(1S:2S)-III, $[\alpha]_D^{20}$ +188°(c 0.80, $CHCl_3$), whose absolute configuration was determined as follows. The same iodide (+)-III was metallated with n-butyllithium (6), carbonated and then esterified to give back methyl ester of (+)-Ia, $[\alpha]_D^{20}$ +270°(c 1.22, EtOH) (81% optical purity, 48% overall yield). Thus the Barton reaction proceeds with similar stereochemistry as the phenylation reaction. The retention of configuration at the phenyl-substituted carbon of Ia is calculated to be at least 86%. Furthermore the Barton reaction of 2,2-diphenylcyclopropanecarboxylic acid gave only 2,2-diphenylcyclopropyl iodide (m.p. 44-45.5°, 57% yield). These observations exclude the possibility of phenyl migration in this kind of radical reactions.

Now that iododecarboxylation of cis-acid (+)-Ib, $[\alpha]_D^{20}$ +16°(c 1.00, $CHCl_3$), gave (-)-(1R:2R)-III, $[\alpha]_D^{20}$ -128°(c 2.06, $CHCl_3$), the absolute configuration of (+)-Ib was reconfirmed to be 1S:2R.

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