Revised Structure Assignments among the Cyclopentenedicarboxylic Acids

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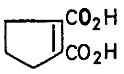
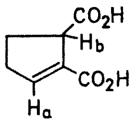
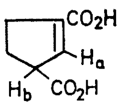
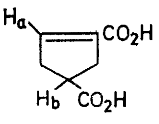
Summary The alleged cyclopentene-1,5-dicarboxylic acid comprises mixtures of cyclopentene-1,2- and -1,5-dicarboxylic acids; the 1,3-isomer has been characterized and the 1,4-isomer prepared for the first time.

Solvolysis of 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-one (**1**) in aqueous acetic acid containing alkali acetate provides a direct synthesis for tropolone.[1] In contrast, the hydrolysis in aqueous alkali-metal carbonate solution results mainly in cleavage of the cyclobutanone ring to give polymeric products as well as a conjugated formylcyclopentenecarboxylic acid (A) which is readily oxidized to the corresponding dicarboxylic acid (B) (m.p. 182—183°). The vinylic substituents in these compounds are readily deduced

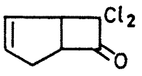
Physical properties

				
M.p.	178°	182—183°	150·5°	181—182°
$\nu_{C=C}$ (cm^{-1})[a]	[b]	1612, 1632	1625	1615
H_a (Hz)[c]	[b]	416	406	400
H_b (Hz)[c]	[b]	222	227	198

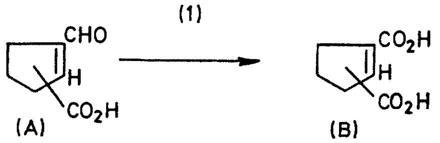
[a] Halocarbon mull used below 1300 cm^{-1} in i.r. spectra.
[b] No signals observed in the indicated frequency range.
[c] ^1H n.m.r. measurements in $(CD_3)_2CO$.

from n.m.r. evidence but the position of the carboxy-group could not be ascertained on the basis of literature data.

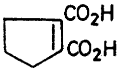
Ultimately, identification of (B) required a complete reassessment of previous structure assignments among the "acrylically conjugated" cyclopentenedicarboxylic acids. Isomers (**2**), (**3**), and (**4**) were reported in the literature[4–7] (reported m.ps 178°, *ca.* 144—147°, and 151·5°, respectively). No useful reference to (**5**) could be located. Consideration was given to the 1,3-dicarboxylic acids (**4**) and (**5**) in view of a possible retroaldo-realdolization sequence by which an initially-formed 1-formylcyclopentene-5-carboxylic acid could have been converted into a 1-formylcyclopentene-4-carboxylic acid and hence into (**5**) or (**4**).



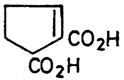
(1)



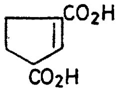
(A) (B)



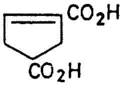
(2)



(3)



(4)



(5)

Isomer (**5**) was prepared from the diethyl ester of *cis,cis,-cis*-3-chlorocyclopentane-1,4-dicarboxylic acid[2] by heating with quinoline.[3] Both the diethyl ester and the acid (**5**) were distinguishable spectroscopically from (B) and its diethyl esters. The m.ps of the two acids were within 1° of each other, as shown in the Table.

By an analogous series of reactions starting with all-*cis*-2-chlorocyclopentane-1,3-dicarboxylic acid[2] the reported[4] structure assignment and m.p. of (**4**) were confirmed.

Isomer (**3**) was first reported by Hassel and Ingold[5] and later by Nandi[6] and Fijise *et al.*[7] Repeating these syntheses based on the isomerization of (**2**) to (**3**) by heating with alkali, we indeed observed products in the m.p. range of 144—147° as described by these authors. However, n.m.r. analysis clearly indicated mixtures of two dibasic acids identified as unchanged (**2**) and the "unknown" isomer (B) (m.p. 182—183°) which is therefore properly assigned structure (**3**).

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