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The Metalation of Indene. The Preparation of Indene-1-carboxylic Acid

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ONLY the 3-carboxylic acid has been obtained by carbonation of metal derivatives of indene.^{1,2} We

now report the synthesis of the hitherto unknown l-carboxylic acid and observations on its isomerism.

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CHEMICAL COMMUNICATIONS

CO₂H

(II)

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CO₂H

(III)

In contrast to other recommendations,³⁻⁵ we find that metalation with butyl-lithium is complete at -70° in 15-20 minutes. Carbonation, followed by rapid acidification at -40° with an

As well as finally resolving the long-standing problem of isolating indene-1-carboxylic acid, this method should lend itself to the preparation of other 1-substituted indenes.

		N.m	ı.r. spec	trum of in	dene-1-carbo	xylic acid (2) i	n CDCl _a /Me ₄ Si ⁴	•	
I	Proton			1	2	3	4, 5, 6	7	CO_2H
τ		••		5.47	3.57	3 ·24	2.76	2.45	-2.39
Multiplicity	••		••	3†	4	4‡	complex	complex	1
Relative inte	ensity	••	••	1	1	1	3	î	1
J (c./sec.)	•••	••	••	$J_{1,2} = J_2$	1,3 = 1.9;	$J_{2,3}=5.7;$	$J_{8,7} = 0.7$;	$J_{1,4} = 0.8.\dagger$	

TABLE

* 1-Methylindene⁶ has $\tau_2 = 3.65$; $\tau_3 = 3.29$; $J_{1,3} = 1.95$ c./sec.; $J_{1,2} = 1.95$ c./sec.; $J_{2,3} = 5.7$ c./sec. † Second-order splitting of 0.8 c./sec. is probably due to long range coupling between positions 1 and 4 or 7. ‡ Elvidge and Foster⁷ record long range coupling of 0.7 c./sec. between positions 3 and 7.

(M = Na, Li, or MgX)

(I)

excess of 10% hydrochloric acid gave the 1-isomer in high yield, m.p. 73.5-74° (from petroleum).

Tautomerism to the 3-carboxylic acid (cf. Ref. 6) is base-catalysed and very rapid, and also occurs above the melting point. The correctness of the 1-carboxylic acid structure is demonstrated by the n.m.r. spectrum (see Table).

The infrared spectra of the two acids, although significantly different, both show carbonyl stretching frequencies at 1675 cm.⁻¹ (KBr).

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