

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 1-carboxylic acid and observations on its isomerism.

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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 indenenes.

TABLE

		<i>N.m.r. spectrum of indene-1-carboxylic acid (2) in CDCl₃/Me₄Si*</i>						
Proton		1	2	3	4, 5, 6	7	CO ₂ H	
τ	5.47	3.57	3.24	2.76	2.45	-2.39	
Multiplicity	3 \dagger	4	4 \dagger	complex	complex	1	
Relative intensity	1	1	1	3	1	1	
J (c./sec.)	$J_{1,2} = J_{1,3} = 1.9$;		$J_{2,3} = 5.7$;	$J_{3,7} = 0.7\dagger$;	$J_{1,4} = 0.8\dagger$		

* 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.

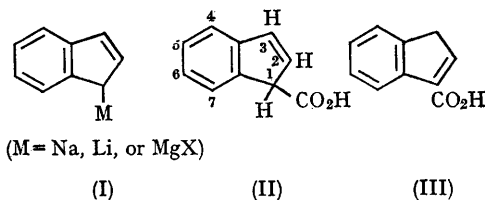
\dagger Second-order splitting of 0.8 c./sec. is probably due to long range coupling between positions 1 and 4 or 7.

\ddagger Elvidge and Foster⁷ record long range coupling of 0.7 c./sec. between positions 3 and 7.

excess of 10% hydrochloric acid gave the 1-isomer in high yield, m.p. $73.5-74^\circ$ (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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