Alkenylation with Lithium Alkenyls. Part XII. Dihydronaphthyl and Indenyl Derivatives.*

By E. A. Braude and E. A. Evans.

[Reprint Order No. 6297.]

4- and 3-Chloro-1 : 2-dihydronaphthalene, prepared from α- and β-tetralone, respectively, have been converted by direct metallation into 3 : 4-dihydro-1- and -2-naphthyl-lithium and thence into 3 : 4-dihydro-1- and -2-naphthoic acid.

3-Chloroindene failed to react with lithium, while 2-chloroindene underwent metallation at the $-CH_2-$ rather than at the $=CCl-$ group, as shown by the formation of 2-chloroindene-3-carboxylic acid on carboxylation.

Since it has been shown that lithium alkenyls can readily be obtained from 1-chloro*cyclo*alkenes (Braude and Coles, *J.*, 1950, 2014; Braude and Forbes, *J.*, 1951, 1755, and later papers) as well as from 2-arylated vinyl halides (Wright, *J. Org. Chem.*, 1936, **1**, 457), it might be expected that the same would be true of derivatives combining these structural features. Dihydronaphthyl-lithium and similar derivatives are of interest as possible synthetical reagents in the field of hydroaromatic systems and in the present paper a study of their formation and stability is reported.

α-Tetralone, which is most conveniently prepared by the oxidation of tetralin with chromic acid [Nazarov and Burmistrova, *Zhur. obshchei Khim.*, 1950, **20**, 1304], was converted by phosphorus pentachloride into a mixture of 3-chloro-1 : 2-dihydronaphthalene (II) and 1 : 1-dichlorotetralin, which are readily separated by fractionation. The ethylenic chloride was attacked slowly by lithium in refluxing ether, about 60 hours being required for complete reaction. Carboxylation furnished 3 : 4-dihydro-1-naphthoic acid (IV; see Table) (12%), together with polymeric products, possibly formed through self-addition or exchange metallation of the lithium alkenyl. The acid has previously been prepared by other methods (Baeyer, *Annalen*, 1891, **266**, 169, 175; Kay and Morton, *J.*, 1914, 1565, 1574; Fieser and Holmes, *J. Amer. Chem. Soc.*, 1936, **58**, 2319): it was characterised as a benzylamine salt. On dehydrogenation with palladium–charcoal at 290°, it gave mainly naphthalene (68%), in contrast to dehydrogenation with sulphur at 230° which yields mainly 1-naphthoic acid (Fieser, Fieser, Hershberg, Holmes, and Newman, *Science*, 1936, **83**, 558). Attempted formylation of 3 : 4-dihydro-1-naphthyl-lithium with dimethylformamide (Part XI, *loc. cit.*) yielded a mixture from which only a small amount of a 2 : 4-dinitrophenylhydrazone, corresponding to the hydrate of the derivative of 3 : 4-dihydro-1-naphthaldehyde, could be isolated.

3-Chloro-1 : 2-dihydronaphthalene (III), similarly prepared from β-tetralone, was

---

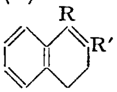
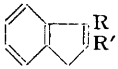
* Part XI, preceding paper.

metallated somewhat more rapidly (24 hours) than the 4-chloro-derivative; in both cases, the reaction was accompanied by an intense red coloration previously observed only with alkadienyl-lithium derivatives (Part VIII, Braude and Evans, *J.*, 1954, 607). Carboxylation gave 3 : 4-dihydro-2-naphthoic acid (V) (8%), again accompanied by polymeric material from which it was separated by sublimation in a high vacuum. The acid was characterised by a benzylamine salt which contained two molar proportions of acid to one of amine, a phenomenon previously encountered with 2 : 4-dimethylpentadienoic acid (Part IX, Braude and Evans, *J.*, 1955, 3324); it is presumably a freak of crystal lattice structure rather than a chemical effect.

3-Chloroindene (VII) prepared from indan-1-one (cf. Braun and Ostermayer, *Ber.*, 1937, **70**, 1006) was not appreciably attacked by lithium in refluxing ether after 50 hours. 2-Chloroindene (VIII), prepared by dehydrochlorination of 1 : 2-dichloroindane (Suter and Lutz, *J. Amer. Chem. Soc.*, 1938, **60**, 1360), reacted very slowly, over 110 hours being required for complete consumption of the metal. Carboxylation gave a chloro-carboxylic acid, which was characterised as the methyl ester and from its ultraviolet-light absorption (see below) is formulated as 2-chloroindene-3-carboxylic acid (IX). The $-CH_2-$ group in 2-chloroindene is evidently more reactive towards metallation than the $=CCl-$ group, and carboxylation appears to be accompanied by a migration of the double bond into the most highly conjugated position.

Light-absorption Data.—Ultraviolet-absorption data for the dihydronaphthyl and indenyl derivatives described above are collected in the Table. Like the parent chromophore, styrene [$\lambda_{max.}$ 2110 (ε 16,000) and 2440 Å (ε 12,000)], they all show two bands: one near 2200 Å which may be regarded as a displaced phenyl (E_2-)band (cf. Braude, *Ann. Reports*, 1945, **42**, 105) and the other in the 2500-Å region which is associated with the substituted Ph·C=C system. The locations of the short-wavelength bands are almost independent of the substituents, but the intensities are only about half as high for the indenyl as for the dihydronaphthyl or styryl derivatives. The reason for this difference is uncertain; it is unlikely to be due to steric effects (cf. Braude and Waight in "Progress in Stereochemistry," ed. W. Klyne, Vol. I, Chapter 4, Butterworths, London, 1954), since the indenyl will, if anything, be more planar than the dihydronaphthyl system. It is therefore presumably to be ascribed either to the greater hyperconjugation in the five-membered ring or to transannular conjugation between the benzene ring and the double bond, though either effect might also be expected to lead to a wavelength displacement (cf. Braude, *Chem. and Ind.*, 1954, 1557).

Ultraviolet-light absorption of dihydronaphthyl and indenyl derivatives.

			"Phenyl" band		"Styryl" band		
	R	R′	$\lambda_{max.}$ (Å)	ε	$\lambda_{max.}$ (Å)	ε	Solvent
							
(I)	H	H	—	—	2620	10,000 [a]	Hexane
(II)	Cl	H	2250	16,500	2640	8000	Hexane
(III)	H	Cl	2190	17,500	2700	6500	Hexane
			2260	13,100			
(IV)	CO_2H	H	2230	12,500	2740	6000	Ethanol
(V)	H	CO_2H	2250	20,000	2910	15,000	Ethanol
							
(VI)	H	H	—	—	2490	11,500 [a]	Ethanol
(VII)	Cl	H	2230	10,000	2510	9500	Hexane
(VIII)	H	Cl	2250	9000	2610	10,000	Hexane
(IX)	CO_2H	Cl	2280	11,000	2760	5500	Ethanol
(X)	CO_2Me	Cl	2270	16,500	2780	5500	Ethanol
					2800	6500	Dioxan

[a] Morton and de Gouveia, *J.*, 1934, 911, 916.

The long-wavelength bands show normal bathochromic displacements which, as usual, are larger for a 2-substituent which is in a terminal position with respect to the conjugated system than for a 1-substituent (cf. Bowden, Braude, and Jones, *J.*, 1946, 948; Bowden and Braude, *J.*, 1952, 1068). Thus the values of $\Delta\lambda$ are: 1-Cl, 20 Å; 2-Cl, 120 Å; 1-CO_2H, 120 Å; and 2-CO_2H, 290 Å. On this basis, the calculated $\lambda_{max.}$ for the acid (IX) is 2730 Å ($2490 + \Delta\lambda_{1\text{-}CO_2H} + \Delta\lambda_{2\text{-}Cl}$), in close agreement with that observed.

EXPERIMENTAL

For general methods, see Part IX, *J.*, 1955, 3324. Spectral data are only given when not included in the Table.

α-Tetralone.—A solution of chromium trioxide (450 g.) in water (230 ml.) and acetic acid (1200 ml.) was added, dropwise (*ca.* 500 ml./hr.) with vigorous stirring, to tetralin (240 g.) in glacial acetic acid (1300 ml.) during 3 hr.; the temperature was not allowed to rise above 12° (ice-cooling). After the mixture had been kept at 12° for a further 6 hr., it was allowed to attain room temperature and kept for 10 days. The dark green solution was diluted with water (8 l.) and extracted with ether until the extracts were almost colourless. The combined ether extracts (3 l.) were washed several times with 2N-sodium carbonate (1-l. portions) to remove acetic acid. The ether layer was dried (Na_2SO_4–K_2CO_3) and the ether removed through an 8″ Dufton column. The residue was distilled, giving unchanged tetralin (42 g.), b. p. 93—97°/10 mm., and α-tetralone (75 g., 28%), b. p. 129—135°/12 mm., n_D^{21} 1·5675. Yields up to 50% of α-tetralone can be obtained on a smaller scale [cf. Nazarov and Burmistrova, *Zhur. obshchei Khim.*, 1950, **20**, 1904].

4-*Chloro*-1 : 2-*dihydronaphthalene.*—α-Tetralone (50 g.) was added dropwise with stirring and cooling to phosphorus pentachloride (84 g.), and the mixture was stirred overnight at room temperature. Next morning, the solution was poured into ice-water (1 l.) and extracted with ether (4 × 100 ml.), and the ether extracts were washed with water (100 ml.), dried (Na_2SO_4), and fractionated through an 8″ Dufton column, giving: (i) 4-*chloro*-1 : 2-*dihydronaphthalene* (20 g., 36%), b. p. 59°/10^{-3} mm., n_D^{20} 1·5978, which after refractionation from sodium had b. p. 50—51°/10^{-4} mm., n_D^{23} 1·5952 (Found: C, 72·9; H, 5·7; Cl, 22·5. Calc. for $C_{10}H_9Cl$: C, 73·0; H, 5·5; Cl, 21·5%) (Mousseron and Jacquier, *Bull. Soc. chim. France*, 1950, 648, give b. p. 105°/2 mm., n_D^{25} 1·5810); (ii) higher-boiling fractions (16 g.), b. p. 76—82°/10^{-5} mm., n_D^{20} 1·6038—1·6092, which consisted mainly of 1 : 1-dichlorotetrahydronaphthalene and were recovered unchanged on treatment for 24 hr. with 20% alcoholic potassium hydroxide at 35°.

3 : 4-*Dihydro*-1-*naphthoic Acid.*—4-Chloro-1 : 2-dihydronaphthalene (10 g.) in anhydrous ether (25 ml.) was added dropwise to a stirred suspension of finely cut lithium (1 g.) in refluxing anhydrous ether (450 ml.). A faint turbidity appeared after 20 min. After 66 hours' refluxing, all the lithium had reacted and the solution was deep red.

This solution was poured on a large excess of finely powdered solid carbon dioxide (*ca.* 600 g.). After attaining room temperature, the mixture was diluted with water (400 ml.) and acidified dropwise with concentrated hydrochloric acid, and the ether layer was separated and extracted with 2N-sodium hydroxide (2 × 150 ml.). Evaporation of the ethereal solution under reduced pressure gave only a small amount of a dark brown gum. The aqueous alkaline extract was acidified with concentrated hydrochloric acid and extracted with ether (2 × 75 ml.), and the ethereal extracts, which exhibited a strong green fluorescence, were dried (Na_2SO_4) and evaporated under reduced pressure. The residual dark brown gum was sublimed at 10^{-5} mm., giving 3 : 4-dihydro-1-naphthoic acid (1·3 g., 12%) which crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 120—122° (Found: C, 76·2; H, 6·1. Calc. for $C_{11}H_{10}O_2$: C, 75·8; H, 5·8%) (Fieser and Holmes, *J. Amer. Chem. Soc.*, 1936, **58**, 2319, 2321, give m. p. 121°). Infrared absorption (paraffin mull): $\nu_{max.}$ 2650, 2580 (OH stretching), 1670 (C=O stretching), 1608 (C=C stretching), and 917 cm.$^{-1}$ (OH deformation). The *benzylamine salt* crystallised from ethyl acetate–ethanol in needles, m. p. 145—146° (Found: C, 76·1; H, 6·35; N, 4·9. $C_{18}H_{19}O_2N$ requires C, 76·8; H, 6·8; N, 5·0%).

When the acid (0·2 g.) was heated with 10% palladium–charcoal (0·05 g.) at 290—300° for 5—6 hr. in a stream of nitrogen, naphthalene (0·1 g., 68%), m. p. and mixed m. p. 80°, was obtained.

Attempted Formylation of 3 : 4-*Dihydro*-1-*naphthyl-lithium.*—Dimethylformamide (3·8 g.) in anhydrous ether (25 ml.) was added dropwise to 3 : 4-dihydro-1-naphthyl-lithium (from metal, 0·8 g., and 4-chloro-1 : 2-dihydronaphthalene, 7·5 g.), in ether (300 ml.) at 0°. The mixture was stirred at room temperature for 2 hr. and then treated with a saturated solution of ammonium chloride (300 ml.). The ether layer was separated, dried (Na_2SO_4), and fractionated, giving a mixture (2·4 g.), b. p. 135—145° (bath-temp.)/10^{-5} mm., n_D^{19} 1·6352, which did not give a semicarbazone but yielded a 2 : 4-*dinitrophenylhydrazone*, which after chromatography on alumina in benzene–chloroform crystallised from ethyl acetate–methanol in orange plates, m. p. 203—204°, $\lambda_{max.}$ 3860 Å (ε 27,000 in $CHCl_3$) (Found : C, 58·3; H, 4·6; N, 15·3. $C_{17}H_{14}O_4N_4,H_2O$ requires C, 57·3; H, 4·5; N, 15·7%). The analytical data correspond to a hydrate of the derivative of 3 : 4-dihydro-1-naphthaldehyde.

4-*Chloro*-1 : 2-*dihydronaphthalene*.—β-Tetralone (56 g., prepared by the method of Birch, *J.*, 1944, 430) was added dropwise with stirring and cooling to phosphorus pentachloride (100 g.) during 15 min. The mixture was stirred for 3 hr. at room temperature and then poured into ice-water (1 l.). Working up as above gave 3-*chloro*-1 : 2-*dihydronaphthalene* (21 g., 34%), b. p. 60°/0·1 mm., n_D^{21} 1·5870 (Found : C, 73·3; H, 5·55. $C_{10}H_9Cl$ requires C, 73·0; H, 5·5%).

3 : 4-*Dihydro*-2-*naphthoic Acid*.—3-Chloro-1 : 2-dihydronaphthalene (10 g.; redistilled from sodium) was added to a stirred suspension of finely cut lithium (1 g.) in refluxing anhydrous ether (400 ml.). The solution became slightly turbid after 15 min., then gradually acquired a violet colour which was intense after 1 hr. and gradually changed to orange after 6 hr. After 24 hours' refluxing, all the metal had been consumed and the solution was deep red.

Carboxylation of this solution as above gave 3 : 4-dihydro-2-naphthoic acid (0·9 g., 8%) which was isolated from the accompanying polymeric material by sublimation at 10^{-4} mm. and crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 118° (Found : C, 76·0; H, 5·6. Calc. for $C_{11}H_{10}O_2$: C, 75·9; H, 5·75%) (Derick and Kamm, *J. Amer. Chem. Soc.*, 1916, **38**, 400, 409, give m. p. 118·5°). Infrared absorption (paraffin mull) : $\nu_{max.}$ 2710, 2660 (OH stretching), 1675 (C=O stretching), and 1623 cm.$^{-1}$ (C=C stretching). The *benzylamine salt* crystallised in colourless needles (from ethyl acetate), m. p. 154—155° (Found : C, 76·8; H, 6·6; N, 3·2. $2C_{11}H_{10}O_2,C_7H_9N$ requires C, 76·5; H, 6·4; N, 3·1%).

2-*Chloroindene*.—Dry chlorine was passed into a well-cooled solution of indene (156 g.) in carbon tetrachloride (400 ml.). The theoretical amount of chlorine (95 g.) was taken up during 1·5 hr. The solvent was distilled off through an 8" Dufton column and the residue fractionated under reduced pressure, giving 1 : 2-dichloroindane (185 g.), b. p. 86—90°/2 mm., n_D^{23} 1·5715 (Suter and Lutz, *J. Amer. Chem. Soc.*, 1938, **60**, 1360, give b. p. 98—102°/5 mm., n_D^{25} 1·5710).

1 : 2-Dichloroindane (75 g.) was heated for 5 hr. at 225—235° until the vigorous evolution of hydrogen chloride subsided. Fractionation of the residue gave 2-chloroindene (35 g.), b. p. 110—116°/13 mm., n_D^{23} 1·5797—1·5817, which on refractionation from sodium had b. p. 100—104°/11 mm., n_D^{23} 1·5823 (Suter and Lutz, *loc. cit.*, give b. p. 95—98°/11 mm., n_D^{25} 1·5824). Infrared absorption (liquid film) : strong peaks at 1642, 1592, 1563, and 749 cm.$^{-1}$.

2-*Chloroindenyl*-3-*carboxylic Acid*.—2-Chloroindene (12 g.), freshly distilled from sodium, was added to a stirred suspension of lithium (1·4 g.) in refluxing anhydrous ether (450 ml.). After 10 min. the mixture became slightly turbid, after approximately 12 hours' refluxing it had a violet colour, but most of the lithium had not reacted, and after a total reflux time of 112 hr. it was greyish-green. Filtration through glass wool gave unchanged lithium (0·6 g.) which was pyrophoric. The solution was added to a large excess of powdered carbon dioxide (*ca.* 600 g.) and then allowed to attain room temperature. Water (300 ml.) was added, the solution was acidified with concentrated hydrochloric acid, and the ether layer was separated and extracted with 2N-sodium carbonate (2 × 250 ml.). Acidification of the sodium carbonate solution with concentrated hydrochloric acid gave a yellow solid (2·8 g.), and a further quantity (0·3 g.) was obtained by extraction with ether. Recrystallisation of the solid product from benzene gave 2-*chloroindenyl*-3-*carboxylic acid* as very pale yellow needles, m. p. 184—185° [Found : C, 61·6; H, 3·85; Cl, 18·1%; *M* (in camphor), 197; equiv., 193. $C_{10}H_7O_2Cl$ requires C, 61·7; H, 3·6; Cl, 18·2%; *M* and equiv., 195). Infrared absorption (paraffin mull) : main peaks at 2618 (OH stretching), 1692 (CO_2H), and 1587 cm.$^{-1}$ (C=C stretching). Treatment of the acid in ether with ethereal diazomethane gave the *methyl ester*, which crystallised from pentane at −60° in pale yellow needles, m. p. 47° (Found : C, 63·2; H, 4·5; Cl, 17·2. $C_{11}H_9O_2Cl$ requires C, 63·3; H, 4·3; Cl, 17·0%).

3-*Chloroindene*.—Indan-1-one (60 g.) in dry benzene (30 ml.) was added dropwise with cooling to phosphorus pentachloride (100 g.), in dry benzene (50 ml.), during 1 hr. The mixture was stirred for a further 3 hr. and then poured on crushed ice (*ca.* 500 g.). Isolation of the product with ether and fractionation gave 1-chloroindene (35 g.), b. p. 109—110°/16 mm., n_D^{23} 1·5808 (Found : C, 72·1; H, 5·2; Cl, 22·8. Calc. for C_9H_7Cl : C, 71·8; H, 4·7; Cl, 23·7%) (Braun and Ostermayer, *Ber.*, 1937, **70**, 1006, give b. p. 105°/15 mm.). Infrared absorption (paraffin mull) : main peaks at 1613, 1590, 1560, and 757 cm.$^{-1}$.

Attempts to metallate 3-chloroindene with lithium in refluxing ether were unsuccessful; most of the metal was recovered unchanged even after 60 hours' refluxing, and only a slight turbidity and a pale green colour were observed.

DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

[*Received, April 4th*, 1955.]