642. *The Effect of Conformation on the Rate of Unimolecular Solvolysis of Aralkyl Chlorides.*

By G. BADDELEY, J. W. RASBURN, and R. ROSE.

The rates of solvolysis of 1-chloroindane and 1-chlorotetralin and of their 2-methyl and 2 : 2-dimethyl derivatives in ethanol at several temperatures have been measured. The 2-methyl groups hinder solvolysis to nearly the same extent as do 2-methyl substituents in 1-phenylpropyl chloride. The similarity casts doubt on the correctness of our previous conclusion [1] that differences between the reactivities of the chlorides R•CHPhCl, where R is a primary, secondary, and tertiary alkyl group severally, are caused *mainly* by differences in steric hindrance of ionisation.

The rate of ethanolysis of 1-chloro-2-deuteroindane is 87% of that of 1-chloroindane.

Comparison of the ultraviolet absorption spectra of indan-1-one and tetral-1-one with those of their 2-methyl and 2 : 2-dimethyl derivatives shows that the 2-methyl groups, unlike the methyl groups of *tert.*-butyl phenyl ketone, do not hinder conjugation of the carbonyl group and the benzene ring.

THE reactivity of the aralkyl chlorides R•CHPhCl towards solvolysis in 80% aqueous ethanol decreases in the order R = Me > Et > Pr^i > Bu^t and we have argued [1] that this is the order of increasing steric hindrance of ionisation of the chlorides. These compounds will prefer those conformations in which R, being a bulky group, avoids the plane of the benzene ring whereas R must lie in or near this plane in the benzyl cation if this is to have maximum resonance energy; thus ionisation of the chloride is hindered by the increase of steric interaction as R approaches the plane of the ring and by loss of resonance energy in the benzyl cation if this, for steric reasons, is not approximately planar. It was recognised at that time that other interpretations of the decrease in reactivity might invoke decrease in hyperconjugation in, and increase of steric hindrance of solvation of, the aralkyl cation in the above order, but these effects were largely discounted since they might be expected to apply also to the solvolysis of the alkyl chlorides R•CMe_2Cl and it was already known that the reactivity of these compounds is only little affected by change of R from primary to secondary to tertiary alkyl group. The comparatively high reactivity of 1-chloroindane and 1-chlorotetralin [2] was offered as further evidence for our argument: these compounds have nearly the same conformation of the carbon skeleton as is required for maximum resonance stabilisation in the transition state of the ionisation process and, not having to change conformation during reaction, are essentially free from steric hindrance of ionisation.

The present paper is concerned with the relative reactivities of 1-chloroindane and 1-chlorotetralin and their 2-methyl and 2 : 2-dimethyl derivatives (I and II; R = R′ = H; R = Me, R′ = H; R = R′ = Me). According to the above steric considerations, these replacements of a hydrogen atom by a methyl group should provide a steric hindrance of ionisation of the resulting chloride which is negligible or, in any case, small in comparison with that given by the corresponding replacements in 1-phenylpropyl chloride (III; R = R′ = H). This expectation finds support, if this is needed, in the comparison of the ultraviolet absorption spectra of the series of ketones (V) and (VI) with those of the series (VII) (see Table 1). It is seen that conjugation of a carbonyl group and a benzene ring in *tert.*-butyl phenyl ketone (VII; R = R′ = Me) is hindered whereas that in the 2 : 2-dimethyl derivatives of indan-1-one and tetral-1-one (V and VI respectively; R = R′ = Me) is not. The absorption spectra of the semicarbazones are given in the

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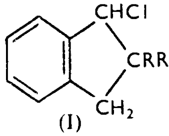
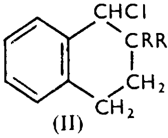
[1] Baddeley, Chadwick, and Taylor, *J.*, 1954, 2405.
[2] Baddeley and Chadwick, *J.*, 1951, 368.

TABLE 1. *The ultraviolet absorption spectra of the ketones.*

	$\lambda_{max.}$ (Å)		ε	
Indan-1-one	2430	2880	12,650	3000
2-Methylindan-1-one	2450	2900	9,900	2100
2 : 2-Dimethylindan-1-one	2450	2920	11,450	2650
Tetral-1-one	2475	2900	11,550	1900
2-Methyltetral-1-one	2465	2900	9,600	1500
2 : 2-Dimethyltetral-1-one	2465	2880	10,900	1600
Ph·CO·R				
R = Et	2380	2770	11,450	880
R = Pr^i	2375	2770	11,500	850
R = Bu^t	2360	no max.	8,100	no max.

Experimental section. The semicarbazone of 2 : 2-dimethylindanone was difficult to prepare; that of 2 : 2-dimethyltetralone was not obtained. The kinetic data are assembled in Table 2, while in Table 3 the reactivities of the series of chlorides (I), (II), and (III)


(I)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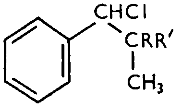
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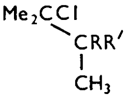
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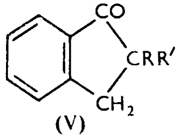
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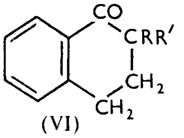
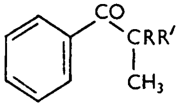

(VI)


(VII)

are compared with one another and with those of the series of tertiary alkyl chlorides (IV). It is noteworthy that the 1-chloro-2-methyl derivatives of indane and tetralin are almost identical in their behaviour towards anhydrous ethanol.

TABLE 2. *Constants of the Arrhenius equation, $k = Ae^{-E/RT}$, for the formation of hydrogen chloride by ethanolysis of the chlorides.*

	10^4k_t (min.$^{-1}$)					E (kcal. mole^{-1})	$10^{-13}A$ (min.$^{-1}$)
	0·0°	15·0°	25·0°	40·0°	50·0°		
1-Chloroindane	3·35	26·1	90·8	—	—	21·6	6·76
1-Chloro-2-methylindane	0·316	2·75	10·6	66·1	—	22·8	4·27
1-Chloro-2 : 2-dimethylindane	—	0·462	1·76	10·9	36·0	23·0	1·07
1-Chlorotetralin	0·521	5·01	19·7	132	—	23·2	17·4
1-Chloro-2-methyltetralin	—	2·51	9·6	58·9	174	22·9	4·68
1-Chloro-2 : 2-dimethyltetralin	—	—	1·78	13·8	52·5	26·4	324

TABLE 3. *Relative reactivities of the chlorides* (I) *and* (II) *in absolute ethanol and of the chlorides* (III) *and* (IV) *in* 80% *aqueous ethanol.*

	(I)		(II)		(III)[1]		(IV)[a]	
	log $k_{25\cdot0}$ (rel.)	E	log $k_{25\cdot0}$ (rel.)	E	log $k_{45\cdot0}$ (rel.)	E	log $k_{25\cdot0}$ (rel.)	E
R = R′ = H	2·93	21·6	2·31	23·2	2·67	20·7	2·25	21·0
R = Me, R′ = H	2·00	22·8	2·00	22·9	2·00	22·9	2·00	21·4
R = R′ = Me	1·22	23·0	1·27	26·4	0·57	25·4	2·13	21·4

[a] Brown, Davies, Dostrovsky, Evans, and Hughes, *Nature*, 1951, **167**, 987.

Contrary to expectation, the reactivities of the chlorides (I) and (II) decrease in the order R = R′ = H > R = Me, R′ = H > R = R′ = Me and to an extent which is similar to, if somewhat less than, that for the reactivities of the chlorides (III). The similarity casts doubt on our previous conclusion that differences between the reactivities of the chlorides in series (III) are caused *mainly* by differences in steric hindrance of ionisation. The sequence of decreasing reactivity in the three series of aralkyl chlorides is also that of decreasing hyperconjugation in the corresponding series of aralkyl cations, but change in hyperconjugation does not usually provide differences in reactivity as large as those reported here. Further, change in hyperconjugation does not provide correspondingly large differences in reactivity between the members of the alkyl chlorides (IV). That hyperconjugation contributes to the ease of ionisation of 1-chloroindane is indicated by the data in Table 4: they show that replacement of hydrogen by deuterium atom at the 2-position effects a decrease of 13% in the rate of ionisation.

TABLE 4. *Comparison of the reactivities of* 1-*chloroindane and its* 2-*deutero-derivative in absolute ethanol.*

	$10^4k_{0\cdot0}$ (min.$^{-1}$)	$10^4k_{15\cdot0}$ (min.$^{-1}$)	$10^4k_{25\cdot0}$ (min.$^{-1}$)	E (kcal. mole^{-1})	10^{-13} A (min.$^{-1}$)
1-Chloroindane	3·35	26·1	90·8	21·6	6·76
1-Chloro[2-$^2H_1$]indane	2·89	22·8	79·7	21·7	5·43
k_D/k_H	0·86	0·87	0·88	—	—

EXPERIMENTAL

Materials.—Ketones. Indan-1-one, b. p. 129—131°/12 mm., m. p. 40—41° (semicarbazone, m. p. 237—238°), was afforded in 94% yield by interaction of β-phenylpropionyl chloride and aluminium chloride in thiophen-free benzene. 2-Methylindan-1-one, b. p. 132—134°/18 mm., n_D^{20} 1·5430 (semicarbazone, m. p. 195°), was similarly prepared from α-methyl-β-phenylpropionyl chloride. 2 : 2-Dimethylindan-1-one was given by the methylation of indan-1-one. This ketone (20 g.) and methyl iodide (30 g.) were added to sodamide [from sodium (4·5 g.)] in liquid ammonia (200 c.c.). Additional amounts of sodamide (from sodium, 4·5 g.) and methyl iodide (30 g.) were added to the mixture. After evaporation of the ammonia, water was added to the residue, and the mixture was extracted with ether. The ether extract was dried (K_2CO_3) and the ether was evaporated. The residue was further methylated as described above and gave 2 : 2-dimethylindan-1-one (13·5 g.), b. p. 113—115°/13 mm., m. p. 43—44° (Found: C, 82·6; H, 7·3. Calc. for $C_{11}H_{12}O$: C, 82·5; H, 7·5%) [semicarbazone, m. p. 195—197° (Found: C, 66·5; H, 7·0; N, 19·2. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·4%)]. Tetral-1-one, b. p. 122—124°/9 mm. (semicarbazone, m. p. 222—223°), and 2-methyltetral-1-one, b. p. 129—131°/11 mm., n_D^{20} 1·5516 [semicarbazone, m. p. 200—201° (Found: C, 66·4; H, 6·7; N, 19·4. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·3%)], were prepared from γ-phenylbutyryl chloride and its α-methyl derivative respectively through the agency of aluminium chloride in thiophen-free benzene. 2 : 2-Dimethyltetral-1-one, b. p. 128—130°/13 mm., was afforded by the action of sulphuric acid (80% v/v) on γ-phenyl-αα-dimethylbutyric acid and did not give a semicarbazone.

Alcohols. These were obtained from the ketones by the action of lithium aluminium hydride and crystallised from light petroleum: indan-1-ol,[3] b. p. 119—120°/9 mm., m. p. 52—53°; 2-*methylindan*-1-*ol*, b. p. 122—123°/15 mm., m. p. 78—79° (Found: C, 81·0; H, 8·2. $C_{10}H_{12}O$ requires C, 81·1; H, 8·1%) [*phenylurethane*, m. p. 89° (Found: C, 76·8; H, 6·4; N, 5·3. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%)]; 2 : 2-*dimethylindan*-1-*ol*, b. p. 138—140/°10 mm., m. p. 56—57° (Found: C, 81·1; H, 8·5. $C_{11}H_{14}O$ requires C, 81·5; H, 8·6%) [*phenylurethane*, m. p. 90—91° (Found: C, 77·0; H, 7·0; N, 5·0. $C_{18}H_{19}O_2N$ requires C, 76·8; H, 6·8; N, 5·0%)]; tetral-1-ol, b. p. 132—134°/12 mm., n_D^{20} 1·5672 (phenylurethane, m. p. 121°); 2-*methyltetral*-1-*ol*, b. p. 138—140°/15 mm., m. p. 69—70° (Found: C, 81·8; H, 9·1. $C_{11}H_{14}O$ requires C, 81·5; H, 8·6%) [*phenylurethane*, m. p. 90—92° (Found: C, 77·5; H, 6·9; N, 5·1. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 5·0%)]; 2 : 2-*dimethyltetral*-1-*ol*, b. p. 136—138°/16 mm., m. p. 44·5—45·5° (Found: C, 81·7; H, 8·7. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%) [*phenylurethane*, m. p. 90—91° (Found: C, 77·2; H, 7·2; N, 5·0. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·1; N, 4·7%)].

When required for solvolysis in absolute ethanol, the chlorides were obtained by the action of dry hydrogen chloride on the alcohols in light petroleum in the presence of calcium chloride. 1-Chloroindane, b. p. 90—92°/10 mm. (Found: Cl, 22·3. Calc. for C_9H_9Cl: Cl, 23·3%), was

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[3] Weissgerber, *Ber.*, 1911, **44**, 1445.

also obtained by the method of Haworth, Lindley, and Woodcock.[4] It reacted with thiourea in dioxan and the product, with picric acid, gave 1-*indanylthiouronium picrate*, m. p. 158° (Found: C, 45·7; H, 3·7; N, 16·7. $C_{16}H_{15}O_7N_5S$ requires C, 45·6; H, 3·6; N, 16·6%). 1-*Chloro*[2-$^2H_1$]*indane*, b. p. 95—96°/12 mm. (Found: C, 70·5; H + D, 6·6; Cl, 22·9. C_9H_8DCl requires C, 70·4; H + D, 6·6; Cl, 23·1%), was given by interaction of dry deuterium chloride, prepared from benzoyl chloride and deuterium oxide (99·77%) as described by Brown and Groot,[5] and indene at −15° in a closed system, and was purified by repeated distillation under reduced pressure. It gave a *thiuronium picrate*, m. p. 158—158·5° (Found: C, 45·8; H + D, 3·7; N, 16·1. $C_{16}H_{14}DO_7N_5S$ requires C, 45·5; H + D, 3·8; N, 16·6%).

Ethanolysis of the Chlorides.—The ethanol was dried over magnesium ethoxide by the method of Lund and Bjerrum [6] and redistilled from magnesium ethoxide before each experiment. Ethanol (120—150 c.c.) in a flask (250 c.c.) fitted with ground-glass stopper was placed in a thermostat at the selected temperature. After an hour, the chloro-compound (0·25—0·4 c.c.) was quickly added by dropper-pipette, and the mixture was vigorously agitated. Samples (10 c.c.) were removed at selected times, run into dry acetone (40 c.c.) and titrated (lacmoid indicator) with ethanolic 0·01N-sodium ethoxide. Each determination was repeated several times; the average rate constants are listed in Tables 2 and 4. When the selected temperature was 50°, samples (10 c.c.) of the reaction mixture were heated in sealed tubes.

TABLE 5. *Ultraviolet absorption spectra of the semicarbazones.*

	$\lambda_{max.}$ (Å)				ε			
Indan-1-one	2700	2790	2975	3090	15,600	16,000	14,500	12,800
2-Methylindan-1-one	2700	2790	2970	3075	15,000	15,600	13,400	12,300
2 : 2-Dimethylindan-1-one	2720 *	2810	2975	3090 *	9,600 *	10,200	11,900	10,400 *
Tetral-1-one	2780	2850	—	—	18,000	17,900	—	—
2-Methyltetral-1-one	2800	2850	—	—	15,800	15,500	—	—

* Shoulder.

The ultraviolet absorption spectra of the ketones (see Table 1) and semicarbazones (Table 5) in hexane were measured with a Hilger Uvispek Photoelectric Spectrophotometer.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER, 1.

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[4] Haworth, Lindley, and Woodcock, *J.*, 1947, 369.
[5] Brown and Groot, *J. Amer. Chem. Soc.*, 1942, **64**, 2223.
[6] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.