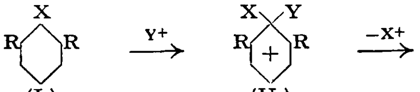
80. *The Effect of Intramolecular Configuration on the Rate of Unimolecular Solvolysis of Aralkyl Chlorides.*

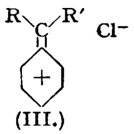
By G. Baddeley and J. Chadwick.

3-Hydroxy- and 3-chloro-1 : 2-benz*cyclo*heptene have been prepared. The rates of ethanolysis of 1-phenyl-, 1-*o*-tolyl- and 1-mesityl-ethyl chlorides and of 1-chloroindane, 1-chlorotetralin, and 3-chloro-1 : 2-benz*cyclo*heptene have been measured at two temperatures; in general, increased reactivity is caused by diminution in activation energy. The high reactivity of 1-chloroindane and 1-chlorotetralin is related to the essentially planar structure of the respective carbon skeletons. It is argued that ionisation of the other chlorides is accompanied by intramolecular reorientation and that this is subject to steric hindrance.

One of us pointed out (*Nature*, 1939, **144**, 444; 1942, **150**, 178) that, whereas some reactions are sterically hindered, others are sterically facilitated. In the latter, steric interaction in the transition state is less than that in the reactant. The naïve assumption that bimolecular reactions are of the former type while unimolecular ionisation processes are of the latter is to be avoided. There are many instances in which the bimolecular replacement of a bulky group X in a benzene derivative (I) is possible only when bulky *ortho*-substituents are present, and it has been suggested (*loc. cit.*) that this arises from the decrease in steric interaction in passing from (I) to the transition state (II). On the other hand, we now show that the ionisation of an aralkyl chloride, $\mathrm{Ar{\cdot}CRR'Cl} \longrightarrow \mathrm{Ar{\cdot}\overset{+}{C}RR'} + \mathrm{Cl^-}$, is subject to steric hindrance.

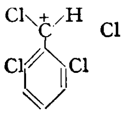


(I.) (II.)



(III.)

The ionisation process, which is the rate-determining step in the unimolecular solvolysis of alkyl and aralkyl halides, entails a tetrahedral carbon atom becoming a planar carbonium ion (Hughes, Ingold, *et al.*, numerous papers since 1935) and provides an intramolecular reorientation of the carbon skeleton which alters the magnitude of intramolecular steric interaction. Thus unimolecular solvolysis is subject to steric effects which arise solely from this change in the configuration of the carbon skeleton. For example, solvolysis of a *tert.*-alkyl halide is facilitated sterically by the decrease in the energy of steric interaction between alkyl groups which accompanies the process $\mathrm{RR'R''CCl} \longrightarrow \mathrm{RR'R''C^+} + \mathrm{Cl^-}$, the alkyl groups being more widely separated in the cation than in the chloride. Ionisation of an aralkyl chloride Ar·CRR′Cl, however, is subject to more stringent steric requirements; it is facilitated by conjugation between the side-chain and the benzene ring in the cation $Ar\cdot\overset{+}{C}RR'$, and this activating effect of the aryl group, on the basis of resonance with quinonoid structures like (III), is fully operative only when the cation is planar. The formation of such structures is known to be obstructed by one bulky *ortho*-substituent when both R and R′ (of III) are large atoms or groups and by two bulky *ortho*-substituents when R only is large; thus the steric inhibition of resonance which was first recognised more than ten years ago (Hampson *et al.*, *J.*, 1937, 10; 1939, 981; Baddeley, *loc. cit.*) and is one of several causes of "*ortho*-effects" (Hughes, *Quart. Reviews*, 1948, **2**, 107), can be a feature of the unimolecular solvolysis of a benzyl halide. This argument is difficult to substantiate as the introduction of bulky *ortho*-substituents provides additional inductomeric and possibly electromeric effects which are hard to disentangle from steric effects. For example, the low reactivity of 2 : 6-dichlorobenzylidene chloride in 50% aqueous acetone (Loch and Asinger, *Monatsh.*, 1932, **59**, 152, record 2 : 6-dichloro- $\leqslant$ 2-chloro-benzylidene chloride $<$ benzylidene chloride) is due, at least in part, to the inductive effect of the chlorine atoms attached directly to the benzene ring, and cannot be assigned to the steric inhibition of resonance in the cation (IV). Again, we have now observed that 1-mesitylethyl chloride, no doubt as a consequence of the inductive effect of its methyl groups, reacts rapidly with ethanol (Table I), despite the probable steric inhibition of resonance in the cation (V).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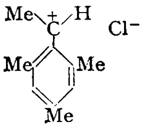
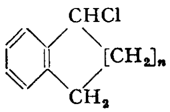

(V.)


(VI.)

The absorption spectrum of 1-methyl-2 : 3-benz-1-aza*cyclo*hept-2-ene and its low reactivity in the hydrogen-exchange reaction are both quoted as evidence that the conformation of the seven-membered ring partly inhibits conjugation between the nitrogen atom and the benzene ring (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838; Brown, Widiger, and Letang, *ibid.*, 1939, **61**, 2597), and we recognised that a comparison of 3-chloro-1 : 2-benz*cyclo*heptene (VI; $n = 3$) with 1-chlorotetralin (VI; $n = 2$), 1-chloroindane (VI; $n = 1$) and 1-*o*-tolylethyl chloride would demonstrate unambiguously, the uncertainties arising from the introduction of additional *ortho*-substituents being avoided, the effect of intramolecular configuration on the rate of unimolecular solvolysis of benzyl chloride derivatives.

Benzosuberone was obtained in good yield (*ca.* 80%) by the interaction of δ-phenyl-*n*-valeryl chloride and aluminium chloride in ethylene chloride; lower yields were obtained in light petroleum (Kipping and Hunter, *J.*, 1901, 602) or carbon disulphide (Borsche and Roth, *Ber.*, 1921, **54**, 174). Benzosuberol was readily obtained by reduction of this with aluminium *iso*propoxide and, like 1-phenylethyl alcohol, was readily converted into the corresponding chloride by thionyl chloride in the presence of pyridine. This procedure was unsatisfactory for the preparation of the readily hydrolysed 1-chloroindane and 1-chlorotetralin, and these were obtained by the addition of hydrogen chloride to indene and 1 : 2-dihydronaphthalene respectively. Their times of half-reaction in 50% aqueous acetone at 17° are 3—10 seconds. Unimolecular solvolysis occurs less readily in solvents of lower dielectric constant (Hughes, Ingold, *et al.*, *loc. cit.*), and the data in Table I were obtained in absolute ethanol. The rates of hydrogen chloride formation were measured conductometrically.

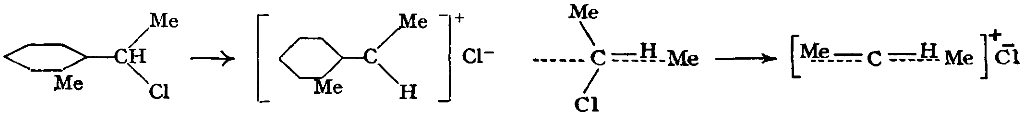
TABLE I.

Constants of Arrhenius equation, $k = A\mathrm{e}^{-E/RT}$, for the formation of hydrogen chloride by the ethanolysis of the chlorides.

	$10^7\,k_{0\cdot0}$ (mins.$^{-1}$).	$10^5\,k_{25\cdot0}$ (mins.$^{-1}$).	E, kcals./mole.	$10^{-10}A$ (secs.$^{-1}$).
1-Mesitylethyl chloride	6800	1960	21·9	290
1-Chloroindane	4000	870	20·0	5·9
1-Chlorotetralin	1070	239	20·2	2·1
1-*o*-Tolylethyl chloride	66	22·0	22·8	15
3-Chloro-1 : 2-benz*cyclo*heptene	23·5	9·2	23·9	38
1-Phenylethyl chloride	1·94	0·99	25·6	93

These reactions, like that of 1-phenylethyl chloride (Ward, *J.*, 1927, 445; Hughes, Ingold, and Scott, *J.*, 1937, 1201), are unimolecular, their rates being unaffected by small additions of sodium ethoxide. When these chlorides were added to very dilute ethanolic sodium ethoxide, the conductivity remained constant while sodium ethoxide was present and then rose sharply as the solution became acidic. Greater concentrations of sodium ethoxide provided a conductivity which was constant at first but subsequently fell gradually, owing to precipitation of sodium chloride, and passed through a sharp minimum as the mixture became acidic. The rates of reaction, obtained by measuring the times required for the neutralisation of known quantities of sodium ethoxide, were in good agreement with those obtained in the absence of ethoxide ions.

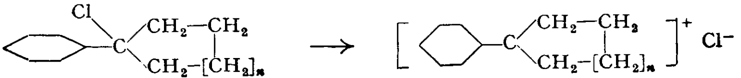
The results in Table I show that, in general, increased reactivity is caused by a diminution in activation energy (E) and that the action constant (A) varies so as to compensate partly for the change in E; such compensation effects have been discussed by Hinshelwood (" Kinetics of Chemical Change," Oxford, 1940, p. 257) and Christiansen (*Acta Chem. Scand.*, 1949, **3**, 61). The relative rates of ethanolysis, 1-chloroindane $>$ 1-chlorotetralin $\gg$ 3-chloro-1 : 2-benz*cyclo*heptene, are strikingly similar to the relative rates of hydrogen exchange, 1-methylindoline $>$ 1-methyltetrahydroquinoline $\gg$ 1-methyl-2 : 3-benz-1-aza*cyclo*heptene, observed by Brown, Widiger, and Letang (*loc. cit.*), and can be explained in terms of partial steric inhibition of resonance by a puckered seven-membered ring. When 1-*o*-tolylethyl chloride is included in the comparison, however, the outstanding feature is the high reactivity of 1-chloroindane and 1-chlorotetralin. The carbon skeletons of these two chlorides have essentially the same planar configuration as is required for maximum resonance energy in the corresponding cations; this does not apply to 3-chloro-1 : 2-benz*cyclo*heptene or 1-*o*-tolylethyl chloride, and the additional energy needed to ionise them can arise because (i) ionisation is accompanied by intramolecular reorientation in which non-bonded atoms or groups are brought closer together so that their energies of interaction consequently increase (ii) steric interaction provides a non-planar cation of comparatively low resonance energy. The latter circumstance arises when deviation from planarity effects a diminution in steric interaction which more than compensates for the loss in resonance energy. It is plausible to assume that this does not obtain in the 1-*o*-tolylethyl cation, and the manner in which steric interaction may hinder the ionisation of 1-*o*-tolyl ethyl chloride is illustrated below. The formulæ on the right, in which the broken line represents the benzene ring, are projections on a plane perpendicular to the Ar–CHMeCl bond. If the chloride is given the configuration in which steric interaction is a minimum, the methyl group of the side-chain being well separated from the *ortho*-positions, then, as resonance ensures the planarity of the cation, *ionisation of the chloride is hindered by the energy needed to bring the methyl group into the plane of the benzene ring.* This incursion of steric interaction is not in doubt.



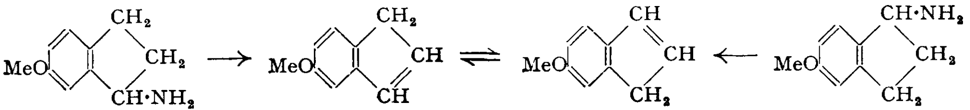
The distance separating the side-chain methyl group from the *ortho*-position in the cation is comparable with that separating (i) the *o*- and the *o*′-position in diphenyl or (ii) the methyl groups in *cis*-but-2-ene. The concomitant steric interactions in these substances are reflected respectively by the non-planar structure of diphenyl in the liquid and the gaseous state (Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408) and by the difference of *ca.* 1 kcal./g.-mol. between the *cis*- and the *trans*-form of but-2-ene (Kistiakowsky *et al.*, *J.*, *Amer. Chem. Soc.*, 1935, **57**, 876).

Although the comparatively slow ethanolysis of 3-chloro-1 : 2-benz*cyclo*heptene may, on the above argument, be derived from the energy which is needed to bring the α-methylene group into the plane of the benzene ring, there is also the possibility that it is caused by partial inhibition of resonance in the cation obtained when this chloride is ionised. There is no definite evidence to support the latter possibility. The rates of interaction of semicarbazide with indan-1-one, 1-tetralone, and benzosuberone, ultra-violet absorption data for these ketones and for their oximes and semicarbazones, the Raman frequencies for the carbonyl group in these ketones, and ultra-violet absorption data for indene, 1 : 2-dihydronaphthalene, and 1 : 2-benz*cyclo*hepta-1 : 3-diene are assembled in the Experimental section; they provide on definite evidence that those substances containing a seven-membered ring are subject to steric hindrance of resonance.

These steric considerations lead to the view that the ionisation of a tertiary aralkyl halide Ar·CRR′X, in contrast with that of a *tert.*-alkyl halide, is sterically hindered, energy being needed to bring the alkyl groups R and R′ into the plane of the ring. This view can account for our observation (details will be communicated later when the rates of unimolecular solvolysis of *cyclo*pentyl and *cyclo*hexyl chloride are available for comparison) that the rate of unimolecular ethanolysis of 1-phenyl*cyclo*pentyl chloride (VII; $n = 1$) is many times faster than that of the corresponding *cyclo*hexyl chloride (VII; $n = 2$); in fact, this difference in rate was expected since, in the cation (VIII; $n = 1$) the *cyclo*pentyl group holds the α-methylene groups away from the *ortho*-positions of the benzene ring and so effects a diminution in steric interaction. This effect of the five-membered ring has been substantiated in other instances; the comparatively stable complex of tetrahydrofuran with boron trifluoride (Brown and Adams, *J. Amer. Chem. Soc.*, 1942, **64**, 2557) and the greater stability of pyrrolidine–trimethylboron compared with piperidine–trimethylboron (Brown and Gernstein, *ibid.*, 1950, **72**, 2926) have been attributed to the reduced steric effect of the α-methylene groups of a five-membered ring.


(VII.) (VIII.)

The comparatively high reactivity of reactants which have the same configuration, usually planar, as is required for maximum resonance energy in the transition state, *e.g.*, that of 1-chloroindane and 1-chlorotetralin, is further illustrated by the hydrochlorides of the aminoindanes (IX) and (X) which form ammonium chloride " with quite remarkable ease " (Ingold and Piggott, *J.*, 1923, 1472). These authors made the further significant observation that unlike 1 : 3-diphenylpropene, " which is definitely static, indene is mobile, being strictly comparable in this respect with aziminobenzene and benziminazole."


(IX.) (X.)

Discussion of the products of interaction of the chlorides (Table I) with ethanol will form part of a further communication. It is known that 1-phenylethyl chloride provides 1-phenylethyl alcohol and styrene on interaction with aqueous formic acid (Hughes, Ingold, and Scott, *loc. cit.*), and that indan-1-ol, indene, and di-1-indanyl ether are the products of hydrolysis of 1-chloroindane (Weisgerber, *Ber.*, 1911, **44**, 1444).

EXPERIMENTAL.

Materials.—Ketones. Acetophenone was carefully fractionated. Its 2-methyl derivative (b.p. 98—99°/25 mm.; semicarbazone, m. p. 205°) was obtained by the addition of *o*-tolunitrile (*Org. Synth.*, Vol. IV, p. 69) to methylmagnesium iodide as described by Baddeley (*J.*, 1944, 235). Addition of aluminium chloride to a solution of mesitylene and acetyl chloride in carbon disulphide (Dittrich and Meyer, *Annalen*, 1891, **264**, 138) provided mesityl methyl ketone (b. p. 120—121°/18 mm.). 1-Tetralone (b. p. 129—130°/12 mm.; semicarbazone, m. p. 217—218°; Kipping and Hunter, *J.*, 1899, 149) was obtained by the oxidation of tetralin with atmospheric oxygen (Brown, Widiger, and Letang, *loc. cit.*) and freed from a little 1-tetralol (phenylurethane, m. p. 120—121°; Brochet and Cornubert, *Compt. rend.*, 1921, **172**, 1499) by oxidation with chromic acid.

Indan-1-one [m. p. 40—41°, from light petroleum; semicarbazone, m. p. 237° (decomp.) from ethanol] was obtained in 83% yield by interaction of β-phenylpropionyl chloride (b. p. 112—115°/15 mm.) and aluminium chloride (Kipping, *J.*, 1894, 480). β-Phenylpropionic acid (m. p. 46—47°, from light petroleum) was obtained by the reduction of ethyl cinnamate in methanolic solution with hydrogen and Raney nickel, and hydrolysis of the product (250 g.) in ethanol (250 c.c.) by addition of a solution of sodium hydroxide (120 g.) in water (150 c.c.). Sodium β-phenylpropionate was filtered off and dissolved in water (1200 c.c.), and the organic acid (190 g.) precipitated by concentrated hydrochloric acid. The recrystallised acid was converted into the acid chloride by interaction with excess of thionyl chloride.

Benzosuberone was prepared from δ-phenyl-*n*-valeryl chloride by a modification of the method described by Kipping and Hunter (*loc. cit.*). Finely powdered aluminium chloride (40 g.) was placed in a three-necked flask fitted with a mercury-sealed stirrer, a reflux condenser closed with a drying tube

($CaCl_2$), and a dropping funnel, and covered with dry ethylene dichloride (150 c.c.). The acid chloride (25 g.) in dry ethylene dichloride (500 c.c.) was added dropwise during 3 hours, with vigorous stirring. When the evolution of hydrogen chloride was complete, the mixture was poured into dilute hydrochloric acid–ice. The organic layer was separated, ethylene dichloride removed on the steam-bath, and the residue distilled with steam. The distillate was extracted with ether, dried (K_2CO_3), and distilled. Benzosuberone (15·5 g.; b. p. 145—146°/12 mm.) was obtained and provided a semicarbazone, m. p. 207—208° (from ethanol), and an oxime, m. p. 107—108° (from light petroleum), as described by Kipping and Hunter (*loc. cit.*). δ-Phenyl-*n*-valeric acid was prepared as follows: cinnamylidenemalonic acid (m. p. 208°) was obtained by condensing cinnamaldehyde with malonic acid (Liebmann, *Ber.*, 1895, **28**, 1439) and converted into its dimethyl ester (m. p. 66—67°; Thiele and Meisenheimer, *Annalen*, 1899, **306**, 253) which was readily hydrogenated over Raney nickel in methanol to dimethyl 3-phenyl-*n*-propylmalonate, b. p. 185—186°/15 mm. [Borsche (*Ber.*, 1912, **45**, 622) employed colloidal palladium.] Sodium hydroxide solution (25%; 625 c.c.) was added to an ice-cold solution of the ester (200 g.) in methanol (2 l.). The sodium salt of the organic acid was collected, washed with methanol, and dissolved in the minimum of water, the solution extracted with ether (2 × 500 c.c.) to remove unchanged ester, and the aqueous layer acidified with sulphuric acid. The mixture was extracted with ether, the extract dried (Na_2SO_4), and the dicarboxylic acid (160 g.; m. p. 96—97°) heated at 120—140° for 6 hours, *i.e.*, until evolution of carbon dioxide was complete. δ-Phenyl-*n*-valeric acid (m. p. 57—58°; Kipping and Hunter, *loc. cit.*, give m. p. 59°) and excess of thionyl chloride provided the acid chloride (b. p. 140—145°/20 mm.).

Secondary alcohols. Mesityl methyl ketone was reduced to the carbinol (m. p. 70—71°; phenylurethane, m. p. 123—124°) by sodium in absolute ethanol as described by Klages and Allendorff (*Ber.*, 1898, **31**, 998). Each of the other ketones was reduced to the corresponding secondary alcohol by aluminium *iso*propoxide in boiling *iso*propyl alcohol in the manner described by Lund (*Ber.*, 1937, **70**, 1520) for the reduction of acetophenone. A rough estimate of the relative rates of reduction under comparable conditions was obtained as follows. Freshly distilled aluminium *iso*propoxide (151 g.; b. p. 140—150°/12 mm.) was dissolved in *iso*propyl alcohol (249 g.); a mixture of this solution (40 g.) and ketone (M/30) was refluxed for 0·5 hour and then distilled at a rate of 1 c.c. of distillate per minute until 20 c.c. had been collected. The acetone in the distillate was converted by excess of the hydrazine in dilute hydrochloric acid into its 2 : 4-dinitrophenylhydrazone which was weighed. The results are assembled in the following table. 1-Phenylethyl alcohol (b. p. 96—97°/12 mm.; phenylurethane m. p. 93—94°) was obtained in 84% yield, 1-tetralol (b. p. 134—136°/15 mm.; phenylurethane m. p. 121—122°) in 76% yield, and *benzosuberol*, m. p. 100—101° (from light petroleum) (Found: C, 81·6; H, 8·6. $C_{11}H_{14}O$ requires C, 81·5; H, 8·6%), in 89% yield. Oxidation by chromic acid in glacial acetic acid provided benzosuberone (semicarbazone, m. p. and mixed m. p. 206—207°).

Ketone.	Wt. of acetone derivative (g.).	Reduction, %.	Relative rate.
Acetophenone	2·33	30	6
Indan-1-one	0·42	5	1
1-Tetralone	0·76	10	2
Benzosuberone	2·36	30	6

Olefins. Reduction of ketones with aluminium *iso*propoxide at higher temperatures is known to provide olefins in some instances (*e.g.*, Bachmann and Struve, *J. Org. Chem.*, 1939, **4**, 461) and we have now observed that the reduction of 1-tetralone in boiling xylene provides 1 : 2-dihydronaphthalene [b. p. 95—97°/15 mm.; dibromide m. p. 69—70° (from light petroleum)] in 72% yield. 1 : 2-Benz*cyclo*hepta-1 : 3-diene was obtained in 25% overall yield as described by Kipping and Hunter (*J.*, 1903, 146): benzosuberone oxime was reduced by sodium amalgam to 3-amino-1 : 2-benz*cyclo*heptene which provided the desired diene (b. p. 120—122°/18 mm.) when the hydrochloride was placed in a bath at 240°.

Chlorides. 1-Phenylethyl chloride and 3-chloro-1 : 2-benz*cyclo*heptene were obtained from the corresponding alcohols by the action of thionyl chloride in the presence of pyridine. In aqueous acetone, 3-chlorobenz*cyclo*heptene provided the corresponding alcohol, m. p. and mixed m. p. 101°. 1-Chloroindane and 1-chlorotetralin were obtained by the addition of dry hydrogen chloride to indene (Haworth, Lindley, and Woodcock, *J.*, 1947, 367) and 1 : 2-dihydronaphthalene respectively at −10°; being sensitive to moisture they were kept in sealed tubes. 1-*o*-Tolylethyl chloride and 1-mesitylethyl chloride were obtained from benzene solutions of the corresponding alcohols by hydrogen chloride. The water formed was removed by calcium chloride. Each chloride was distilled under reduced pressure in an atmosphere of dry nitrogen (cf. appended table).

Compound.	B. p. (0·5 mm.).	Cl, %, found.	Cl, %, calc.	Compound.	B. p. (0·5 mm.).	Cl, %, found.	Cl, %, calc.
1-Phenylethyl chloride	39—40°	25·2	25·3	1-Chloroindane	68—69°	23·0	23·3
1-*o*-Tolylethyl chloride	96—97 (15 mm.)	22·8	23·0	1-Chlorotetralin	76—77	21·2	21·3
1-Mesitylethyl chloride	83—84	19·2	19·45	3-Chlorobenz*cyclo*heptene	95—96	19·6	19·65

Physical Data.—The ultra-violet absorption spectra of most of the ketones and olefins employed in this work were measured with a Hilger E3 quartz spectrograph fitted with a Spekker photometer. A tungsten-steel high-tension spark was employed as the source of light. Immediately before use, each substance was either recrystallised or redistilled under reduced pressure. Relevant data from other sources are also assembled; our own are given in parentheses.

Compound.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	Ref.	Raman frequency for the carbonyl group (cm.$^{-1}$).	Ref.
1-Indanone	2350 (2400)	12,000 (11,000)	(*a*)	1714 *	(*c*)
1-Tetralone	2400 (2450)	10,000 (11,000)	(*a*)	1682	(*c*)
Benzosuberone	2350 (2400)	9,000 (9,000)	(*a*)	1676	(*c*)
Acetophenone	2400 (2350)	12,000 (10,000)	(*b*)	1684	(*c*)
2 : 4 : 6-Trimethylacetophenone	2400 †	4,000	(*b*)	1700	(*d*)

* This frequency is as high as that for a carbonyl group which is not conjugated with a benzene ring (cf. benzyl methyl ketone, 1714 cm.$^{-1}$), but is not evidence of lack of conjugation as the frequency for indan-2-one is also abnormally high (1739 cm.$^{-1}$; cf 2-tetralone, 1717 cm.$^{-1}$).

† Maximum absorption occurs at a shorter wave-length.

	Semicarbazones.		Oximes [Ref. (*e*)].	
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
I-Indanone	(2705)	(18,000)	2500	10,000
1-Tetralone	(2800)	(18,000)	2500	10,000
Benzosuberone	(2650)	(17,000)	2450	10,000
Acetophenone	(2750)	(18,000)	2500	10,000

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	Ref.
Indene	2500	10,000	(*f*)
1 : 2-Dihydronaphthalene	2500	10,000	(*f*)
1 : 2-Benz*cyclo*hepta-1 : 3-diene	(2550)	(10,000)	
Styrene	2460	10,000	(*f*)

(*a*) Ramart-Lucas and Hoch, *Bull. Soc. chim.*, 1935, [v], **2**, 327; 1938, [v], **5**, 848. (*b*) O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906. (*c*) Bicquard, *Bull. Soc. chim.*, 1941, [v], **8**, 55. (*d*) Saunders, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3121. (*e*) Ramart-Lucas and Hoch, *Bull. Soc. chim.*, 1938, [v], **5**, 987. (*f*) Morton and de Gouveia, *J.*, 1934, **911**, **916**.

Rates of Semicarbazone Formation.—The method was based on that described by Conant and Bartlett (*J. Amer. Chem. Soc.*, 1932, **54**, 2881). A solution (0·200M.; 60 c.c.) of the ketone in ethanol and a mixture of an aqueous solution (0·200M.; 30 c.c.) of semicarbazide hydrochloride and an aqueous solution (0·400M.; 30 c.c.) of potassium acetate were placed in a thermostat at 25·0° or 41·0° and subsequently mixed together. Samples (10 c.c.) were removed after selected intervals of time and unchanged semicarbazide determined by titration with iodine solution. The reaction is reversible and the bimolecular velocity constants (k_2) were obtained by substitution in the equation :

$$k_2 = [138/(t - t_1)Z] \log_{10}(2S + A)(2S_1 + B)/(2S + B)(2S_1 + A).$$

S, the concentration of semicarbazide at time t, is given by $0{\cdot}025T$ where T is the titre, expressed in c.c. N/10-iodine solution, of 10 c.c. of reaction mixture. $A = (0{\cdot}05 + RS_\infty + Z)$, $B = (0{\cdot}05 + RS_\infty - Z)$, $Z = [(0{\cdot}05 + RS_\infty)^2 + 0{\cdot}2RS_\infty]^{1/2}$, $R = (0{\cdot}05 + S_\infty)/(0{\cdot}05 - S_\infty)$, and the subscripts have their usual significance. This equation assumes pseudo-unimolecular hydrolysis of the semicarbazone (velocity constant k_1) and gives values of k_2 which are somewhat lower than those obtained by applying Conant and Bartlett's equation. Details of a typical experiment are given in Table II, and the velocity constants are assembled in Table III.

TABLE II.

Interaction of acetophenone and semicarbazide at 25·0°.

Directly measured end-point, $T_\infty = 0{\cdot}82$; $T_0 = 20{\cdot}00$ c.c.

$(t - t_1)$, min.	0	21	40	60	80	103	127
T, c.c.	17·82	15·02	13·00	11·34	9·88	8·48	7·36
k_2	—	5·40	5·40	5·33	5·39	5·45	5·43

Mean value of $k_2 = 5{\cdot}41$ hr.$^{-1}$ g.-mol.$^{-1}$ l. at 25·0°.
$k_1 = k_2RS_\infty = 0{\cdot}0123$ hr.$^{-1}$ at 25·0°.

TABLE III.

Velocity constants.

Compound.	Temp.	k_2, hr.$^{-1}$ g.-mol.$^{-1}$ l.	k_1, hr.$^{-1}$.	Compound.	Temp.	k_2, hr.$^{-1}$ g.-mol.$^{-1}$ l.	k_1, hr.$^{-1}$.
Acetophenone	25·C°	5·41	0·0123	1-Tetralone	25·0°	1·03	0·0169
	41·0	7·9	0·0223		41·0	2·00	0·0337
1-Indanone	25·0	1·40	0·0167	Benzosuberone	25·0	0·59	0·0164
	41·0	3·29	0·0391		41·0	1·03	0·0253

Ethanolysis of the Chlorides.—One batch of absolute alcohol, obtained by the method of Lund and Bjerrum (*Ber.*, 1931, **64**, 210), was used for the entire investigation and was redistilled from magnesium ethoxide before each experiment. The chlorides provided hydrogen chloride which was determined conductometrically or by titration with a solution of sodium ethoxide in absolute ethanol (lacmoid indicator). These two methods gave comparable results but the former was the more accurate and the more convenient. Although the conductivities of solutions of hydrogen chloride in absolute ethanol have been determined by a number of workers (*e.g.*, Lapworth and Partington, *J.*, 1911, 1426; Partington, *J.*, 1911, 1939; Goldschmidt, *Z. physikal. Chem.*, 1914, **89**, 129), we calibrated our conductivity cell by introducing ethanolic solutions of hydrogen chloride of known concentration and measuring the conductivities at 0·0° and again at 25·0° (cf. Norris *et al.*, *J. Amer. Chem. Soc.*, 1928, **50**, 1795; 1935, **57**, 1415). Resistances were measured on a Universal Impedance Bridge of the Dawe Instrument Co. Ltd., kindly provided by Imperial Chemical Industries Ltd. It was energised by a 1000-cycle audio-oscillator, and the system was sensitised by a variable condenser in parallel with the conductivity tube. The same tube subsequently constituted reaction vessel and conductivity cell. It had lightly platinised electrodes which did not need to be re-platinised during the course of the work. The electrode unit was attached to the tube by a ground-in joint. Measurements made under nitrogen did not differ by more than the experimental error from those obtained in air (cf. Norris *et al.*, *loc. cit.*). Solutions of hydrogen chloride in ethanol, and solutions in which ethanolysis of a chloride was complete, showed no variation in conductivity when kept under air at 0·0° or 25·0° for several days. Hughes, Ingold, and Scott (*loc. cit.*) observed a ready reaction between ethanol and hydrogen chloride at 70°.

General Experimental Procedure.—The conductivity cell, charged with absolute ethanol (10 c.c.), was placed in the thermostat and after *ca.* 20 minutes a volume, selected to provide an approx. 0·05M-solution, of the chloride was added and the mixture vigorously agitated. A stop watch was started as the first conductivity measurement was made and further measurements were made at selected intervals of time. When the reaction was complete, or when a sufficient range of readings had been obtained (usually after 24 hours), a sample (5 c.c.) was pipetted into 50% aqueous acetone (20 c.c.), refluxed gently for 30 minutes, and titrated with standard alkali. The molarity of the ethanolic solution was calculated from the titre and agreed with that obtained conductometrically in those instances where the reaction went to completion in the conductivity cell. A detailed example is shown in Table IV.

Actually, owing to the presence of the aromatic material, the concentrations of hydrogen chloride as determined by the conductivity method were about 3% low. This discrepancy was also observed by Norris.

Ethanolysis in the Presence of Sodium Ethoxide.—If the ethanolysis is bimolecular, the rate of reaction should be greatly increased by the presence of ethoxide ions: no such effect has been found. The conductivity cell was charged with absolute ethanol (10 c.c.) and 0·100N-sodium ethoxide (0·500 c.c.) and placed in a thermostat at 25·0°. After 20 minutes, the chloride (*ca.* 0·0010 mole) was added and the resistance measured at frequent intervals. As previously described, change in resistance indicated when the reaction mixture was neutral and the time was then recorded. Further additions of 0·100N-sodium ethoxide solution were made from a micro-burette, precautions being taken to prevent access to atmospheric moisture, and the intervals of time to reach neutrality were recorded. The final titration was obtained by washing the reaction mixture into a flask with 50% aqueous acetone (20 c.c.) and titration with sodium ethoxide solution. A detailed example is shown in Table V.

TABLE IV.

Ethanolysis of 1-*chlorindan at* 25·0°.

The chloride (0·16 c.c.) was added to ethanol (10 c.c.).

Time (mins.).	Conductance (mhos × 10^4).	Molarity of HCl.	$10^4 k$ (mins.$^{-1}$).	Time (mins.).	Conductance (mhos × 10^4).	Molarity of HCl.	$10^4 k$ (mins.$^{-1}$).
0	2·47	0·0032	—	87	26·60	0·0612	89
12	8·00	0·0142	90	103	28·17	0·0663	86
21	11·24	0·0211	87	120	30·30	0·0727	87
37	15·87	0·0325	86	139	32·15	0·0765	83
57	20·62	0·0446	85	153	33·33	0·0832	89
				After 24 hours	39·50	0·1105	—
73	24·15	0·0541	88	Final molarity by titration		0·115	—

Mean value of k = 0·0087 mins.$^{-1}$ at 25·0°.

TABLE V.

Ethanolysis of 1-*chlorindan at* 25·0° *in the presence of small concentrations of sodium ethoxide.*

0·1N-NaOEt, c.c.	0·50	1·50	3·00	4·00	5·00	6·00	7·00	8·00	11·00
Time (mins.)	5·5	17	38	53	70	92	118	152	∞
$10^4 k$	84	87	84	85	86	86	86	85	—

Mean value of k = 0·0085 mins.$^{-1}$ at 25·0°.

The Chlorides and Potassium Iodide in Acetone.—Potassium iodide (AnalaR) was recrystallised twice from distilled water, thoroughly dried in an oven at 120°, and stored in the dark in air-tight containers. Acetone (2 l.) was refluxed for 6 hours over potassium permanganate (20 g.) and sodium hydroxide (20 g.) and fractionally distilled. The fraction of b. p. 56·5—57·0° was collected separately and access to moisture was prevented. Each chloride (0·01 mole) in turn was added to a 0·04M-solution (50 c.c.) of potassium iodide in acetone; samples (5 c.c.), in sealed tubes, were placed in a thermostat at 100·0°. In each instance there was no precipitate of potassium chloride after several hours. Precipitation was apparently complete after 30 minutes when benzyl chloride was employed.

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