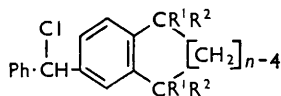**887.** *Relation between Hyperconjugation and Conformation. Part III.* Ethyl Alcoholysis of Some Derivatives of Diphenylmethyl Chloride.*

By G. BADDELEY and M. GORDON.

Derivatives (II, $n = 5$, 6, and 7) and (III, $n = 5$ and 6) have been prepared and their reactivities in ethanolysis measured and compared with those for the chlorides (I, $n = 5$, 6, and 7). The comparison affords evidence for the view [1] that hyperconjugation of methylene and phenyl groups varies with change in the conformational relationship of the groups.

The reactivities of 4-*cyclo*pentyl-, 4-*cyclo*hexyl-, and 4-*iso*propyl-diphenyl-methyl chloride in ethanolysis decrease in this order.

RATES of unimolecular solvolysis of the chlorides (I; $n = 5$, 6, and 7) decrease in this order and have been offered [2] as evidence for the view [1] that hyperconjugation of methylene group and aromatic ring in the system $Ar-\overset{\alpha}{C}H_2-\overset{\beta}{C}{<}$ decreases progressively as the β-carbon atom lies at increasing distances from the plane of the ring. According to this interpretation, should one or both of the hydrogen atoms of the α-methylene group be replaced by methyl as in the chlorides (II and III; $n = 5$, 6, and 7) the reactivities of the chlorides should depend less on the value of n. In fact, the contribution by hyperconjugation to the reactivities of the chlorides (III), though not zero since it is generally accepted that the C–C bond can hyperconjugate though to a less extent than the C–H bond, should not be altered by change in the value of n. This follows from the assumption that the *tert.*-butyl group resembles the methyl group in having its hyperconjugative effect unaffected by rotation of the group about the bond joining it to the benzene ring. We have prepared the chlorides (II; $n = 5$, 6, and 7) and (III; $n = 5$ and 6); the kinetic data for their solvolysis in dry ethyl alcohol are assembled in Table 1 together with those previously reported for the chlorides (I; $n = 5$, 6, and 7). Table 2 provides a comparison of the relative rates of solvolysis at 0° for each series of chlorides.

(1 ; $R^1 = R^2 = H$)

(II ; $R^1 = H$; $R^2 = Me$)

(III ; $R^1 = R^2 = Me$)

TABLE 1. *Arrhenius parameters for the formation of hydrogen chloride by the ethanolysis of the chlorides.*

Chloride	At 0·0° $10^5 k$ (sec.$^{-1}$)	At 20·0° $10^5 k$ (sec.$^{-1}$)	E (kcal./ mole)	$10^{-10} A$ (sec.$^{-1}$)	Chloride	At 0·0° $10^5 k$ (sec.$^{-1}$)	At 20·0° $10^5 k$ (sec.$^{-1}$)	E (kcal./ mole)	$10^{-10} A$ (sec.$^{-1}$)
I; $n = 5$ ...	23·3	205	17·3	1·5	II; $n = 5$	14·8	160	18·9	15·8
$n = 6$ ...	17·9	172	17·9	1·7	$n = 6$	11·9	130	19·1	15·5
$n = 7$ ...	15·1	147	18·0	2·0	$n = 7$	12·1	142	19·4	15·8
					III; $n = 5$	10·9	123	19·2	25·1
					$n = 6$	9·6	113	19·6	37·4

2-Phenylmethyl chlorides	At 0·0° $10^5 k$ (sec.$^{-1}$)	At 20·0° $10^5 k$ (sec.$^{-1}$)	At 25·0° $10^5 k$ (sec.$^{-1}$)	E (kcal./mole)	$10^{-10} A$ (sec.$^{-1}$)
4-*cyclo*Pentyl-	7·51	82·9	144	19·1	11·6
4-*cyclo*Hexyl-	5·75	67·9	122	19·3	13·8
4-*iso*Propyl- [3]	—	—	106	—	—

As expected, change in reactivity is greatest in series (I) and least in (III); thus the data provide evidence for the view that hyperconjugation of methylene and phenyl groups

* Part II, *J.*, 1958, 3171.

[1] Baddeley, Chadwick, and Rawlinson, *Nature*, 1949, **164**, 833; Baddeley and Gordon, *J.*, 1952, 2190.

[2] Arnold and Truett, *J. Amer. Chem. Soc.*, 1951, **73**, 5508.

[3] Hughes, Ingold, and Taher, *J.*, 1940, 949.

is altered by change in the conformational relationship of the groups. It is noteworthy that whereas the contribution of hyperconjugation to the reactivity of (III; $n = 6$) is expected to be about the same as that to the reactivity of (III; $n = 5$), these compounds have different reactivities. It follows, therefore, that the differences in reactivity between members of the series of chlorides (I) and (II) cannot be attributed wholly to differences in hyperconjugation.

TABLE 2. *Relative rates of ethanolysis at* $0·0°$ *for each of the series of chlorides,*
(I), (II), *and* (III).

	(I)	(II)	(III)
$n = 5$	100	100	100
$n = 6$	77	80	88
$n = 7$	65	82	—

The reactivity of 4-*cyclo*pentyldiphenylmethyl chloride is greater than that of the corresponding *cyclo*hexyl derivative (see Table 1) as expected since the *cyclo*pentyl group holds its α-methylene group away from the *ortho*-positions of the benzene ring and so diminishes steric interaction. This effect of the five-membered ring has been observed in other instances. However, other effects, such as the greater aptitude of the *cyclo*pentyl group to provide an exocyclic double bond, may contribute to the difference in reactivity.

EXPERIMENTAL

Materials.—*Hydrocarbons.* *iso*Propyl-, *cyclo*pentyl-, and *cyclo*hexyl-benzene were prepared by previously described methods. 1 : 3-Dimethylindane, b. p. 199—201°, was obtained by catalytic hydrogenation of 1 : 3-dimethylindene,[4] the product of distillation of 1 : 3-dimethyl-indan-1-ol at atmospheric pressure. 1 : 2 : 3 : 4-Tetrahydro-1 : 4-dimethylnaphthalene, b. p. 104—105°/12 mm., was given by hydrogenation of 1 : 2-dihydro-1 : 4-dimethylnaphthalene,[5] the product of dehydration of 1 : 2 : 3 : 4-tetrahydro-1-hydroxy-1 : 4-dimethylnaphthalene with formic acid. 5-Phenylhexanoyl chloride, b. p. 145—147°/16 mm., was obtained from the acid [6] by the action of thionyl chloride, and gave 3-methyl-1 : 2-benzo*cyclo*hepten-7-one, b. p. 148—150°/16 mm., *semicarbazone*, m. p. 204—205° (Found: C, 68·1; H, 7·5; N, 17·7. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·4; N, 18·2%), when cyclised with aluminium chloride as described by Baker and Aspinall.[7] This ketone afforded 3 : 7-dimethyl-1 : 2-benzo*cyclo*-hepten-3-ol which gave 3 : 7-*dimethyl*-1 : 2-benzo*cyclo*hepta-1 : 3-*diene*, b. p. 123—124°/17 mm. (Found: C, 90·5; H, 9·4. $C_{13}H_{16}$ requires C, 90·7; H, 9·3%). 3 : 7-*Dimethylbenzo*cyclo*-heptene*, b. p. 121—123°/18 mm. (Found: C, 90·0; H, 10·0. $C_{13}H_{18}$ requires C, 89·7; H, 10·3%), was obtained by catalytic hydrogenation. 1 : 1 : 3 : 3-Tetramethylindane,[8] b. p. 208—210°, was readily afforded by the action of 85% sulphuric acid on 2 : 5-dimethyl-4-phenylpentan-2-ol or the olefin obtained from it by the action of formic acid.

1 : 2 : 3 : 4-Tetrahydro-1 : 1 : 4 : 4-tetramethylnaphthalene,[9] b. p. 248°/760 mm., was given by the interaction of 2 : 5-dichloro-2 : 5-dimethylhexane (the product of interaction of the corresponding diol, m. p. 88—89°, and hydrogen chloride), benzene, and aluminium chloride. The preparation of *cyclo*hexylbenzene,[10] b. p. 239°/760 mm., involved 1-phenyl*cyclo*hexanol and 1-phenyl*cyclo*hexane as intermediates. *cyclo*Pentylbenzene, b. p. 216—217°/760 mm., was similarly obtained.

Ketones. Aluminium chloride (1·5 mol.) was covered with redistilled ethylene dichloride and benzoyl chloride (1·25 mol.) was gradually added together with sufficient ethylene dichloride to keep the acid chloride–aluminium chloride complex in solution. The solution was decanted on the appropriate aromatic hydrocarbon, and after being kept overnight the mixture was

[4] von Braun and Kirschbaum, *Ber.*, 1913, **46**, 3041.
[5] Kloetzel, *J. Amer. Chem. Soc.*, 1940, **62**, 1710.
[6] Nenitzescu and Gavat, *Annalen*, 1935, **519**, 271.
[7] *J.*, 1950, 745.
[8] Bogert and Davidson, *J. Amer. Chem. Soc.*, 1934, **56**, 187.
[9] Bruson and Kroeger, *ibid.*, 1940, **62**, 36.
[10] Sabatier and Murat, *Compt. rend.*, 1912, **154**, 1390.

poured on ice and hydrochloric acid. The organic layer was separated, dried (K_2CO_3), and distilled.

The following derivatives of benzophenone were obtained: 3 : 4-(3 : 5-dimethyl*cyclo*penteno)-, 204—205°/0·25 mm. (Found: C, 86·5; H, 7·1. Calc. for $C_{18}H_{18}O$: C, 86·4; H, 7·2%); 3 : 4-(3 : 6-dimethyl*cyclo*hexeno)-, b. p. 205—206°/0·25 mm. (Found: C, 86·2; H, 7·5. Calc. for $C_{19}H_{20}O$: C, 86·4; H, 7·6%); 3 : 4-(3 : 7-dimethyl*cyclo*hepteno)-, b. p. 198°/0·07 mm. (Found: C, 86·5; H, 8·0. Calc. for $C_{20}H_{22}O$: C, 86·3; H, 7·9%); 3 : 4-(3 : 3 : 5 : 5-*tetramethyl*cyclo*penteno)-, b. p. 190°/0·5 mm., needles, m. p. 70—71° from ethanol (Found: C, 85·9; H, 7·9. $C_{20}H_{22}O$ requires C, 86·3; H, 7·9%); 3 : 4-(3 : 3 : 6 : 6-*tetramethyl*cyclo*hexeno)-, b. p. 196—198°/0·3 mm., needles, m. p. 77—78° from ethanol (Found: C, 86·2; H, 8·3. $C_{21}H_{24}O$ requires C, 86·3; H, 8·2%); 4-*cyclo*pentyl-, b. p. 175—177°/0·06 mm. (Found: C, 86·1; H, 7·4. Calc. for $C_{18}H_{18}O$: C, 86·4; H, 7·2%); 4-*cyclo*hexyl-,[11] b. p. 197—199°/0·12 mm. (Found: C, 86·2; H, 7·4. Calc. for $C_{19}H_{20}O$: C, 86·4; H, 7·6%).

Alcohols. The following derivatives of diphenylmethanol were obtained from the corresponding benzophenones by reduction with lithium aluminium hydride or with zinc dust and alkali;[3] 3 : 4-(3 : 5-*dimethyl*cyclo*penteno)-, b. p. 213—215°/13 mm., needles, m. p. 62·5—63·5° from light petroleum (Found: C, 85·5; H, 7·8. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%); 3 : 4-(3 : 6-dimethyl*cyclo*hexeno)-, b. p. 189—191°/0·1 mm. (Found: C, 85·5; H, 8·5. Calc. for $C_{19}H_{22}O$: C, 85·7; H, 8·3%); 3 : 4-(3 : 7-dimethyl*cyclo*hepteno)-, b. p. 190—192°/0·07 mm. (Found: C, 85·4; H, 8·6. Calc. for $C_{20}H_{24}O$: C, 85·7; H, 8·6%); 3 : 4-(3 : 3 : 5 : 5-*tetramethyl*cyclo*penteno)-, needles, m. p. 118—119° from light petroleum (Found: C, 84·9; H, 9·0. $C_{21}H_{24}O$ requires C, 85·7; H, 8·9%); 4-*cyclo*pentyl-, needles, m. p. 52—53° from light petroleum (Found: C, 85·9; H, 8·1. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%); 4-*cyclo*hexyl-, needles, m. p. 53—54° (Found: C, 85·8; H, 8·7. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%).

Chlorides. The following derivatives of diphenylmethyl chloride were prepared by passing dry hydrogen chloride for 24 hours into a solution or suspension of the corresponding alcohols in light petroleum (b. p. 60—80°). The petroleum was then decanted from a lower aqueous layer and dried ($CaCl_2$); the solvent was removed under reduced pressure and in the absence of moisture and oxygen and the residue was rapidly distilled at 0·1 mm., using a preheated oil-bath. In all instances, the chloride before and after distillation provided rates of ethanolysis which, for a given temperature, did not differ by more than 2%. The approximate b. p.s were: 3 : 4-(dimethyl*cyclo*penteno)-, b. p. 170° (Found: Cl, 13·1. Calc. for $C_{18}H_{19}Cl$: Cl, 13·1%); 3 : 4-(3 : 6-dimethyl*cyclo*hexeno)-, b. p. 175° (Found: Cl, 12·3. Calc. for $C_{19}H_{21}Cl$: Cl, 12·5%); 3 : 4-(3 : 7-dimethyl*cyclo*hepteno)-, b. p. 180° (Found: Cl, 11·8. Calc. for $C_{20}H_{23}Cl$: Cl, 11·9%); 3 : 4-(3 : 3 : 5 : 5-tetramethyl*cyclo*penteno)-, b. p. 180° (Found: Cl, 11·6. Calc. for $C_{20}H_{23}Cl$: Cl, 11·9%); 3 : 4-(3 : 3 : 6 : 6-tetramethyl*cyclo*hexeno)-, b. p. 185° (Found: Cl, 11·1. Calc. for $C_{21}H_{25}Cl$: Cl, 11·4%); 4-*cyclo*pentyl-, b. p. 187° (Found: Cl, 13·2. Calc. for $C_{18}H_{19}Cl$: 4-*cyclo*hexyl-, b. p. 193°, needles m. p. 62—63° from light petroleum (Found: C, 79·5; H, 7·2; Cl, 12·8. $C_{19}H_{21}Cl$ requires C, 80·1; H, 7·4; Cl, 12·5%).

Alcoholysis of the Chlorides in Anhydrous Ethyl Alcohol.—The procedure was that described by Hughes, Ingold, and Taher.[3] Experiments were carried out at 0·0°, at 20·0°, or 25·0° (±0·05°) by sampling, the samples being run into a large volume of ice-cold acetone to stop the

TABLE 3. *Ethanolysis of* 4-*cyclopentyldiphenylmethyl chloride at* 0·0°.

t	0	50	100	135	176	230	295	348
$a - x$	11·32	9·02	7·15	6·08	5·15	4·02	2·99	2·37
$10^5 k$	—	7·57	7·66	7·67	7·46	7·49	7·51	7·48

Mean $10^5 k = 7·55$; other runs gave $10^5 k = 7·40$ and 7·58 severally.

reaction, and titrated with sodium hydroxide (0·01N) with lacmoid as indicator. Table 3 illustrates one run. 4-*cyclo*Pentyldiphenylmethyl chloride was initially in 0·01132M-solution. Its concentration, $a - x$, at time t, in minutes, is expressed in c.c. of 0·0100N-sodium hydroxide per 10 c.c. of sample. All first-order rate constants, k, are in sec.$^{-1}$.

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[11] Kleene, *J. Amer. Chem. Soc.*, 1940, **62**, 3523.