

643. *Relation between Hyperconjugation and Conformation. Part II. The Ethyl Alcoholysis of Some Homologues of Diphenylmethyl Chloride.*

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The reactivities of the 4-alkyldiphenylmethyl (4-alkylbenzhydryl) chlorides $R\cdot CH_2\cdot C_6H_4\cdot CHPhCl$, where R is H, Me, Et, Prⁱ, and Bu^t, in dry ethyl alcohol are shown to decrease in this order. 3 : 5-Dimethyl-, 3 : 4 : 5-trimethyl-, 4-ethyl-3 : 5-dimethyl-, and 3 : 5-dimethyl-4-propyl-diphenylmethyl chloride have been prepared. Their reactivities in the ethanolysis reaction indicate that the hyperconjugative effect of the 4-ethyl and the 4-propyl group is not hindered by methyl groups in the 3- and 5-positions and, therefore, that in these instances hyperconjugation of a primary alkyl group is unaffected by torsional rotation of the group about the bond attaching it to benzene ring.

RATES of solvolysis decrease in the series 3 : 4-cyclopenteno- > 3 : 4-cyclohexeno- > 3 : 4-cyclohepteno-benzhydryl chloride and have been offered ¹ as evidence for the view ² that

¹ Part I, Baddeley and Gordon, *J.*, 1952, 2190; Arnold and Truett, *J. Amer. Chem. Soc.*, 1951, **73**, 5508.

² Baddeley, Chadwick, and Rawlinson, *Nature*, 1949, **164**, 833.

the hyperconjugative release of electrons by a methylene group is a maximum when its hydrogen atoms are placed one on either side of the plane of the attached benzene ring and is hindered by forces which oppose this conformation. Several groups of workers have shown that primary alkyl groups CH_2R attached to an aromatic system provides a hyperconjugative release of electrons which decreases in the order $\text{R} = \text{H} > \text{Me} > \text{Et} > \text{Pr}^i > \text{Bu}^t$; this has been interpreted in terms of second-order hyperconjugation, partial suppression of hyperconjugation of the CH_2 group by the inductive effect of R, steric hindrance of solvation, and steric hindrance of hyperconjugation severally. The last interpretation is based on the assumption that hyperconjugation in the system $\text{Ar}\cdot\text{CH}_2\text{R}$, like conjugation in ArOR , $\text{Ar}\cdot\text{NHR}$, $\text{Ar}\cdot\text{COR}$, etc., is a maximum when R is in the plane of the aromatic ring and diminishes progressively as the side-chain of which R is a part is rotated through an angle of 90° . It follows that non-bonding interaction of R and the ring, in the order $\text{R} = \text{Me} < \text{Et} < \text{Pr}^i < \text{Bu}^t$, will hinder hyperconjugation. The work reported in this paper was designed to check the validity of this interpretation and involves the following argument. Should the positions *ortho* to the CH_2R group be occupied by bulky substituents, steric hindrance of hyperconjugation should be nearly independent of the size of the alkyl group R, for R, even when only a methyl group, would avoid the plane of the ring. Thus in the presence of bulky *ortho*-substituents the usual sequence of hyperconjugative effects, $\text{R} = \text{H} > \text{Me} > \text{Et} > \text{Pr}^i > \text{Bu}^t$, should become $\text{R} = \text{H} \gg \text{Me} = \text{Et} = \text{Pr}^i = \text{Bu}^t$. The former is conveniently illustrated by the solvolysis of the 4-alkylbenzhydryl chlorides $\text{R}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHPhCl}$; our data are assembled in Table 1. Since this work was completed Shiner and Verbanic³ have reported the preparation of these chlorides and their rates of solvolysis in aqueous ethanol and aqueous acetone.

TABLE 1. Arrhenius parameters for the solvolysis of 4-alkyldiphenylmethyl chlorides in dry ethyl alcohol.

4-Substituent	$10^5 k_{0.0}$ (sec. ⁻¹)	$10^5 k_{20.0}$ (sec. ⁻¹)	$10^5 k_{25.0}$ (sec. ⁻¹)	E (kcal. mole ⁻¹)	$10^{-11} A$ (sec. ⁻¹)
None	0.188	2.88	5.37	21.8	4.47
Methyl (R = H)	6.12	70.8	123	19.5	2.14
Ethyl (R = Me)	5.50	67.6	120	20.0	5.13
Propyl (R = Et)	4.70	58.9	105	20.2	5.89
2-Methylpropyl	4.41	56.2	100	20.3	6.46
2 : 2-Dimethylpropyl	3.93	51.8	93.3	20.6	10.0

TABLE 2. Arrhenius parameters for the solvolysis of 4-alkyl-3 : 5-dimethyldiphenylmethyl chlorides in dry ethyl alcohol.

4-Substituent	$10^5 k_{0.0}$ (sec. ⁻¹)	$10^5 k_{20.0}$ (sec. ⁻¹)	E (kcal. mole ⁻¹)	$10^{-11} A$ (sec. ⁻¹)
None	0.810	11.4	21.1	5.5
Methyl (R = H)	27.3	286	18.8	2.5
Ethyl (R = Me)	25.1	273	19.1	3.8
Propyl (R = Et)	22.8	255	19.3	5.4

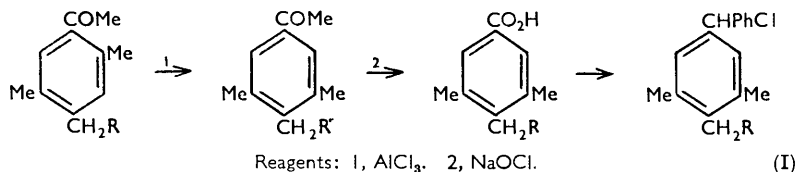
TABLE 3. Comparison of the rate constants and activation energies for ethanolysis of the 4-alkyldiphenylmethyl chlorides with those for ethanolysis of the 3 : 5-dimethyl derivatives.

4-Substituent	H	Me (R = H)	Et (R = Me)	Pr (R = Et)
3 : 5-Substituents:				
H	$k_{20.0}$ (rel.)	1.00	24.6	23.5
Me	$k_{20.0}$ (rel.)	1.00	25.1	24.0
H	E (kcal. mole ⁻¹)	21.8	19.5	20.0
Me	E (kcal. mole ⁻¹)	21.1	18.8	19.1
	ΔE	0.7	0.7	0.9

Our present purpose would be served if the reactivities of these chlorides could be compared with those of their 3 : 5-dimethyl derivatives (I). These compounds are accessible by the formulated route only when the 4-alkyl group is methyl, ethyl, or *n*-propyl

³ Shiner and Verbanic, *J. Amer. Chem. Soc.*, 1957, **79**, 369.

and the comparison has been confined to these instances; the Arrhenius constants for their solvolysis in dry ethanol are listed in Table 2. In Table 3 the relative reactivities of the 4-alkylbenzhydridyl chlorides are compared with, and shown to be similar to, those of their 3:5-dimethyl derivatives. The comparison, therefore, does not provide evidence for the view that the hyperconjugative effect of primary alkyl group is affected by torsional rotation of the group about the bond attaching it to benzene ring.



EXPERIMENTAL

Materials.—3:5-Dimethyldiphenylmethyl chloride. 3:5-Dimethylbenzophenone,⁴ m. p. 69°, with lithium aluminium hydride gave 3:5-dimethyldiphenylmethanol (73%), b. p. 161—163°/1.0 mm., radiating needles, m. p. 50—51° (from light petroleum), which has previously been obtained⁵ only as a liquid (Found: C, 84.5; H, 7.3. Calc. for C₁₅H₁₆O: C, 84.9; H, 7.6%). The alcohol with hydrogen chloride⁶ gave 3:5-dimethyldiphenylmethyl chloride, b. p. 143°/0.1 mm. (Found: Cl, 15.4. C₁₅H₁₅Cl requires Cl, 15.6%).

3:4:5-Trimethyldiphenylmethyl chloride. Hypochlorite oxidation of 3:4:5-trimethylacetophenone⁷ gave the corresponding benzoic acid,⁸ m. p. 214°; Friedel-Crafts interaction at 70° of its chloride, b. p. 140°/15 mm. (Found: Cl, 19.4. C₁₆H₁₁OCl requires Cl, 19.45%) (obtained by the action of thionyl chloride), and benzene gave 3:4:5-trimethylbenzophenone, b. p. 198—200°/14 mm., $n_D^{17.5}$ 1.6002 (Found: C, 85.5; H, 7.3. C₁₆H₁₆O requires C, 85.7; H, 7.1%). Use of lithium aluminium hydride gave 3:4:5-trimethyldiphenylmethanol as prisms, m. p. 81—82° (from light petroleum) (Found: C, 84.7; H, 7.9. C₁₆H₁₈O requires C, 85.0; H, 8.0%), from which the required chloride, b. p. 154—155°/0.06 mm. (Found: Cl, 14.4. C₁₆H₁₇Cl requires Cl, 14.5%), was obtained.

4-Ethyl-3:5-dimethyldiphenylmethyl chloride, b. p. 162°/0.1 mm. (Found: Cl, 13.8. C₁₇H₁₉Cl requires Cl, 13.7%), was similarly obtained from 4-ethyl-3:5-dimethylacetophenone.⁷ 2-Ethyl-3:5-dimethylbenzoic acid separated from benzene in plates, m. p. 178—179° (Found: C, 74.6; H, 7.6. C₁₁H₁₄O₂ requires C, 74.2; H, 7.8%), and its chloride, b. p. 152—154°/19 mm. (Found: Cl, 18.0. C₁₁H₁₃OCl requires Cl, 18.1%), gave 4-ethyl-3:5-dimethylbenzophenone, b. p. 149—152°/0.12 mm. (Found: C, 85.2; H, 7.4. C₁₇H₁₈O requires C, 85.7; H, 7.6%). 4-Ethyl-3:5-dimethyldiphenylmethanol separated from light petroleum in needles, m. p. 75—76° (Found: C, 84.7; H, 8.1. C₁₇H₂₀O requires C, 85.0; H, 8.3%), and gave the required chloride, b. p. 162°/0.1 mm. (Found: Cl, 13.8. C₁₇H₁₉Cl requires Cl, 13.7%).

3:5-Dimethyl-4-n-propyldiphenylmethyl chloride, b. p. 165—167°/0.4 mm. (Found: Cl, 12.8. C₁₈H₂₁Cl requires Cl, 13.0%), was prepared from 3:5-dimethyl-4-n-propylacetophenone.⁷ 3:5-Dimethyl-4-n-propylbenzoic acid, needles, m. p. 105° (Found: C, 74.9; H, 8.1. C₁₂H₁₆O₂ requires C, 75.0; H, 8.3%), its chloride, b. p. 153—153.5°/15 mm. (Found: Cl, 16.7. C₁₂H₁₅OCl requires Cl, 16.9%). 3:5-Dimethyl-4-n-propylbenzophenone, b. p. 217—218°/18 mm. (Found: C, 85.4; H, 7.9. C₁₈H₂₀O requires C, 85.7; H, 7.9%), and 3:5-dimethyl-4-n-propyldiphenylmethanol, b. p. 182—183°/0.65 mm. (Found: C, 85.0; H, 8.5. C₁₈H₂₂O requires C, 85.1; H, 8.7%), were the intermediates.

4-neopentyldiphenylmethyl chloride,³ b. p. 179°/1.0 mm. (Found: Cl, 12.9. Calc. for C₁₈H₂₁Cl: Cl, 13.0%), was prepared from 4-neopentylbenzophenone, b. p. 213—215°/20 mm., needles, m. p. 84° (from light petroleum) (Found: C, 85.2; H, 7.8. Calc. for C₁₈H₂₀O: C, 85.7; H, 7.9%). The intermediate, 4-neopentyldiphenylmethyl alcohol, b. p. 168—170°/0.5 mm., separated from light petroleum in needles, m. p. 82—83° (Found: C, 84.7; H, 8.9. Calc. for C₁₈H₂₂O: C, 85.0; H, 8.7%); addition of the ketone depressed the m. p.

⁴ Baddeley, *J.*, 1944, 236.

⁵ Grunert, Nichol, and Sandin, *J. Amer. Chem. Soc.*, 1947, **69**, 2255.

⁶ Hughes, Ingold, and Taher, *J.*, 1940, 949.

⁷ Baddeley and Varma, *J.*, 1957, 2727.

⁸ Bielefeldt, *Annalen*, 1879, **198**, 385.

Diphenylmethyl chloride and its 4-methyl, 4-ethyl, 4-propyl (Found: Cl, 14.3. Calc. for $C_{18}H_{21}Cl$: Cl, 14.5%), and 4-isobutyl (Found: Cl, 13.5. Calc. for $C_{17}H_{19}Cl$: Cl, 13.7%) derivatives were similarly obtained.^{3, 6}

Kinetic Measurements.—The method employed was that described by Hughes, Ingold, and Taher⁶ for alcoholysis in anhydrous ethyl alcohol. Approximately 0.01M-solutions were used. The first-order rate constants (sec.^{-1}) are summarised in the Tables. Each rate constant represents the average of several values.

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