

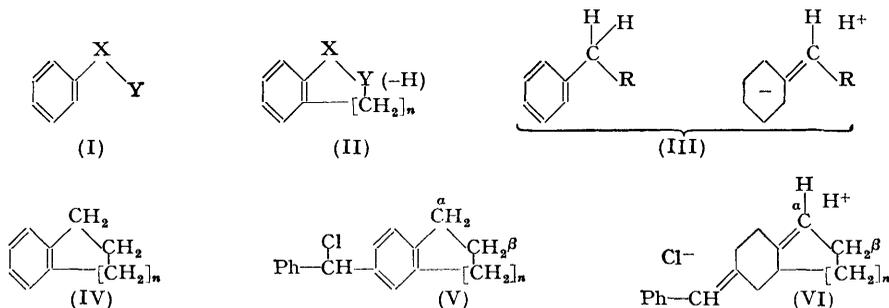
**407.** *Relationship between Hyperconjugation and Intramolecular Configuration. Part I. The Ethyl Alcoholysis of Some Derivatives of Diphenylmethyl Chloride.*

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Rates of alcoholysis decrease in the series 3:4-cyclopenteno->3:4-cyclohexeno->3:4-cyclohepteno->3:4-diethyl-benzhydryl chloride. These chlorides are subject to the same inductive and inductomeric effects, and decreases in reactivity can probably be related to decreases in magnitude of hyperconjugation. Thus the tautomeric release of electrons by a methylene group is a maximum when the hydrogen atoms are placed one on either side of the plane of the attached benzene ring, and is hindered by intramolecular steric interactions which oppose this configuration. The interpretation of the decrease in hyperconjugation in the order  $\text{Me} > \text{Et} > \text{Pr}^1$  is discussed.

In 1949 we pointed out (*Nature*, 1949, **164**, 833) that, when resonance interaction between the benzene ring and X in compounds of type (I) is insufficient to hold Y in the plane of the ring, then the planar or near-planar configuration which obtains in compounds of type (II) when *n* is 1 or 2, but not 3, leads to anomalous properties indicative of a comparatively high resonance interaction. We indicated that Berliner and Berliner (*J. Amer. Chem. Soc.*, 1949, **71**, 1195), by showing that the rate of bromination of ethyl-, *n*-propyl-, isobutyl-, and neopentyl-benzene decreases in this order, had provided evidence that hyperconjugation between the methylene group and the benzene ring in these hydrocarbons (III; R = Me, Et, Pr<sup>1</sup>, and Bu<sup>1</sup> respectively) is probably a maximum when R is closest to the plane of the

ring, and is subject to hindrance by steric factors which oppose this configuration. Finally, we announced that the properties of indane, tetralin, and benzocycloheptene (IV;  $n = 1, 2,$  and  $3$  respectively) and of some of their derivatives are being studied in these laboratories with the intention of clarifying the Baker-Nathan effect by demonstrating whether hyperconjugation of methylene groups is subject to steric effects, *i.e.*, whether the properties of indane and tetralin and of some of their derivatives indicate the presence of a comparatively large hyperconjugation.



Recently, Arnold and Truett (*ibid.*, 1951, **73**, 5508) have compared the rates of hydrolysis, in aqueous acetone, of 3 : 4-cyclopenteno-, 3 : 4-cyclohexeno-, and 3 : 4-cyclohepteno-benzhydryl chloride \* respectively ( $V$ ;  $n = 1, 2,$  or  $3$  respectively); we have compared the rates of reaction of these chlorides and of 3 : 4-dimethyl- and 3 : 4-diethyl-benzhydryl chloride \* with absolute ethanol.

Our data are assembled in the table and are comparable with those of Arnold and Truett (cf. Arnold, Murai, and Dodson, *ibid.*, 1950, **72**, 4193). Some of the chlorides, in their behaviour towards ethanol, resemble one another rather closely and, in consequence, rate constant determinations were duplicated.

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

Derivative	At 0.0° $10^3k$ (sec. <sup>-1</sup> )	At 20.0° $10^4k$ (sec. <sup>-1</sup> )	$E$ , kcal./mole	$10^{-10} A$ (sec. <sup>-1</sup> )
4-Methyl- *	7.33	7.12	—	—
	—	7.18	18.2	2.2
3 : 4-Dimethyl- .....	17.8	15.1	—	—
	18.2	15.1	17.0	0.6
3 : 4-Diethyl- .....	11.2	12.2	—	—
	11.5	12.1	18.9	13
3 : 4-cycloPento- .....	23.3	20.3	—	—
	23.3	20.6	17.3	1.5
3 : 4-cycloHexeno- .....	17.9	17.3	—	—
	17.8	17.1	18.1	1.7
3 : 4-cycloHepteno- .....	15.1	14.7	—	—
	15.0	14.6	18.2	2.0
	15.2	—	—	—

\*  $10^3k$  (at 25.0°) = 1.19; Hughes, Ingold, and Taher (*J.*, 1940, 949) give 1.22.

The ionisation process, which is the rate-determining step in the unimolecular alcoholysis of these chlorides (Ward, *J.*, 1927, 2285), is facilitated by hyperconjugation because this contributes especially, as illustrated in (VI), to the resonance stabilisation of the corresponding cations. In consequence, the sequence of reactivities: 3 : 4-cyclopenteno- > 3 : 4-cyclohexeno- > 3 : 4-cyclohepteno- > 3 : 4-diethyl-benzhydryl chloride provides definite evidence that hyperconjugation of the  $\alpha$ -methylene group with the benzene ring decreases progressively as the  $\beta$ -methylene group lies at increasing distances from the plane of this ring. 3 : 4-Dimethylbenzhydryl chloride is not strictly comparable with the other chlorides

\* Although not sanctioned by I.U.P.A.C., the name benzhydryl provides the simple basis for the discussion in this paper. Systematic names are used in the Experimental section.

as the methyl group has a smaller inductive and inductomeric effect than have other alkyl groups; under the experimental conditions, this chloride is not more reactive than 3 : 4-cyclohexenobenzhydryl chloride and, apparently, the methyl group is not more susceptible to hyperconjugation than an  $\alpha$ -methylene group when the corresponding  $\beta$ -methylene group is held near to the plane of the aromatic ring.

It is generally assumed, after Baker and Nathan (*J.*, 1936, 236), that hyperconjugation between the benzene ring and a methyl, ethyl, and *isopropyl* group, respectively, decreases in this order owing to a corresponding decrease in the number of "effective hydrogen atoms" (3, 2, and 1 respectively). As an alternative interpretation, we have suggested (*loc. cit.*) that this decrease in hyperconjugation may be the consequence of an increasing steric inhibition of a hyperconjugation which, for each of these alkyl groups, involves, at any instant, interaction of the electrons of no more than *one* CH-bond with the  $\pi$ -orbitals of the benzene ring (cf. Coulson, *Quart. Reviews*, 1947, 1, 144); thus, when the alkyl group is ethyl or *isopropyl*, hyperconjugation is hindered by the increase in intramolecular steric interaction incurred by bringing the methyl group of the former or the two methyl groups of the latter close to the plane of the benzene ring. The data we now communicate are supported by other work we have in hand; they indicate that hyperconjugation is subject to steric inhibition and, at least to this extent, support our interpretation.

#### EXPERIMENTAL

*Materials.—Ketones.* A solution of aluminium chloride (1.5 mol.) and benzoyl chloride (1.25 mol.) in ethylene dichloride was added gradually to a solution of the appropriate aromatic hydrocarbon in ethylene dichloride. After being kept overnight, the mixture was poured on ice and hydrochloric acid, and the organic layer separated, washed with water, dried ( $K_2CO_3$ ), and distilled.

The following derivatives of benzophenone were obtained: 4-methyl-, b. p. 171—172°/12 mm., m. p. 54—55° after recrystallisation from ligroin (Linke and Plascuda, *Ber.*, 1873, 6, 908; 1874, 7, 982); 3 : 4-dimethyl-, b. p. 190—191°/13 mm., m. p. 45—46° after recrystallisation from ethanol (Elbs, *J. pr. chem.*, 1887, 35, 467); 3 : 4-diethyl-, b. p. 160—163°/0.34 mm.; 3 : 4-cyclopenteno-, b. p. 194—196°/9 mm., m. p. 40—41° after recrystallisation from ethanol (Borsche and Pommer, *Ber.*, 1921, 54, 102); 3 : 4-cyclohexeno-, b. p. 219—221°/11 mm., rhombic plates, m. p. 40—41°, from light petroleum (Found: C, 86.7; H, 6.5. Calc. for  $C_{17}H_{16}O$ : C, 86.4; H, 6.8%) (Scharwin, *Ber.*, 1902, 35, 2511, describes it as an oil, b. p. 222—223°/12 mm.); and 3 : 4-cyclohepteno-, b. p. 219°/8 mm., needles, m. p. 38—42°, crystallising with difficulty from light petroleum.

*Alcohols.* The following derivatives of diphenylmethanol were obtained from the corresponding benzophenones by reduction with zinc dust and alkali (Hughes, Ingold, and Taher, *J.*, 1940, 949); 4-methyl-, m. p. 51—52° (Hughes, Ingold, and Taher give m. p. 52—53°); 3 : 4-dimethyl-, m. p. 65—66° (Elbs, *loc. cit.*, gives m. p. 68°); and 3 : 4-diethyl-, b. p. 160—161°/0.45 mm.; 5- $\alpha$ -hydroxy-benzylindane, fine needles, m. p. 65—66°, from light petroleum (Found: C, 86.0; H, 7.24. Calc. for  $C_{16}H_{16}O$ : C, 85.7; H, 7.14%); 6- $\alpha$ -hydroxybenzyltetralin, needles, m. p. 66—67°, from light petroleum (Found: C, 85.6; H, 7.4. Calc. for  $C_{17}H_{18}O$ : C, 85.7; H, 7.6%); 2'- $\alpha$ -hydroxybenzylbenzocycloheptene, clusters of needles, m. p. 72.5—73.5°, from light petroleum (Found: C, 85.7; H, 7.6.  $C_{18}H_{20}O$  requires C, 85.7; H, 7.9%).

*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 removed under reduced pressure and in the absence of moisture, and the residue rapidly distilled at 0.1—0.5 mm. Slow distillation caused some decomposition and provided distillates which, by hydrolysis, were found to contain considerably less halogen than was required. In all instances, the chloride before and after distillation provided rates of ethanolysis which did not differ by more than 2%. Physical data were: 4-methyl-, b. p. 140°/0.4 mm. (Found: Cl, 16.0. Calc. for  $C_{14}H_{13}Cl$ : Cl, 16.4%), 3 : 4-dimethyl-, b. p. 155°/0.11 mm. (Found: Cl, 15.3. Calc. for  $C_{15}H_{15}Cl$ : Cl, 15.4%), and 3 : 4-diethyl-diphenylmethyl chloride, b. p. 160°/0.18 mm. (Found: Cl, 13.5. Calc. for  $C_{17}H_{19}Cl$ : Cl, 13.7%); 5- $\alpha$ -chlorobenzylindane, b. p. 162°/0.04 mm. (Found: Cl, 14.2. Calc. for  $C_{16}H_{15}Cl$ : Cl, 14.6%); 6- $\alpha$ -chlorobenzyltetralin, b. p. 177°/0.05 mm. (Found: Cl, 13.5. Calc. for  $C_{17}H_{17}Cl$ : 13.8%); 2'- $\alpha$ -chloro-

benzylbenzocycloheptene, b. p. 187—189°/0.24 mm. (Found: Cl, 13.5. Calc. for  $C_{18}H_{19}Cl$ : Cl, 13.1%).

*Alcoholysis of the Chlorides in Anhydrous Ethyl Alcohol.*—The alcohol was purified by Lund and Bjerrum's method (*Ber.*, 1931, **64**, 210). The experiments were carried out either at 0.0° or at 20.0° ( $\pm 0.05^\circ$ ) by the sampling method described by Hughes, Ingold, and Taher (*loc. cit.*), the samples being run into a large volume of cold acetone in order to stop the reaction, and titrated with *ca.* 0.01N-sodium hydroxide with lacmoid as indicator.

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