

### 278. Stability of Carbonium Ions.

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The rates of solvolysis of some  $\alpha$ -arylbenzyl chlorides in 9 : 1 ethanol-acetone show that the 2-fluorenyl and the 2-biphenylenyl systems are more able to stabilise carbonium ions derived from them than are the 4-biphenylyl or the 2-phenanthryl systems. The implications of these results are discussed.

BERLINER AND SHIEH<sup>1</sup> studied the rates of hydrolysis on many  $\alpha$ -arylethyl chlorides in aqueous acetone. Especially, they found that the 2-fluorenyl reacted far more rapidly than the 4-biphenylyl derivative; this was tentatively attributed to the planarity of the fluorene system, which permitted more complete resonance stabilisation of the carbonium ion formed in the rate-determining stage of the reaction.<sup>1,2</sup>

We have found that not only the 2-fluorenyl, but also the 2-biphenylenyl system, can behave as a "planar biphenyl" structure, although the 2-phenanthryl system, which is formally similar, does not do so; this is in accord with other results.<sup>1,3</sup>

#### EXPERIMENTAL

The course of the solvolyses was followed by direct titration of the reaction mixture at intervals, by use of the technique described by Swain.<sup>4</sup> Since this technique requires that the rate of the reaction under study is unaltered by the presence of varying *low* concentrations of sodium alkoxide, it is specific to  $S_N1$  reactions. The internal indicator used was a mixture of Bromothymol Blue and Phenol Red. Quantities of sodium ethoxide solution were added to the reaction mixture, and the time at which neutralisation of each aliquot occurred was noted. In this way, kinetic plots comprised of thirty points could be drawn, and integrated first-order rate coefficients were derived. The secondary halides were generally prepared by treating the corresponding alcohol with thionyl chloride; these alcohols were obtained by reduction of the appropriate ketone with lithium aluminium hydride. Benzophenone was a commercial product which was purified by distillation under reduced pressure. 4-Benzoylbiphenyl<sup>5</sup> and 2-benzoylfluorene<sup>6</sup> were synthesised from the hydrocarbons by the action of benzoyl chloride and aluminium chloride, with carbon disulphide as solvent. 2-Benzoylphenanthrene was prepared from phenanthrene-2-carboxylic acid by way of the acid chloride; the parent acid was obtained from 2-acetylphenanthrene.<sup>7,8</sup> The ketones and alcohols thus obtained had melting points in agreement with literature values.

2-Benzoylbiphenylene has been reported<sup>9</sup> since we prepared it; use of the benzoyl chloride-aluminium chloride complex (1 mol.) in carbon disulphide at 15° gave a slightly better yield (75%) of a product of somewhat higher melting point (118.8—119.6°). The derived *alcohol*, m. p. 112—112.5° (Found: C, 88.1; H, 5.5.  $C_{19}H_{14}O$  requires C, 88.4; H, 5.4%) was obtained as small white needles from ether-light petroleum (b. p. 40—60°). Neither thionyl chloride, acetyl chloride, nor dry hydrogen chloride in ether, or in pentane at 0°, gave a pure chloride from this alcohol. A product, m. p. 109° (decomp.), was obtained in the latter case, but it appeared to be a mixture. However, the impurities had no effect upon the reaction of the chloride with ethanol-acetone; identical rates of reaction were obtained by use of products obtained from the alcohol by different means, and the kinetic plots showed no tendency to be non-linear.

The ethanol and acetone were purified by standard techniques.<sup>10,11</sup>

<sup>1</sup> Berliner and Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849.

<sup>2</sup> Brown, "Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958.

<sup>3</sup> Dewar and Sampson, *J.*, 1956, 2789; 1957, 2946, 2952.

<sup>4</sup> Swain, Esteve, jun., and Jones, *J. Amer. Chem. Soc.*, 1949, **71**, 965.

<sup>5</sup> Long and Henze, *J. Amer. Chem. Soc.*, 1941, **63**, 1939.

<sup>6</sup> Ray and Levine, *J. Org. Chem.*, 1938, **2**, 267.

<sup>7</sup> Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 558.

<sup>8</sup> Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704.

<sup>9</sup> Blatchly, McOmie, and Thatte, *J.*, 1962, 5090.

<sup>10</sup> Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

<sup>11</sup> Conant and Kirner, *J. Amer. Chem. Soc.*, 1924, **46**, 232.

An example of the kinetic results obtained is given in Table 1.

TABLE 1.

Solvolysis of  $\alpha$ -(2-biphenylenyl)benzyl chloride.

Time (sec.)	44	63	79	100	126	145	168	197
Volume (ml.)	0.700	0.810	0.900	1.000	1.124	1.200	1.300	1.400
Percentage reaction	25.55	29.56	32.85	36.50	41.02	43.80	47.44	51.09
$10^3k$ (sec. <sup>-1</sup> )	2.56	2.68	2.74	2.72	2.74	2.72	2.75	2.71
Time (sec.)	226	258	297	330	368	417	477	4000
Volume (ml.)	1.500	1.600	1.718	1.800	1.900	2.000	2.100	2.740
Percentage reaction	54.74	58.39	62.70	65.69	69.34	72.99	76.64	99.82
$10^3k$ (sec. <sup>-1</sup> )	2.70	2.69	2.71	2.69	2.72	2.70	2.67	—

Mean  $k$ :  $(2.71 \pm 0.02) \times 10^{-3}$  sec.<sup>-1</sup> at 4.6°.

The measured rate constants are given in Table 2.

TABLE 2.

Measured rate constants in 9 : 1 ethanol-acetone.\*

$\alpha$ -(2-Fluorenyl)benzyl chloride: $10^3k$ (sec. <sup>-1</sup> ) = 0.886 (3.2°), 1.91 (7.0°), 2.29 (10.0°), 2.34 (11.2°), 2.55 (12.2°), 3.58, 3.59 (15.0°), 4.43 (17.4°), 6.13 (20.0°), 8.15 (23.2°), 9.88 (25.0°), 13.00 (27.2°), 13.74 (30.0°).
$\alpha$ -(4-Biphenyl)benzyl chloride: $10^3k$ (sec. <sup>-1</sup> ) = 0.705 (29.2°), 0.824 (30.0°), 1.28, 1.30 (34.4°), 2.00 (38.5°), 2.19 (39.2°), 2.38 (40.0°), 3.10 (42.5°), 3.79 (44.8°).
$\alpha$ -(2-Phenanthryl)benzyl chloride: $10^3k$ (sec. <sup>-1</sup> ) = 0.390 (25.5°), 0.628 (30.3°), 1.15 (35.0), 1.33 (37.3°), 2.16 (42.0°), 2.94 (44.8°), 3.54 (47.0°), 4.42 (49.5°), 5.25 (52.0°), 6.50 (54.5°).
$\alpha$ -(2-Biphenylenyl)benzyl chloride: $10^3k$ (sec. <sup>-1</sup> ) = 2.71 (4.6°), 4.16 (6.6°), 5.00 (9.9°), 6.23 (12.8°), 8.07 (14.8°), 8.80 (16.0°), 13.30 (20.0°).

\* All rate constants were consistent to within 1.5% (mean deviation).

Table 3 summarises the derived activation energies for the solvolysis of the  $\alpha$ -arylbenzyl chlorides. These values, from least-squares analysis, show a probable error of  $\pm 0.3$  kcal. per mole.

TABLE 3.

Summary of the kinetic results for the solvolysis of  $\alpha$ -arylbenzyl chlorides in 9 : 1 ethanol-acetone.

Aryl group	$E$ (kcal. mole <sup>-1</sup> )	$\log_{10} A$	$k_{rel}$ , at 25°
Phenyl *	21.6	11.4	1.00
4-Biphenyl	20.4	11.7	12.2
2-Phenanthryl	19.0	10.5	10.1
2-Fluorenyl	17.5	10.8	250
2-Biphenylenyl	16.2	10.2	560

\* The values for benzhydryl chloride were taken from a previous study.<sup>12</sup>

## DISCUSSION

The fluorene, phenanthrene, and biphenylene systems may all be formally derived from biphenyl; since all three hydrocarbons are planar, we had expected their derived secondary halides to show the enhanced reactivity, compared with the biphenyl analogue, which Berliner and Shieh noted for  $\alpha$ -(2-fluorenyl)ethyl chloride.<sup>1</sup> However, theoretical calculations<sup>3,13,14</sup> and experimental observations<sup>1,3,13</sup> both show that the 2-phenanthryl system is less effective in delocalising charge in a derived carbonium ion than is the 4-biphenyl system; our analogy is thus not valid, and it seems more correct to compare the 2-phenanthryl with the 2-naphthyl system. Our results show that, in the  $\alpha$ -arylbenzyl chlorides also, the apparent relationship between the biphenyl and the phenanthrene systems is unreal.

<sup>12</sup> Bolton, Ph.D. Thesis, Hull, 1961; Bolton, Chapman, and Shorter, *J.*, 1964, in the press.

<sup>13</sup> Dewar, "Progress in Organic Chemistry," ed. Cook, Butterworths, London, 1953.

<sup>14</sup> Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265 *et seq.*

Neither electrophilic nor nucleophilic reactions of biphenylene derivatives have received great attention. Longuet-Higgins<sup>15</sup> drew attention to the discrepancy between the predictions of resonance theory and of molecular-orbital theory for the position of attack on 2-substituted biphenylenes; Baker and his co-workers<sup>16</sup> have shown that electrophilic substitution occurs predominantly (65% yield) at the 3-position of 2-acetaminobiphenylene, verifying the predictions of molecular-orbital theory, and also that electrophilic attack on the hydrocarbon itself takes place mainly at the 2-position. X-ray<sup>17</sup> and electron-diffraction studies show that the central ring of biphenylene has little cyclobutadienoid character, in keeping with the known instability of such systems. Resonance forms of the 2-biphenylenylmethyl carbonium ion which involve a cyclobutadiene system would probably be less preferred, energetically, to those in which the central four-membered ring system is cyclobutenoid. Such structures are similar to those which would stabilise the 4-biphenylylmethyl and the 2-fluorenylmethyl carbonium ions, but the planarity of biphenylene and fluorene would make such resonance stabilisation more effective. This is shown in Table 3; replacement of the phenyl group by the 4-biphenyl system increases the rate of solvolysis (or the rate of formation of the carbonium ion, since these reactions proceed by the  $S_N1$  mechanism) by a factor of twelve, but replacement of a phenyl group by either the 2-fluorenyl system or the 2-biphenylenyl system increases the rate by a factor of several hundred.

The influence of planarity upon the reactivity of the fluorene system has already been described by Brown<sup>18</sup> and his co-workers in a comprehensive series of studies on the electrophilic substitution of fluorene and of biphenyl. In all these reactions, fluorene reacted about two hundred times as fast as biphenyl; it was concluded that the effect was almost certainly due to the lack of steric inhibition of resonance in fluorene, in contrast with biphenyl. However, no kinetic studies seem to have been made of electrophilic substitution in biphenylene, where, for the same reasons, a similar enhancement of reactivity would be expected; such investigations are now in progress.\*

The general trend of activation energies for solvolysis (Table 3) parallels the reactivities of the halides; some, at least, of the changes in reactivity seem to be due to the lower energies of activation, which implies either that the fluorenyl and the biphenylenyl derivatives have ground states which are somewhat more polarised, or that the derived carbonium ions have lower resonance energies. This may be a result of the planarity of the aryl groups, or of the strain inherent in the two systems. Changes in the environment around each reaction centre do not seem sufficiently great to make real differences in the degree of solvation.

Longuet-Higgins has also derived figures which represent the probability of charge residing on the  $\alpha$ -carbon atom of a number of arylmethyl carbonium ions,<sup>14</sup> and Berliner and Shieh<sup>1</sup> found that these values paralleled the free energies of reaction in the large number of arylchloroethanes which they studied. The present results show a similar relationship, although it is not strictly linear.

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\* Since this Paper was submitted, Streitwieser and Schwager (*J. Amer. Chem. Soc.*, 1963, **85**, 2855) have reported the rates of tritideprotonation at both positions of biphenylene.

<sup>15</sup> Longuet-Higgins, *Proc. Chem. Soc.*, 1957, 157.

<sup>16</sup> Baker, McOmie, Rogers, and Preston, *J.*, 1960, **414**; Baker, McOmie, and Rogers, *Chem. and Ind.*, 1958, 1236.

<sup>17</sup> Waser and Schomaker, *J. Amer. Chem. Soc.*, 1943, **65**, 1451; Waser and Lu, *ibid.*, 1944, **66**, 2035; Mak and Trotter, *Proc. Chem. Soc.*, 1961, 163.

<sup>18</sup> Brown, Dubeck, and Goldman, *J. Amer. Chem. Soc.*, 1962, **84**, 1229; Brown and Neyens, *ibid.*, p. 1233; Brown and Marino, *ibid.*, p. 1236; Brown and Stock, *ibid.*, pp. 1238, 1242.