Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Acetates. Part VIII.[1] The 1-Position of Biphenylene

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1-Biphenylen-1-ylethyl acetate has been prepared and its rate of pyrolysis (together with that of 1-phenylethyl acetate) measured between 399·3 and 349·2 °C. The former ester eliminates 1·205 times faster than the latter at 625 K which leads to a σ^+-value of −0·13 for the 1-position of biphenylene in this reaction. The weak activation of the 1-position is less than in hydrogen exchange but contrasts with protodesilylation where weak deactivation occurs. The reactivity in the pyrolysis is predicted by our theory attributing the differential reactivity of the α- and β-positions in biphenylene (and strained aromatic molecules in general) to bond strain in the transition state, and is *counter* to the prediction of the alternative theory based upon increased electronegativity of bridgehead carbons in strained rings.

The chemistry of biphenylene is interesting not only because it is a relatively simple aromatic molecule about which comparatively little is known, but also because it is a strained molecule and the manner in which this strain affects the reactivity is important, especially since similar strains occur in a wide range of aromatic molecules.[2] The inaccessibility of the derivatives has meant however that very few quantitative studies of its electrophilic reactivity, for example, have been made. Previously, one of us showed that the 2-position is much more reactive than the 1-position in both protodetritiation[3] and protodesilylation,[4] and that the latter position was weakly activated in the former reaction ($f_1 = 104$, $\rho = ca. -8{\cdot}5$), and weakly

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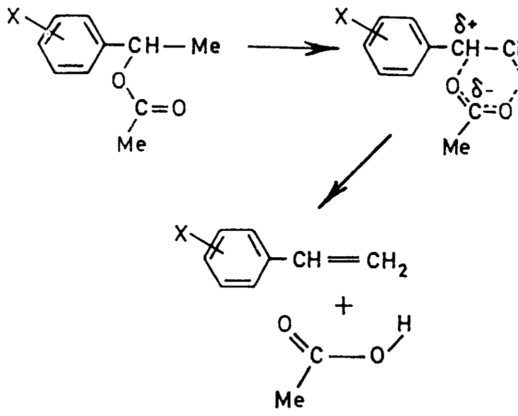
[1] Part VII, R. Taylor, *J. Chem. Soc.* (*B*), 1971, 2382.

[2] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1559.

[3] J. M. Blatchly and R. Taylor, *J. Chem. Soc.* (*B*), 1964, 4641.

[4] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 536.

deactivated in the latter reaction ($f_1 = 0{\cdot}68$, $\rho = -5{\cdot}0$). This variation in reactivity relative to a single position in benzene is so far unique amongst polycyclic reactivities, but is explicable in terms of variable demands for resonance stabilisation of transition states superimposed upon a $-I$ effect of the phenylene substituent.[4] In both reactions the 2-position was of closely similar reactivity to that of a 2-position in fluorene and this was true also in the pyrolysis of 1-arylethyl acetates (Scheme).[5] Obviously it would be of interest to measure the reactivity of the 1-position in other reactions, and particularly so in the pyrolysis reaction because the results would afford a method (described below) of distinguishing between the two alternative mechanisms proposed to account for the different reactivities at the 1- and 2-positions; in addition the reaction possesses all the advantages described in earlier papers in this series. Until recently however, routes to the preparation of the quantities of 1-isomer required for the pyrolysis were unavailable, but recent work on the synthesis of 1-biphenylene derivatives by one of us[6] has now made this possible.



SCHEME

RESULTS AND DISCUSSION

The rates of pyrolysis of 1-biphenylen-1-ylethyl acetate (reproducible to ±1·5%) are given in the Table together with those for 1-phenylethyl acetate (reproducible to ±1%), log $k_{\text{rel.}}$ at 625 K, the energies, and the entropies of activation, the latter being calculated at 600 K for consistency with the previous paper on biphenylene.[5] Good first-order kinetics were obtained with both esters for at least 95% of reaction. The biphenylen-1-yl ester reaction product showed a slight tendency to polymerise as did that from pyrolysis of the 2-isomer,[5] but since this polymerisation reaction in this case was very slow compared to the elimination of acetic acid from the ester, it did not introduce a significant error in the measured first-order rate coefficients. The kinetic data for both esters produced an excellent Arrhenius plot (see Figure) from which a $k_{\text{rel.}}$ value of 1·205 at 625 K is interpolated. This, coupled with the ρ-factor for the reaction (—0·63 at 625 K) leads to a σ^+-value of —0·13.

Pyrolysis of $RCH(Me){\cdot}O{\cdot}COCH_3$

T/°C	10^3k/s^{-1}	log A/s^{-1}	$\frac{E}{\text{kcal mol}^{-1}}$	$\frac{S}{\text{cal mol}^{-1}\text{ K}^{-1}}$	log k/k_0 (at 625 K)
		R = Phenyl			
399·2	38·0	12·75	43·7	−1·7	0
393·5	28·8				
385·9	19·9				
377·9	12·5				
366·4	7·21				
349·2	2·79				
		R = Biphenylen-1-yl			
399·2	44·3	12·56	42·3	−2·45	0·081
393·3	33·0				
385·9	23·0				
377·9	15·5				
366·4	8·50				
349·2	3·49				

Thus the 1-position is predicted to be weakly activated in electrophilic substitution. This result may be compared to that obtained in hydrogen exchange which requires a σ^+-value of —0·23 and that in protodesilylation which requires a value of +0·035. These differences are not inconsistent however since the demand for resonance stabilisation of the transition states increases along the reaction series protodesilylation < pyrolysis < protodetritiation. The results for pyrolysis then is as expected and fits in with the general pattern for biphenylene substitution, namely that the ratio of 2 : 1-substitution is much greater than predicted by theoretical calculations.[7] This observation is very important because it permits us to make a further evaluation of two theories which have been proposed to account for the large difference in reactivity of the 1- and 2-positions in biphenylene[4,5,8,9] (and the α- and β-positions in strained aromatic molecules in general). One theory attributes the low reactivity of the 1-position to the increased electronegativity of the adjacent bridgehead carbon atom, the enhanced electronegativity arising out of the strain present in the cyclic substituent.[9] The other due to one of us, attributes the low reactivity to the increase in bond strain that occurs on going to the transition state for 1-substitution.[4,5,8] An important difference in the theories is that the former predicts the reactivity of the 2-position to be less than expected,

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[5] J. M. Blatchly and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1402.

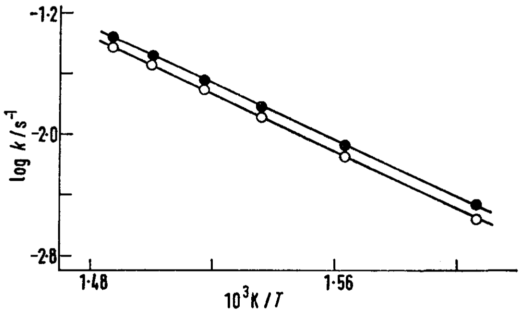
[6] P. R. Constantine, G. E. Hall, C. R. Harrison, J. F. W. McOmie, and R. J. G. Searle, *J. Chem. Soc.* (*C*), 1966, 1767; A. J. Boulton, J. B. Chadwick, C. R. Harrison, and J. F. W. McOmie, *J. Chem. Soc.* (*C*), 1968, 328.

[7] R. D. Brown, *Trans. Faraday Soc.*, 1950, **46**, 146; F. H. Burkitt, C. A. Coulson, and H. Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553; A. Streitwieser and J. Schwager, *J. Amer. Chem. Soc.*, 1963, **85**, 2855.

[8] R. Taylor, G. J. Wright, and A. J. Homes, *J. Chem. Soc.* (*B*), 1967, 480; R. Taylor, *Chimia*, 1968, **22**, 1; *J. Chem. Soc.* (*B*), 1968, 1559; A. R. Bassindale, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.* (*B*), 1969, 12.

[9] A. Streitwieser, G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, 1968, **90**, 1357.

whereas the latter predicts it to be greater than expected; in every single case where the reactivity of the 2- (or β-) position in a strained aromatic molecule has been measured, it comes out to be greater than expected.[4,5,8,10] The only fact which argues for continuing to consider the electronegativity theory is the enhanced acidity of the 1-position of biphenylene, benzo[b]biphenylene, and triptycene observed in base-catalysed hydrogen exchange. Now in the pyrolysis of 1-arylethyl acetates a partial carbonium ion is generated at the side-chain α-carbon atom[11] and therefore inductive effects will have a smaller influence upon the stability of this carbonium ion than upon the stability of the positive reaction site in an electrophilic substitution.* Consequently the reactivity of the 1-position in pyrolysis should be very significantly higher relative to electrophilic substitutions; this is not observed. By contrast, the theory based upon strain effects predicts that the 1-position will suffer the *same* diminution in reactivity observed in electrophilic substitutions. Once again therefore the theory based on electronegativity effects fails to predict the experimental observation.



Arrhenius plots for the pyrolysis of 1-arylethyl acetates: aryl = ○ phenyl, ● biphenyl-1-yl

EXPERIMENTAL

The apparatus and method have been described.[1]

1-*Phenylethyl Acetate*.—This compound was available from previous work.[1]

1-*Biphenylen*-1-*ylethyl Alcohol*.—A slight excess of sodium borohydride was added in portions to a stirred solution of 1-acetylbiphenylene.[6] When the initial deep yellow colour had faded (*ca.* 2 h), dilute hydrochloric acid was added to the reaction mixture to decompose unchanged borohydride. The ethanol was removed under reduced pressure and the residual suspension of oil in water was further diluted with water. The product was collected in ether from which it was obtained as a greenish yellow oil (800 mg, 79%), which gave only one spot on thin-layer chromatography (silica-gel–benzene and silica-gel–methylene chloride). Most of the material was used directly for the next experiment but a sample was purified by distillation at 84—86°/0·15 mm (Found: C, 85·6; H, 6·3. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%), $\lambda_{max.}$ (EtOH) 221sh, 237sh, 243, 252, 327, 341, 344, and 360 nm (log ε 3·82, 4·44, 4·73, 4·96, 3·36, 3·66, 3·64, 3·82), τ (CCl_4), 3·52 (m, 7ArH), 5·50, (q, CH), 7·84 (s, OH), and 8·64 (d, CH_3), J_{H,CH_3} 6·2 Hz.

1-*Biphenylen*-1-*ylethyl Acetate*.—Acetic anhydride (10 ml) was added to an ice-cooled solution of 1-biphenylen-1-ylethyl alcohol (800 mg) in pyridine (5 g). The mixture was stirred at room temperature for 2 h and then more acetic anhydride (10 ml) was added to it. After being stirred for 3 more h the mixture was poured into dilute hydrochloric acid containing crushed ice. The resulting oily suspension was extracted with ether which yielded an orange oil. This was purified by thick-layer chromatography on Kieselgel G (Merck) in benzene and gave the acetate as a pale yellow oil (750 mg, 77%). A sample was further purified by distillation at 72—74°/0·08 mmHg (Found: C, 80·9; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%), $\lambda_{max.}$ (EtOH) 222sh, 238sh, 243, 252, 327, 342, and 360 nm (log ε 3·75, 4·28, 4·67, 4·96, 3·40, 3·69, and 3·81), τ (CCl_4) 3·34 (m, 7ArH), 4·32 (q, CH), 7·92 (s, $COCH_3$), and 8·48 (d, CH_3), J_{H,CH_3} 6·4 Hz, $\nu_{C=C}$ 1726 cm⁻¹ (liquid film).

[1/1265 *Received, July 23rd*, 1971]

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* We are indebted to Professor A. Streitwieser for drawing our attention to the significance of this point.

[10] A. Streitwieser, A. Lewis, I. Schwager, R. W. Fish, and S. Labana, *J. Amer. Chem. Soc.*, 1970, **93**, 6525.

[11] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.