

## Organic Anions. Part 1. Equilibration of 1,3-Diarylpropenes

By Richard J. Bushby\* and Gerald J. Ferber, Department of Organic Chemistry, The University, Leeds LS2 9JT

A number of 1,3-diarylpropenes, potential precursors of the allylic anions (I), have been synthesised, and the base catalysed equilibration between the double bond isomers (II) and (III) has been investigated. The equilibrium constants correlate satisfactorily with the substituent constant  $\sigma$ . N.m.r. shift reagents aided spectroscopic analysis of certain mixtures.

AMBIDENT reactivity remains one of the problem areas of organic chemistry. Many criteria of ambident reactivity and many reactivity indices have been suggested. Some of these involve comparing the stabilities of the various possible products as, for example, the use of the Hughes–Ingold Rule<sup>1</sup> or of localisation energies.<sup>2</sup> Others are normally derived from MO calculations providing indices such as charge, free valence,  $Z$  value, polarisability, superdelocalisability, *etc.*<sup>2</sup> for the various reactive sites of the substrate. A third line of argument was suggested by Hine in his principle of least motion,<sup>3</sup> which concentrates on the amount of nuclear motion involved in passing from the substrate to the various possible products. Yet another criterion which has been applied is Pearson's essentially qualitative concept of hard and soft acids and bases,<sup>4</sup> and in some systems it is clear that effects such as steric hindrance, solvation, and ion pairing must also be considered. The overall situation is complex and confused. What is clear is that some of these reactivity indices are roughly equivalent to each other<sup>2,5</sup> and also that no one criterion will suffice to cover all situations. However, the hope still remains that within a limited group of ambident reactions it will be possible to discover which of these many criteria is best and many studies of electrophilic aromatic substitution, for example, have been made with this end in view.<sup>2</sup> This paper and the following two are mainly concerned with a rather different group of reactions, the protonation of allylic anions, and the quantitative comparison of two apparently unrelated indices, namely charge and product stability, as criteria of ambident reactivity. These two criteria have been chosen as the only ones which are reasonably easy to measure experimentally.

Although they have also been the subject of many investigations, the ambident reactions of organic anions are particularly difficult to rationalise. The main reason for this is that in the great majority of the systems it is by no means clear what ion, ion pair, or aggregate<sup>6</sup> is the reactive species. Most probably they involve contact ion pairs or ion pair clusters and it is obvious that in such cases any treatment which ignores the effect of the counter-ion is unlikely to succeed. Fortunately for

diaryl allylic anions of the type (I) chosen for the present study the ion pairing behaviour had been investigated extensively by Burley and Young.<sup>7</sup> It was also hoped that in these anions <sup>1</sup>H, or more likely <sup>13</sup>C n.m.r. spectroscopy would provide a measure of the charges at the allylic positions<sup>8</sup> which would be at least as reliable and probably more so than that provided by the normal, rather crude, MO calculations.<sup>9</sup> Finally it was anticipated that positioning of substituents in the *para*- (and in one case *meta*-) positions of the phenyl rings would avoid complications from preferential steric effects. Ammonia was chosen for the solvent partly because it has advantages for n.m.r. work but more because it was anticipated that this strongly solvating medium would support solvent-separated rather than contact ion pairs.<sup>10</sup>

This first paper is concerned with the preparation of the anion precursors and protonation products (II) and (III), the methods used in the analysis of mixtures, trial generations of the anions (I), and determination of the relative stabilities of the protonation products. The second paper deals with spectroscopic studies of the ion pair type and of charge distribution within the anions, and the third with the actual comparison of charge distribution and of product stability as criteria of ambident reactivity.

*Preparation of Diarylpropenes.*—Twelve 1,3-diarylpropenes were made by a modified form of the synthetic route used by Rondestvedt.<sup>11</sup> This involved base-catalysed condensation of acetophenone (IV) with benzaldehyde (V) (either of which may bear a ring substituent) and reduction of the resultant chalcone (VI) with lithium aluminium hydride in tetrahydrofuran (better than ether<sup>11</sup>). The alcohol (VIIa), thus obtained, was then acetylated and converted into the alkene (II) by pyrolysis at 300 °C under nitrogen.<sup>12</sup> This was found to give a better yield than direct dehydration of the alcohol.<sup>11,12</sup> This general route was, however, unsatisfactory for the nitro-substituted system (II; X = H, Y = NO<sub>2</sub>), first because 4-nitrochalcone (VI; X = H, Y = NO<sub>2</sub>) was difficult to reduce selectively and secondly because pyrolysis of the acetate (VIIb; X = H, Y =

<sup>1</sup> A. G. Catchpole, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1948, 8; C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, 1953, 565.

<sup>2</sup> H. H. Greenwood and R. McWeeny, *Adv. Phys. Org. Chem.*, 1966, 4, 73.

<sup>3</sup> J. Hine, *J. Org. Chem.*, 1966, 31, 1236.

<sup>4</sup> R. G. Pearson, *J. Amer. Chem. Soc.*, 1963, 85, 3533; 1967, 89, 1827.

<sup>5</sup> G. Klopman, *J. Amer. Chem. Soc.*, 1968, 90, 223.

<sup>6</sup> M. Szwarc, 'Ions and Ion Pairs in Organic Reactions,' Wiley-Interscience, vol. 1, 1972; vol. 2, 1974.

<sup>7</sup> J. W. Burley and R. N. Young, *Chem. Comm.*, 1969, 1127; *J. Chem. Soc. (B)*, 1971, 1018; *J.C.S. Perkin II*, 1972, 835, 1006.

<sup>8</sup> D. G. Farnum, *Adv. Phys. Org. Chem.*, 1975, 11, 123.

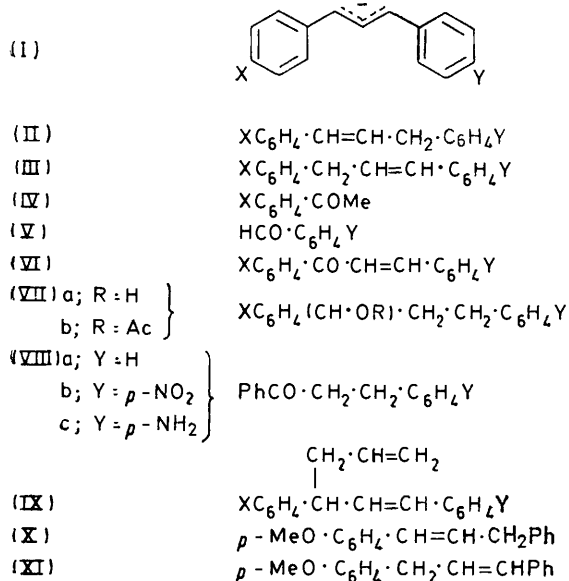
<sup>9</sup> For anionic species in particular calculations employing a small basis set probably give a rather misleading impression of the charge distribution; cf. A. J. Duke, *Chem. Phys. Letters*, 1973, 21, 275.

<sup>10</sup> J.-P. Pascault and J. Gole, *J. Chim. phys.*, 1971, 68, 442; C. Pillot, J.-P. Pascault, and J. Gole, *Bull. Soc. chim. France*, 1974, 357, 362.

<sup>11</sup> C. S. Rondestvedt, *J. Amer. Chem. Soc.*, 1951, 73, 4509.

<sup>12</sup> C. H. Depuy and R. E. Leary, *J. Amer. Chem. Soc.*, 1957, 79, 3705.

NO<sub>2</sub>) produced only tar. In this case chalcone itself (VI; X = Y = H) was hydrogenated<sup>13</sup> to give 1,3-diphenylpropanone (VIIIa), which was then nitrated and the *para*-isomer (VIIIb) separated chromatographically.<sup>14</sup> This was reduced to 3-(4-nitrophenyl)-1-phenylpropan-1-ol (VIIa; X = H, Y = NO<sub>2</sub>) with sodium borohydride in ethanol and converted into the alkene by



the method of Hurd and Jenkins.<sup>15</sup> For the dimethylamino-substituted alkene (II; X = H, Y = NMe<sub>2</sub>) no suitable amino-substituted acetophenone (IV) or benzaldehyde (V) was available as a starting material. It was therefore most convenient to start with 4-nitrochalcone (VI; X = H, Y = NO<sub>2</sub>). This was hydrogenated to give 3-(4-aminophenyl)-1-phenylpropan-1-one (VIIIc). Clark-Eschweiler<sup>16</sup> methylation and reduction with sodium borohydride gave 3-(4-dimethylaminophenyl)-1-phenylpropan-1-ol (VIIa; X = H, Y = NMe<sub>2</sub>), which was converted into the alkene (II; X = H, Y = NMe<sub>2</sub>) in the normal way. The isomer of this alkene (III; X = H, Y = NMe<sub>2</sub>) was obtained by converting (II) into its anion (I; X = H, Y = NMe<sub>2</sub>) with sodamide in liquid ammonia, treating this with acid, and chromatographing the resultant mixture of (II) and (III). The quaternary ammonium-substituted alkenes (II) and (III) (X = H, Y = NMe<sub>3</sub><sup>+</sup>I<sup>-</sup>) were obtained simply by treating the corresponding dimethylamino-substituted alkenes with methyl iodide.

The overall yields of the sixteen alkenes were good (30–50%) except in the *para*-iodo- and *meta*-fluoro-systems where extensive chromatography was required to remove impurities. The only reactions in the general scheme which gave any problems were the acetate pyrolyses. It was anticipated that these would give a mixture

<sup>13</sup> R. Adams, J. W. Kern, and R. L. Shriner, *Org. Synth.*, Coll. Vol. I, 1941, 101.

<sup>14</sup> B. C. Gasson, Ph.D. Thesis, Leeds 1975.

<sup>15</sup> C. D. Hurd and W. W. Jenkins, *J. Org. Chem.*, 1957, **22**, 1418.

of *cis*- and *trans*-isomers but it was also found that under pyrolysis conditions a small and variable amount of double bond migration occurred. This isomerisation was presumably acid-catalysed, even though the apparatus used was designed to distil out the acetic acid as it was formed.<sup>17</sup> As would be expected from the relative stabilities of the *cis*- and *trans*-isomers (see later) the products of double-bond isomerisation were essentially all *trans*. The products of direct elimination, however, contained considerably more than the equilibrium percentage of *cis*-alkene.

*Generation of Diarylpropenides.*—1,3-Diarylpropenes can be converted into the corresponding anions either by butyl-lithium in ether solvents<sup>7,18</sup> or by amide anion in liquid ammonia.<sup>19</sup> As was pointed out in the introduction, ether solvents were expected to give problems both in the n.m.r. and in the ambident reactivity studies and so the latter possibility was chosen. For the parent alkene (II; X = Y = H), the *para*-dimethylamino-, methoxy-, methyl-, *t*-butyl-, fluoro-, and chloro-substituted alkenes, and the *meta*-fluoro-substituted alkene, treatment of a concentrated solution in ether with a slight excess of sodamide in liquid ammonia at -42 ° gave an essentially quantitative formation (as judged by n.m.r.) of the cherry red anion solutions, and on treatment with acid a 91–96% recovery of mixed monomeric alkenes resulted. The anion solutions showed no deterioration after several weeks at -40 °C. However, the *para*-iodo- and nitro-substituted alkenes gave yellow-brown solutions which showed no anion signals in the n.m.r. and, after quenching with acid, gave no monomeric products. The trimethylammonium-substituted alkenes (II) and (III) (X = H, Y = NMe<sub>3</sub><sup>+</sup>I<sup>-</sup>) behaved similarly except that the solution formed on treatment with sodamide was pale red. The trifluoromethyl-substituted alkene (II; X = CF<sub>3</sub>, Y = H) initially gave a cherry red solution but within a few minutes this turned blue. Presumably the anion was formed but quickly decomposed. The yields of the allyl-substituted compounds (IX; X = CF<sub>3</sub>, Y = H; X = H, Y = CF<sub>3</sub>) on treating the solution with allyl chloride reflected this decomposition: 84% immediately after adding the sodamide and 22% 5 min after adding the sodamide.

*Analysis of Alkene Mixtures.*—For all except the unsubstituted system four isomers must be considered, *i.e.* two double-bond positional isomers either of which may be *cis* or *trans*. Satisfactory g.l.c. conditions were found for separating all the isomers in the unsubstituted system and the *para*-dimethylamino-, *para*-*t*-butyl-, *para*-fluoro-, *meta*-fluoro-, and *para*-chloro-substituted systems. For the *para*-methoxy-substituted alkenes only a partial g.l.c. separation was possible and for the *para*-methyl-substituted alkenes g.l.c. only provided a

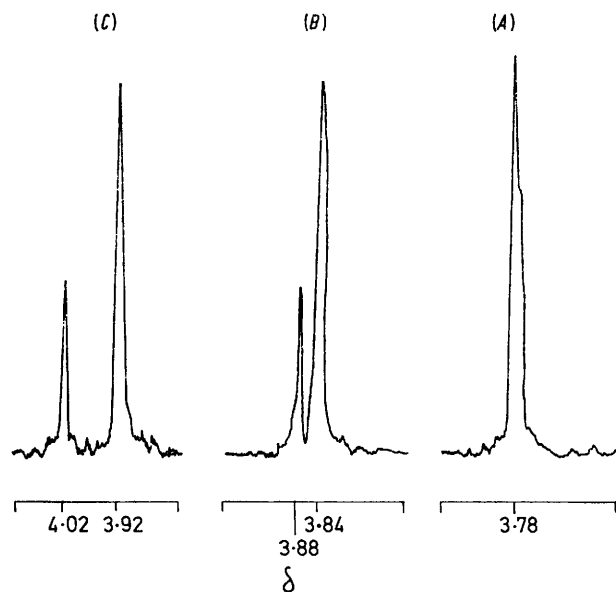
<sup>16</sup> R. N. Icke, B. B. Wisegarver, and G. A. Alles, *Org. Synth.*, Coll. Vol. III, 1955, 723.

<sup>17</sup> P. Hallett, Ph.D. Thesis, Leeds University, 1974.

<sup>18</sup> H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Amer. Chem. Soc.*, 1967, **89**, 1762.

<sup>19</sup> G. J. Heiszwolf and H. Kloosterziel, *Rec. Trav. chim.*, 1967, **86**, 1345.

measure of the total *cis*- versus total *trans*-isomers. For these last two systems spectroscopic methods of analysis were employed. In fact, because of the danger of isomerisation or polymerisation under g.l.c. conditions, whenever possible all g.l.c. analyses were cross checked by n.m.r. spectroscopy. In practice good agreement was always obtained although g.l.c. results proved to be more accurate and reproducible. For the *para*- and *meta*-fluoro-substituted systems the g.l.c. analyses were



(A) Part of the  $^1\text{H}$  n.m.r. spectrum of a 2 : 1 mixture of (X) and (XI) (70 mg) in  $\text{CDCl}_3$  (0.4  $\text{cm}^3$ ); (B)  $\text{Eu}(\text{fod})_3$  (60 mg) added; (C)  $\text{Eu}(\text{fod})_3$  (130 mg) added

cross checked by  $^{19}\text{F}$  n.m.r. For the methyl-substituted system analyses were made from the  $^1\text{H}$  n.m.r. methyl resonances in hexafluorobenzene solution. For the *t*-butyl-substituted system a semiquantitative cross-check on the g.l.c. analyses was possible from the  $^1\text{H}$  n.m.r. of the partially resolved *t*-butyl resonances in the same solvent. Analyses for the methoxy-substituted system were made from the methyl resonances in the  $^1\text{H}$  n.m.r. by using a chloroform solution with added shift reagent. The Figure shows the effect of adding  $\text{Eu}(\text{fod})_3$  to a 2 : 1 mixture of *trans*-(X) and *trans*-(XI). Initially the signals for the two methoxy-groups overlap. As increasing amounts of  $\text{Eu}(\text{fod})_3$  are added the methyl resonance for (XI) is shifted more rapidly to lower field than the methyl resonance of (X). This presumably reflects the greater availability for complexation of the less highly conjugated oxygen lone pair electrons in (XI). A similar method was used to provide a spectroscopic cross check on the g.l.c. analyses of the dimethylamino-substituted system.

**Equilibration of Alkenes.**—The substituted alkenes (II)

† Some of the alkenes were low melting solids and others viscous liquids which made it difficult to handle small quantities by syringe. It was, therefore, more convenient to add them to sodamide-liquid ammonia as a concentrated solution in ether. As it was also necessary to add ether as an internal lock and standard in the n.m.r. studies (Part 2), to maintain comparability, all work was carried out using *ca.* 8 : 1 liquid ammonia-ether as the solvent.

and (III) can be readily equilibrated by using a trace of sodamide in liquid ammonia-ether (8 : 1) at room temperature (sealed tube) and the results of these equilibrations are given in the Table. As the relative stabi-

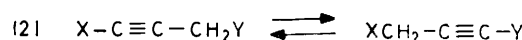
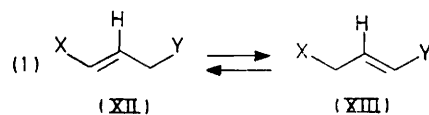
Equilibration of alkenes in liquid ammonia-ether (8 : 1) at room temperature

| X                     | Y | Expt. no.      | % (II)       |                    | % (III)      |                    | Impurities (%) |
|-----------------------|---|----------------|--------------|--------------------|--------------|--------------------|----------------|
|                       |   |                | <i>trans</i> | <i>cis</i>         | <i>trans</i> | <i>cis</i>         |                |
| $\text{Me}_2\text{N}$ | H | 1 <sup>a</sup> | 70.5         | 1.6                | 27.8         | 0.1                | 0              |
|                       |   | 2 <sup>a</sup> | 69.6         | 2.0                | 28.5         |                    | 0              |
| MeO                   | H | 1 <sup>a</sup> | 61.8         | 0.8                | 37.0         | 0.5                | 0              |
|                       |   | 2 <sup>a</sup> | 61.3         | 1.5                | 36.8         | 0.5                | 0              |
| Me                    | H | 1 <sup>a</sup> | 48.9         | (1.6) <sup>c</sup> | 46.3         | (1.6) <sup>c</sup> | 3.2            |
|                       |   | 2 <sup>a</sup> | 53.8         | (1.3) <sup>c</sup> | 42.2         | (1.3) <sup>c</sup> | 2.7            |
| Bu <sup>t</sup>       | H | 1 <sup>b</sup> | 49.9         | 1.5                | 39.9         | 1.5                | 7.6            |
|                       |   | 2 <sup>b</sup> | 49.3         | 1.3                | 39.2         | 1.3                | 8.9            |
| <i>para</i> -F        | H | 1 <sup>b</sup> | 46.2         | 0.3                | 52.1         | 1.3                | 0              |
|                       |   | 2 <sup>b</sup> | 46.2         | 0.5                | 52.2         | 1.2                | 0              |
| Cl                    | H | 1 <sup>b</sup> | 47.5         | 1.7                | 49.5         | 1.3                | 0              |
|                       |   | 2 <sup>b</sup> | 47.5         | 1.5                | 50.0         | 0.9                | 0              |
| <i>meta</i> -F        | H | 1 <sup>b</sup> | 43.4         | 0.2                | 55.5         | 0.9                | 0              |
|                       |   | 2 <sup>b</sup> | 44.0         |                    | 55.5         | 1.5                | 0              |

<sup>a</sup> Starting from different alkenes. <sup>b</sup> Different equilibration times. <sup>c</sup> Total *cis*-isomer (II) and (III).

ties of the two alkenes were primarily required for correlation with ambident reactivity studies<sup>20</sup> only the seven systems which may be cleanly converted to the anion were investigated in any detail.

Normally the effect of substituents X and Y on the equilibrium (1) is a complex sum of electronic and steric factors. That is to say the difference between the electronic interactions of substituents X and Y directly with the double bond (the 'second-order' differences between  $\text{CH}_2\text{X}$  and  $\text{CH}_2\text{Y}$  are much smaller and often ignored) together with other factors which include the difference between the *cis*-interaction of X and the central hydrogen atom in (XII) and that between Y and the central hydrogen atom in (XIII).<sup>21</sup>



The advantage of the phenyl-substituted systems used in the present study is that, whilst the electronic effect is doubtless attenuated by the intervening aromatic rings, the differences in steric effects are virtually eliminated. The resultant 'pure electronic' effects of substituents are much as expected. The double bond, being electron-deficient, is destabilised by those groups that exert a predominantly  $-I$  effect (*para*-Cl and *meta*-F), stabilised by those groups that exert a predominantly  $+I$  or hyperconjugative effect (*para*-Me and Bu<sup>t</sup>), and also by those groups that exert a predominantly  $+M$  effect (*para*- $\text{Me}_2\text{N}$  and MeO). They are in broad agreement with the effect of substituents on equilibrium (2)<sup>22</sup> (where steric factors again seem to

<sup>20</sup> Part 3, R. J. Bushby and G. J. Ferber, *J.C.S. Perkin II*, 1976, 1695.

<sup>21</sup> S. J. Rhoads and E. E. Waali, *J. Org. Chem.*, 1970, **35**, 3358.

<sup>22</sup> R. J. Bushby, *Quart. Rev.*, 1970, **24**, 585.

be unimportant) and on other prototropic equilibria where steric factors have either been allowed for<sup>21</sup> or eliminated.<sup>23,24</sup> On a quantitative level the logarithms of the equilibrium constants [*trans*-(III)]/*trans*-(II)] correlate quite well with the substituent parameters  $\sigma^{25}$  (correlation coefficient  $r = 0.961$ ; 8 points) and  $\sigma^+$  ( $r = 0.979$ ; 8 points) but there is no improvement on using the combination of  $\sigma$  and  $\sigma_R^{26}$  ( $r = 0.936$ ; 6 points omitting Bu<sup>t</sup> and *meta*-F) favoured by Ahlbrecht *et al.* from their work on imine–enamine equilibria.<sup>27</sup> It must be noted, however, that the range of substituents used in the present study is much more limited. The position of the equilibrium for the methoxy-substituted system [63% (X) (*cis* and *trans*) in liquid ammonia at room temperature] may be compared with that determined by Ingold and Shoppee in 1929<sup>23</sup> by the use of refractive indices [70.5% (X) in ethanol at 85 °C].

#### EXPERIMENTAL

**Chalcone** (VI; X = Y = H).—By the procedure of Kohler and Chadwell,<sup>28</sup> benzaldehyde (20 g, 189 mmol) was condensed with acetophenone (22.6 g, 189 mmol) in alkaline aqueous ethanol [sodium hydroxide (9.48 g, 237 mmol), ethanol (54 cm<sup>3</sup>), and water (85 cm<sup>3</sup>)]. Recrystallisation from aqueous ethanol gave a light yellow solid (31.4 g, 80%), m.p. 54–55.5 °C (lit.,<sup>28</sup> 55–57 °C),  $\nu_{\max}$  (Nujol) 1 660 cm<sup>-1</sup> (C=O),  $\delta$  7.0–7.7 (8 H, m, ArH), 7.34 (1 H, d, *J* 7.5 Hz,  $\alpha$ - or  $\beta$ -H), 7.51 (1 H, d, *J* 7.5 Hz,  $\alpha$ - or  $\beta$ -H), and 7.77–7.98 (2 H, m, 2'- and 6'-ArH).

In a similar manner the following substituted chalcones were prepared and recrystallised from absolute alcohol.\* 4'-methylchalcone,<sup>29,30</sup> 4-methylchalcone,<sup>29</sup> 4'-methoxychalcone,<sup>29</sup> 4-methoxychalcone,<sup>29</sup> 4-fluorochalcone,<sup>29</sup> 3-fluorochalcone,<sup>29</sup> 4'-*t*-butylchalcone,<sup>31,32</sup> 4-chlorochalcone,<sup>29</sup> 4-nitrochalcone,<sup>29</sup> 4'-trifluoromethylchalcone, and 4-iodochalcone.<sup>33,34</sup>

**1,3-Diphenylpropan-1-ol** (VIIa; X = Y = H).<sup>11</sup>—A solution of chalcone (12.8 g, 60 mmol) in dry tetrahydrofuran (25 cm<sup>3</sup>) was added dropwise to an ice-cold, stirred solution of lithium aluminium hydride (1.5 g, 40 mmol) in dry tetrahydrofuran (75 cm<sup>3</sup>), under nitrogen. The solution was then allowed to warm up to room temperature and stirring was continued for 1 h. The mixture was cooled to 0 °C; the excess of reagent was decomposed by cautious addition of water with stirring, resulting in a white precipitate. Sufficient 2N-H<sub>2</sub>SO<sub>4</sub> was added to dissolve the precipitate. The bulk of the tetrahydrofuran was evaporated off under reduced pressure at room temperature. The aqueous residue was extracted with ether. The extract was washed with water, dried, and evaporated *in vacuo* to yield a water-white liquid which could not be induced to crystallise;

\* Full preparative, spectroscopic, and, where appropriate, analytical data for these compounds are available in Supplementary Publication No. SUP 21827 (25 pp., 1 microfiche). The names of compounds which have been prepared and/or characterised for the first time are given in italics. The Supplementary Publication also includes details of the general methods and instrumentation employed and tables of g.l.c. data and of product ratios from acetate pyrolyses. For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

<sup>23</sup> C. K. Ingold and C. W. Shoppee, *J. Chem. Soc.*, 1929, 447.

<sup>24</sup> The early work of C. W. Shoppee and others on aryl substituted systems is summarised by J. W. Baker in 'Tautomerism,' Routledge, London, 1934.

crude yield 12.1 g (95%). The product was homogeneous by n.m.r. and showed  $\nu_{\max}$  (film) 3 350 cm<sup>-1</sup> (OH),  $\delta$  1.8–2.3 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH-O), 2.0 (1 H, s, exchangeable with D<sub>2</sub>O, OH), 2.5–2.85 (2 H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH-O), 4.62 (1 H, t, *J* 6.5 Hz, CH<sub>2</sub>-CH<sub>2</sub>-CH-O), and 7.22 and 7.33 (each 5 H, s, ArH).

In a similar manner the following substituted 1,3-diphenylpropan-1-ols were prepared: \* 1-(4-methylphenyl)-3-phenylpropan-1-ol,<sup>11</sup> 3-(4-methylphenyl)-1-phenylpropan-1-ol,<sup>35</sup> 1-(4-methoxyphenyl)-3-phenylpropan-1-ol,<sup>11</sup> 3-(4-methoxyphenyl)-1-phenylpropan-1-ol,<sup>11</sup> 3-(4-fluorophenyl)-1-phenylpropan-1-ol, 3-(3-fluorophenyl)-1-phenylpropan-1-ol, 3-phenyl-1-(4-*t*-butylphenyl)propan-1-ol, 3-(4-chlorophenyl)-4-phenylpropan-1-ol,<sup>11</sup> 3-phenyl-1-(4-trifluoromethylphenyl)propan-1-ol, and 3-(4-iodophenyl)-1-phenylpropan-1-ol.

**3-(4-Aminophenyl)-1-phenylpropan-1-one** (VIIIc).—A solution of 4-nitrochalcone (10 g, 40 mmol) in tetrahydrofuran (220 cm<sup>3</sup>) with 5% palladium–charcoal (0.5 g) was hydrogenated at room temperature and 1 atm., until 160 mmol were absorbed. The crude product was subjected to column chromatography (benzene–ether, 3.5 : 1). The first major product eluted was a yellow crystalline solid, 3-(4-aminophenyl)-1-phenylpropan-1-one (5.9 g, 66%), m.p. 78–79 °C (from aqueous ethanol),  $\nu_{\max}$  (Nujol) 3 440 and 3 360 (NH<sub>2</sub>) and 1 680 cm<sup>-1</sup> (C=O),  $\delta$  2.3–3.4 (4 H, m, CH<sub>2</sub>-CH<sub>2</sub>), 3.42br (2 H, s, exchangeable with D<sub>2</sub>O, ArNH<sub>2</sub>), 6.60 (2 H, d, *J* 9 Hz, 3'- and 5'-ArH), 7.04 (2 H, d, *J* 8.5 Hz, 2'- and 6'-ArH), 7.3–7.6 (3 H, m, 3-, 4-, and 5-ArH), and 7.8–8.1 (2 H, m, 2- and 6-ArH).

Treatment with acetic anhydride in pyridine gave the *N*-acetyl derivative as a white crystalline solid, m.p. 143–144 °C (from aqueous ethanol) (Found: C, 76.3; H, 6.1; N, 5.5. C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> requires C, 76.4; H, 6.4; N, 5.2%),  $\nu_{\max}$  (Nujol) 2 330 (N-H), 1 680 (C=O), and 1 660 cm<sup>-1</sup> (O=C-NH),  $\delta$  2.10 (3 H, s, Ac), 2.8–3.4 (4 H, m, CH<sub>2</sub>-CH<sub>2</sub>), 7.13 (2 H, d, *J* 9 Hz, 3'- and 5'-ArH), 7.3–7.6 (5 H, m, ArH), 7.8–8.1 (2 H, m, 2- and 6-ArH), 8.24br (1 H, s, CONH).

**3-(4-Dimethylaminophenyl)-1-phenylpropan-1-one**.—A solution of 3-(4-aminophenyl)-1-phenylpropan-1-one (10 g, 44 mmol) and 37% formaldehyde (84 ml, 1 100 mmol) in absolute ethanol (500 cm<sup>3</sup>) was refluxed for 1 min. Formic acid (7.2 g, 152 mmol) was added to the hot solution, which was then refluxed for 5 h. The bulk of the ethanol was evaporated off under reduced pressure and the residue taken up in ether. The solution was washed twice with sodium carbonate, twice with water, and dried. The ketone was purified by column chromatography (benzene–ether 9 : 1); yield 3.8 g (34%). Bulb distillation [135 °C (bath) and 0.2 mm Hg] yielded a water-white liquid which solidified overnight at –20 °C; m.p. 49–51 °C (Found: C, 80.9; H, 7.5;

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<sup>27</sup> H. Ahlbrecht, J. Blecher, H. Hanisch, G. Papke, and M. Th. Reiner, *Tetrahedron*, 1973, **29**, 3079, and earlier papers by these authors.

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<sup>32</sup> H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897.

<sup>33</sup> W. Davey and J. R. Guilt, *J. Chem. Soc.*, 1957, 1008.

<sup>34</sup> S. D. Jolad and S. Rajagopal, *Org. Synth.*, 1966, **46**, 13.

<sup>35</sup> R. Huisgen and H. Dohl, *Chem. Ber.*, 1960, **93**, 527.

N, 5.4.  $C_{17}H_{19}NO$  requires C, 80.6; H, 7.6; N, 5.5%,  $\nu_{\max}$  (film) 1 680  $cm^{-1}$  (C=O),  $\delta$  2.8—3.4 (4 H, m,  $CH_2 \cdot CH_2$ ), 2.88 (6 H, s,  $ArNMe_2$ ), 6.66 (2 H, d,  $J$  9 Hz, 3'- and 5'-ArH), 7.11 (2 H, d,  $J$  8.5 Hz, 2'- and 6'-ArH), 7.25—7.6 (2 H, m, 3-, 4-, and 5-ArH), and 7.8—8.05 (2 H, m, 2- and 6-ArH).

3-(4-Dimethylaminophenyl)-1-phenylpropan-1-ol (VIIa; X = H, Y =  $Me_2N$ ).—To a freshly prepared stirred solution of sodium borohydride (0.22 g, 4.4 mmol) in absolute ethanol (60  $cm^3$ ) was added a solution of 3-(4-dimethylamino-phenyl)-1-phenylpropan-1-one (1.73 g, 6.9 mmol) in absolute ethanol (10  $cm^3$ ). The solution was stirred overnight. Water (40  $cm^3$ ) was added and the bulk of the ethanol evaporated off under reduced pressure. The alkaline residue was extracted with ether. The extract was washed with water and dried. Column chromatography (benzene-ether, 4 : 1) yielded 3-(4-dimethylaminophenyl)-1-phenylpropan-1-ol as a light yellow oil (1.60 g, 92%). Bulb distillation [140 °C (bath) and  $10^{-2}$  mmHg] gave a liquid which slowly crystallised; m.p. 44—45 °C (Found:  $M^+$ , 255.1616.  $C_{17}H_{21}NO$  requires  $M$ , 255.1623),  $\nu_{\max}$  (film) 3 400  $cm^{-1}$  (OH),  $\delta$  1.7—2.15 (2 H, m,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 2.35—2.75 (2 H, m,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 2.42br (1 H, s, exchangeable with  $D_2O$ , OH), 2.84 (6 H, s,  $ArNMe_2$ ), 4.56 (1 H, t,  $J$  6.5 Hz,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 6.64 (2 H, d,  $J$  9.5 Hz, 3'- and 5'-ArH), 7.03 (2 H, d,  $J$  9 Hz, 2'- and 6'-ArH), and 7.27 (5 H, s, ArH).

1,3-Diphenylpropan-1-one (VIIIa).<sup>13</sup>—Chalcone (36.3 g, 175 mmol) was hydrogenated by the procedure of Adams *et al.*<sup>13</sup> The product was recrystallised from ethanol; yield 29.3 g (80%) (lit.,<sup>13</sup> 81—95%), m.p. 70—71 °C (lit.,<sup>13</sup> 72—73 °C),  $\nu_{\max}$  (Nujol) 1 675  $cm^{-1}$  (C=O),  $\delta$  2.8—3.5 (4 H, m,  $CH_2 \cdot CH_2$ ), 7.28 (5 H, s, ArH), 7.35—7.6 (3 H, m, 3-, 4-, and 5-ArH), and 7.85—8.1 (2 H, m, 2- and 6-ArH).

3-(4-Nitrophenyl)-1-phenylpropan-1-one (VIIIb).—1,3-Diphenylpropan-1-one was nitrated by the procedure of Gasson.<sup>14</sup> Fuming nitric acid (30  $cm^3$ , 680 mmol) was added dropwise to a slurry of 1,3-diphenylpropan-1-one (10 g, 47 mmol) in glacial acetic acid (10  $cm^3$ ) cooled in ice-salt. The rate of addition was regulated to prevent the temperature rising above -5 °C. The solution was then stirred at -5 °C for 30 min, poured onto ice (100 g), and extracted with ether (250  $cm^3$ ). The extract was twice washed with aqueous sodium hydrogen carbonate and water and then dried and evaporated *in vacuo* to a volume of 30  $cm^3$ ; a white crystalline solid was precipitated. The solid, 3-(4-nitrophenyl)-1-phenylpropan-1-one, was filtered off and recrystallised from aqueous ethanol; yield 3.1 g, m.p. 98—99 °C (lit.,<sup>15</sup> 99—100 °C). More of the *p*-nitro-isomer (1.2 g) was obtained, through separation from the *o*-nitro-isomer, by column chromatography (benzene-ether, 4 : 1). The *o*-nitro-isomer was eluted first, closely followed by the *p*-nitro-isomer; total yield 4.3 g (36%),  $\nu_{\max}$  (Nujol) 1 680  $cm^{-1}$  (C=O),  $\delta$  2.9—3.5 (4 H, m,  $CH_2 \cdot CH_2$ ), 7.2—7.65 (3 H, m, 3-, 4-, and 5-ArH), 7.40 (2 H, d,  $J$  9 Hz, 2'- and 6'-ArH), 7.8—8.15 (2 H, m, 2- and 6-ArH), and 8.12 (2 H, d,  $J$  8.5 Hz, 3'- and 5'-ArH).

3-(4-Nitrophenyl)-1-phenylpropan-1-ol (VIIa; X = H, Y =  $NO_2$ ).<sup>15</sup>—3-(4-Nitrophenyl)-1-phenylpropan-1-one (2 g, 7.8 mmol) in absolute ethanol (10  $cm^3$ ) was reduced with sodium borohydride (0.22 g, 4.4 mmol) in absolute ethanol (60  $cm^3$ ) by the method used before; crude yield 1.9 g (97%), m.p. 105—110 °C (lit.,<sup>15</sup> 112—113 °C),  $\nu_{\max}$  (Nujol)

3 300  $cm^{-1}$  (OH),  $\delta$  1.8—2.35 (2 H, m,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 2.27br (1 H, s, exchangeable with  $D_2O$ , OH), 2.62—2.95 (2 H, m,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 4.64 (1 H, t,  $J$  6 Hz,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 7.28 (2 H, d,  $J$  8.5 Hz, 2'- and 6'-ArH), 7.30 (4 H, s, ArH), and 8.07 (2 H, d,  $J$  8.5 Hz, 3'- and 5'-ArH).

1,3-Diphenylpropyl Acetate (VIIb; X = Y = H).<sup>36</sup>—1,3-Diphenylpropan-1-ol (5.30 g, 25 mmol) was refluxed with acetic anhydride (4.1  $cm^3$ , 40.7 mmol) in pyridine (10  $cm^3$ ) for 1 h. The mixture was poured into *n*-hydrochloric acid (150  $cm^3$ ) and extracted with ether. The extract was washed successively with *n*-hydrochloric acid, sodium carbonate (twice), and water, dried and evaporated to give a water-white liquid (6.3 g, 90%), homogeneous by n.m.r.,  $\nu_{\max}$  (film) 1 735  $cm^{-1}$  (—O—C=O),  $\delta$  1.9—2.4 (2 H, m,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 2.03 (3 H, s, Ac), 2.4—2.8 (2 H, m,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), 5.72 (1 H, t,  $J$  7 Hz,  $CH_2 \cdot CH_2 \cdot CH \cdot O$ ), and 7.06 and 7.20 (each 5 H, s, ArH).

In a similar manner the following substituted 1,3-diphenylpropyl acetates were prepared: \* 1-(4-methylphenyl)-3-phenylpropyl acetate, 3-(4-methylphenyl)-1-phenylpropyl acetate, 1-(4-methoxyphenyl)-3-phenylpropyl acetate,<sup>12</sup> 3-(4-methoxyphenyl)-1-phenylpropyl acetate,<sup>12</sup> 3-(4-fluorophenyl)-1-phenylpropyl acetate, 3-(3-fluorophenyl)-1-phenylpropyl acetate, 3-phenyl-1-(4-*t*-butylphenyl)propyl acetate, 3-(4-chlorophenyl)-1-phenylpropyl acetate, 3-(4-nitrophenyl)-1-phenylpropyl acetate, 3-(4-dimethylaminophenyl)-1-phenylpropyl acetate, 3-phenyl-1-(4-trifluoromethylphenyl)propyl acetate, and 3-(4-iodophenyl)-1-phenylpropyl acetate.

1,3-Diphenylpropene—This was prepared by pyrolysing 1,3-diphenylpropyl acetate (5 g, 20 mmol) in a bulb distillation apparatus.<sup>17</sup> The acetate was placed in the lower bulb and the apparatus was continuously swept out with nitrogen introduced *via* a long syringe needle.

The bulb containing the acetate was lowered into a Woods metal bath at 300 °C. The temperature was maintained at  $300 \pm 10$  °C until the calculated amount of acetic acid (1.2  $cm^3$ , 20 mmol) had distilled into the upper bulb. The total pyrolysis time was 15 min. After the apparatus had cooled to room temperature, the contents of both bulbs were poured into sodium carbonate solution, which was extracted with ether. The extract was washed with sodium carbonate (twice) and water, dried and evaporated to yield a light yellow oil (3.9 g). Column chromatography (petrol) of the crude product gave (in elution order) *cis*-1,3-diphenylpropene (30 mg), a mixed fraction of the two isomers (0.5 g), and *trans*-1,3-diphenylpropene (1.56 g); total yield 2.06 g (54%).

*cis*-1,3-Diphenylpropene<sup>37,38</sup> showed  $\nu_{\max}$  (film) 915, 770, 735, and 700  $cm^{-1}$  (lit.,<sup>37</sup> 915, 765, 735, and 700  $cm^{-1}$ ),  $\delta$  3.66 (2 H, dd,  $J$  7 and 2 Hz,  $CH_2$ ), 5.86 (1 H, t,  $J$  11.5 and 7 Hz, =CH- $CH_2$ ), 6.63 (1 H, dt,  $J$  11.5 and 2 Hz, PhCH=), and 7.27 and 7.33 (each 5 H, s, ArH) [lit.,<sup>38</sup> 3.62 (2 H, dd,  $J$  7.5 and 1.5 Hz), 5.82 (1 H, dt,  $J$  11.5 and 7.5 Hz), 6.52 (1 H, dt,  $J$  11.5 and 1.5 Hz), and 7.2 (10 H, 2 bands)].

*trans*-1,3-Diphenylpropene,<sup>38,39</sup> after bulb distillation [65 °C (bath) and  $10^{-4}$  mmHg], showed  $\nu_{\max}$  (film) 964  $cm^{-1}$  (*trans*-CH=CH-) (lit.,<sup>38</sup> 966  $cm^{-1}$ ),  $\delta_H$  (60 MHz) 3.46—3.62 (2 H, apparent t with centre line of reduced intensity,  $X_2$  of  $ABX_2$  system,  $CH_2$ ), 6.30—6.50 with 'wings' at 6.07 and 6.69 (2 H, m, AB of  $ABX_2$  system, olefinic H), and 7.1—7.5 (10 H, m, ArH) [lit.,<sup>38</sup> (100 MHz) 3.48 (2 H, d,  $J$  5 Hz), 6.25

\* See footnote p. 1686.

<sup>36</sup> L. F. Hewitt and J. Kenyon, *J. Chem. Soc.*, 1925, 1094.

<sup>37</sup> G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, 1965, **87**, 1410.

<sup>38</sup> E. K. Rawnio and W. A. Bonmer, *J. Org. Chem.*, 1966, **31**, 396.

<sup>39</sup> M. M. Bokadia, B. R. Brown, D. Cobern, A. Roberts, and G. A. Sommerfield, *J. Chem. Soc.*, 1962, 1658.

( $J$  16 Hz,  $=CH\cdot CH_2$ ), 6.40 ( $J$  16 Hz,  $PhCH=$ ), and 6.9—7.5 (10 H, m, ArH),  $\delta_C$  39.4med ( $CH_2$ ), 126.3str (3- and 5- or 2- and 6- $C_{ar}$ ), 127.3med (4- $C_{ar}$ ), 128.7vstr, br ( $C_{ar}$ ), 129.4med ( $=CH\cdot CH_2$ ), 131.3med ( $PhCH=$ ), 137.8wk (1- $C_{ar}$ ), and 140.4wk (1'- $C_{ar}$ ).

In a similar manner the following substituted 1,3-diphenylpropenes were prepared.\* Their chromatographic behaviour was similar to that of the parent system in that the *cis*-isomer was eluted from the column just before the *trans*-isomer and in some cases it was not possible to obtain the *cis*-form wholly free from *trans*-impurities. In these systems the spectroscopic data\* refer to a *cis*-enriched fraction: 1-(4-methylphenyl)-3-phenylpropene,<sup>11</sup> 3-(4-methylphenyl)-1-phenylpropene,<sup>35</sup> 1-(4-methoxyphenyl)-3-phenylpropene,<sup>11</sup> 3-(4-methoxyphenyl)-1-phenylpropene,<sup>11</sup> 3-(4-fluorophenyl)-1-phenylpropene, 3-(3-fluorophenyl)-1-phenylpropene, 3-phenyl-1-(4-*t*-butylphenyl)propene, 3-(4-chlorophenyl)-1-phenylpropene,<sup>11</sup> 3-(4-nitrophenyl)-1-phenylpropene,<sup>15</sup> 3-(4-dimethylaminophenyl)-1-phenylpropene, 3-phenyl-1-(4-trifluoromethylphenyl)propene, and 3-(4-iodophenyl)-1-phenylpropene.

*trans*-1-Phenyl-3-(4-Trimethylammonio)phenyl)propene Iodide (III;  $X = Me_3N^+I^-$ ,  $Y = H$ ).—To a solution of *trans*-3-(4-dimethylaminophenyl)-1-phenylpropene (0.3 g, 1.2 mmol) in absolute ethanol (3 cm<sup>3</sup>) was added methyl iodide (0.3 cm<sup>3</sup>, 5.1 mmol). The solution was refluxed for 10 min, and a white precipitate was formed. The solution was cooled, and ether (7 cm<sup>3</sup>) was added. The white precipitate was filtered off and washed with ether. Recrystallisation from methanol gave, as a white crystalline solid, the quaternary ammonium salt (0.35 g, 74%), m.p. 181—182 °C (Found: C, 57.4; H, 5.9; I, 31.7; N, 3.7.  $C_{18}H_{22}IN$  requires C, 57.0; H, 5.9; I, 33.5; N, 3.7%),  $\delta$  [(CD<sub>3</sub>)<sub>2</sub>SO] 3.68 (9 H, s,  $ArNMe_3$ ), 3.5—3.7 (2 H, m,  $CH_2$ ), 6.4—6.6 with 'wings' at 6.23 and 6.80 (2 H, m, olefinic H), 7.15—7.45 (5 H, s, ArH), 7.54 (2 H, d,  $J$  9 Hz, 2'- and 6'-ArH), and 8.00 (2 H, d,  $J$  9 Hz, 3'- and 5'-ArH).

*trans*-3-Phenyl-1-(4-trimethylammonio)phenyl)propene iodide was prepared in a similar manner.\*

\* See footnote p. 1686.

*Alkylation of 1-Phenyl-3-(4-trifluoromethylphenyl)propene* (I;  $X = CF_3$ ,  $Y = H$ ).—Allyl chloride<sup>40</sup> (0.6 cm<sup>3</sup>) was added rapidly from a syringe to a stirred freshly prepared solution of the anion (I) (0.55 mmol) in liquid ammonia at -42 °C.<sup>41</sup> The carbanion colour was instantly dissipated. Water was added followed by ether. The ethereal solution was washed with water, dried, and evaporated. The crude product was purified by preparative t.l.c. (Kieselgel-silver nitrate eluted with benzene-petrol, 1 : 2) to yield a mixture of 1-phenyl-3-(4-trifluoromethylphenyl)hexa-1,5-diene and 3-phenyl-1-(4-trifluoromethylphenyl)hexa-1,5-diene (127 mg, 84%) (Found:  $M^+$ , 302.127 7. Calc. for  $C_{18}H_{17}F_3$ ;  $M$ , 302.128 2),  $\delta$  2.57 (2 H, t,  $J$  6.7 Hz,  $CH_2$ ), 3.3—3.7 (1 H, m,  $PhCH$ ), 4.8—5.2 (2 H, m,  $CH_2=C$ ), 5.4—6.0 (1 H, m,  $C=CH\cdot CH_2$ ), 6.3—6.5 (2 H, m, olefinic H), and 7.0—7.7 (9 H, m, ArH),  $m/e$  302 (5%,  $M^+$ ), 262 (100), 261 (100), 193 (100), and 183 (100).

*Equilibration of 1,3-Diarylpropenes*.—A tube (16 cm  $\times$  13 mm i.d.) with a constriction near the neck was attached to the vacuum line via a B10 joint. A solution of sodamide (0.03 mmol) in liquid ammonia (4 cm<sup>3</sup>) was prepared in this tube and the olefin (1 mmol) in dry diethyl ether (0.5 cm<sup>3</sup>) was added.<sup>41</sup> The ammonia solution was frozen in liquid nitrogen, the system evacuated, and the tube sealed at the constriction. After the tube had reached room temperature it was shaken to ensure the formation of a homogeneous pale red solution and then kept at room temperature for 0.5 h (or 1 h in some cases). The solution was rapidly frozen in liquid nitrogen, the tube opened, and the frozen ammonia matrix extruded into water-ice-ether slurry by warming the closed end of the tube. The ether solution was separated from the aqueous ammonia layer, washed with water, dried, and evaporated *in vacuo*. Samples were stored in frozen benzene matrix at -20 °C.

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<sup>40</sup> D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals', Pergamon, Oxford, 1966, 65.

<sup>41</sup> Full details of the vacuum line methods used in the preparation of allyl anion solutions are given in Part 2, R. J. Bushby and G. J. Ferber, following paper.