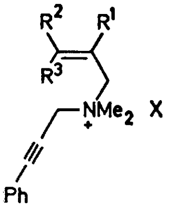
Base-catalysed Rearrangement of Allyl-Propynyl Ammonium Cations and a Novel Synthetic Route to Substituted Biphenyls

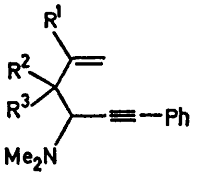
By R. W. JEMISON, T. LAIRD, and W. D. OLLIS*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

Summary Base-catalysed rearrangement of the salts (I) in aprotic media gives the amines (II) and (III); the amines (II) on heating yield the biphenyl derivatives (V).

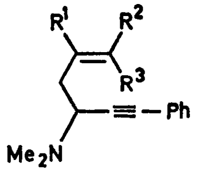
THE salts (I) in dimethyl sulphoxide solution with sodium methoxide (1 equiv.) at room temperature are smoothly transformed into a mixture of amines (II) and (III). The amines (II) which are formed in major yield (*ca.* 90%) are undoubtedly derived by a concerted [2,3]-sigmatropic rearrangement of the intermediate ylide (IV).[1] The relatively minor products (III) (*ca.* 10%) are formed by a Stevens [1,2]-rearrangement of the ylide (IV)[2,3] presumably *via* a radical-pair intermediate.[2,4] Of course, for the salts (I d—f) only one amine (II) is isolated since in these three cases (II) = (III).



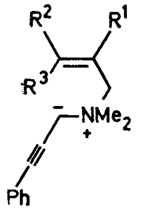
(I)



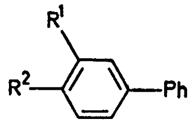
(II)



(III)



(IV)



(V)

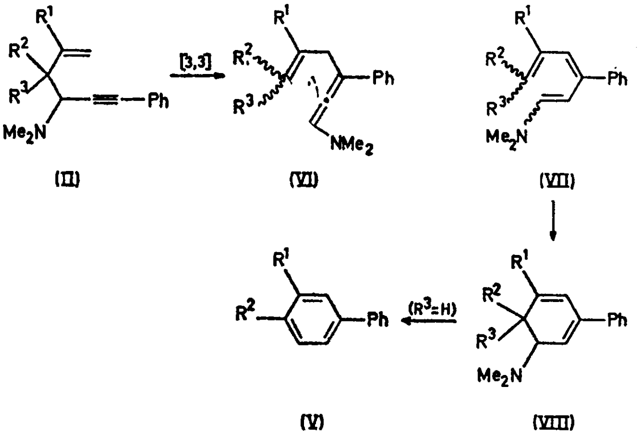
In (I)—(V)

	R^1	R^2	R^3	X
a;	H	Ph	H	Br
b;	H	Me	H	Br
c;	H	Me	Me	Br
d;[5]	H	H	H	Br
e;	Ph	H	H	Br
f;	Me	H	H	Cl

The possibility that the amines (III a—c) are produced by a thermal [1,3]-rearrangement[1] of the corresponding amines (II) is excluded by the following evidence. The amines (II; $R^3 = H$) on heating (Table) are transformed to the biphenyls (V), whereas under similar conditions the amines (III a—c) are recovered. The mechanism proposed for the thermal transformation (II; $R^3 = H$) → (V) is given in the Scheme. It is probably initiated by a [3,3]-sigmatropic rearrangement[6,7] of the ene–yne (II) giving the allenic amine (VI) for which there are good analogies.[4,8–11] The allene (VI) could then undergo a sequence; (i) isomerisation (base-catalysed ?) to the hexatriene (VII), (ii) cyclisation[7] to the cyclohexadiene (VIII), and (iii) aromatisation to the biphenyl by elimination of dimethylamine.

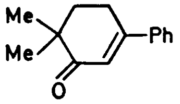
Thermal transformation of the amines (II) *to the biphenyls* (V)

Amine	Temperature (°C)	Time	Yield of (V) (%)
(IIa)	140	1 h	70
(IIb)	200	3 days	60
(IId)	140	7 days	58
(IIe)	140	3 days	95
(IIf)	200	12 h	95

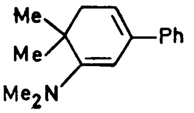


SCHEME

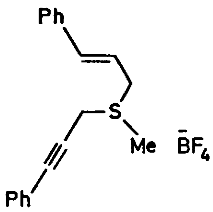
This mechanistic proposal (Scheme) is similar to those already put forward to account for the thermal transformation of aryl prop-2-ynyl ethers to chromenes[10] and vinyl prop-2-ynyl sulphides to thiopyrans.[11] The Scheme is supported by the observation that the amine (IIc) after heating (140°; 3 days) followed by a mild acidic work-up gives the amine (VIII; $R^1 = H$, $R^2 = R^3 = Me$) (12%), the ketone (IX) (30%), and 4-methylbiphenyl (V; $R^1 = H$, $R^2 = Me$) (1%). The ketone (IX) is assumed to have been formed by hydrolysis of the enamine (X) produced by a thermal [1,5]-sigmatropic shift[7] of hydrogen in the cyclo-



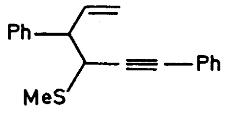
(IX)



(X)



(XI)



(XII)

hexadiene (VIII; $R^1 = H$, $R^2 = R^3 = Me$). The constitution of the ketone (IX) was established by its synthesis[12] from $PhCO{\cdot}CH_2{\cdot}CH_2Cl$, $MeCO{\cdot}CHMe_2$, and $EtMe_2CONa$.

These observations may be compared with results we have obtained with analogous sulphur-containing compounds. The salt (XI) with sodium methoxide–dimethyl sulphoxide gave only the [2,3]-sigmatropic rearrangement product (XII). On heating this compound (XII) gave *p*-terphenyl (Va) in comparatively low yield (*ca.* 30%), and the conditions required (200°; 4 h) were much more vigorous than those for the transformation (IIa) → (Va) (70%) (140°; 1 h). The substituent effect (NMe_2 or SMe) upon the relative rate of the [3,3]-sigmatropic rearrangement [*cf.* (II) → (VI)] is thus similar to the rate effects already observed upon the Cope rearrangement.[8]

We thank the S.R.C. for the award of a Research Fellowship (T.L.).

(*Received, 4th February* 1972; *Com.* 172.)

---

[1] R. W. Jemison and W. D. Ollis, *Chem. Comm.*, 1969, 294.

[2] U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Letters*, 1969, 3415.

[3] R. W. Jemison, S. Mageswaran, W. D. Ollis, S. E. Potter, A. J. Pretty, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Comm.*, 1970, 1201; S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *ibid.*, 1971, 1494.

[4] J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, 1969, **91**, 3646.

[5] I. Iwai and T. Hiroaka, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 1556.

[6] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1962, **18**, 67; *Angew. Chem. Internat. Edn.*, 1963, **2**, 115; S. J. Rhoads in 'Molecular Rearrangements,' ed. P. de Mayo, Interscience, New York, 1963, Part I, p. 655.

[7] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[8] R. W. Jemison, W. D. Ollis, I. O. Sutherland, and J. Tannock, forthcoming publication.

[9] J. A. Berson and E. J. Walsh, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 4730 and references cited therein; S. Swaminathan, K. G. Srinivasan, and P. S. Venkataramani, *Tetrahedron*, 1970, **26**, 1453; A. Viola and E. J. Iorio, *J. Org. Chem.*, 1970, **35**, 856; P. Leriverend and J.-M. Conia, *Bull. Soc. chim. France*, 1970, 1040; R. W. Thies, *Chem. Comm.*, 1971, 237; A. Viola and J. H. MacMillan, *J. Amer. Chem. Soc.*, 1970, **92**, 2404; *Chem. Comm.*, 1970, 301 and references cited therein.

[10] J. Zsindely and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1510 and references cited therein; H.-J. Hansen and H. Schmid, *Chem. in Britain*, 1969, **5**, 111.

[11] L. Brandsma, P. J. W. Schuijl, D. Schuijl-Laros, J. Meier, and H. E. Wijers, *Quart. Reports Sulfur Chem.*, 1971, **6**, 85 and references cited therein.

[12] J.-M. Conia and F. Rouessac, *Bull. Soc. chim. France*, 1963, 1925.