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

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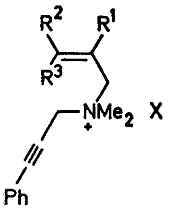
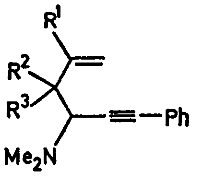
Summary Base-catalysed rearrangement of the salts (I) in aprotic media gives the amines (II) and (III); the amines (II) on heating yield the biphenyl derivatives (V).

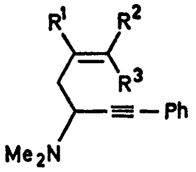
The salts (I) in dimethyl sulphoxide solution with sodium methoxide (1 equiv.) at room temperature are smoothly transformed into a mixture of amines (II) and (III). The amines (II) which are formed in major yield (*ca.* 90%) are undoubtedly derived by a concerted [2,3]-sigmatropic rearrangement of the 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)



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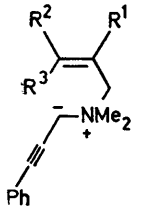

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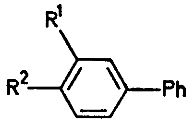


(V)

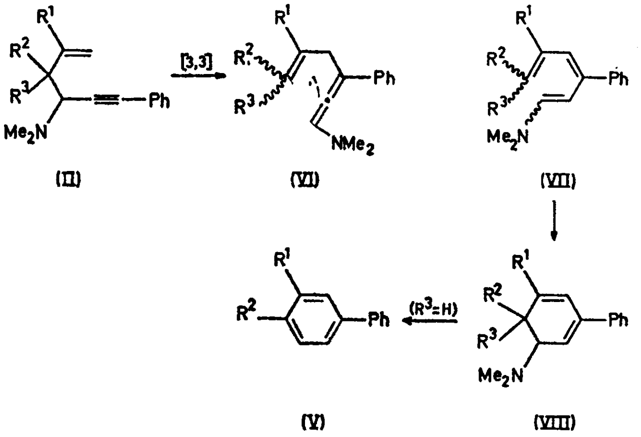
In (I)—(V)

	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.

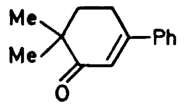
Thermal transformation of the amines (II) *to the biphenyls* (V)

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

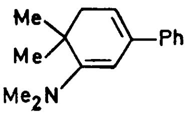


Scheme

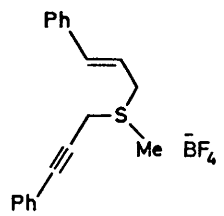
This mechanistic proposal (Scheme) is similar to those already put forward to account for the thermal transformation of aryl prop-2-ynyl ethers to chromenes[10] and vinyl prop-2-ynyl sulphides to thiopyrans.[11] The Scheme is supported by the observation that the amine (IIc) after heating (140°; 3 days) 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-



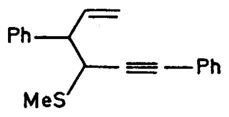
(IX)



(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 $EtMe_2{\cdot}CONa$.

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]

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