Anion Rearrangements: a Case of a Non-degenerate All-carbon [3,2]-Sigmatropic Process

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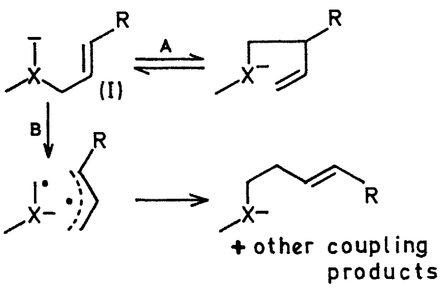
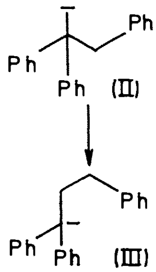
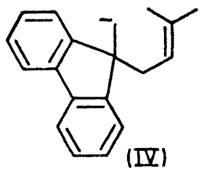
Summary The first example of an all-carbon anionic [3,2]-sigmatropic rearrangement has been observed in the conversion of 9-(3-methylbut-2-enyl)-9-(lithiomethyl)-fluorene into 9-(2,2-dimethylbut-3-enyl)-9-lithiofluorene, the reaction being accompanied by a temperature-dependent dissociation–recombination process.





(II)

(III)



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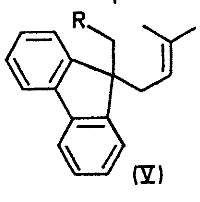

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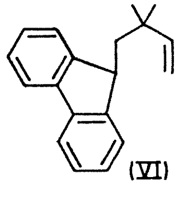

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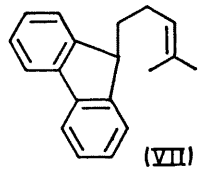

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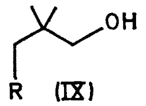

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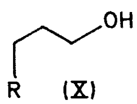
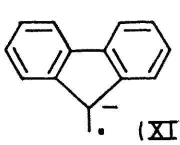
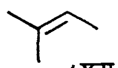


(X)

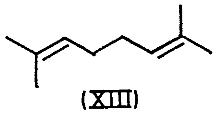
(R = 9-Fluorenyl)



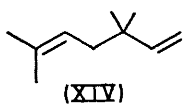
(XI)



(XII)



(XIII)



(XIV)

As a result of earlier studies on ylide rearrangements[1,2] we have delineated[3,4] two pathways by which an ylide (I) may rearrange, *i.e.* by a concerted [3,2]-sigmatropic process with retention of orbital symmetry[5] (path A) or by a radical dissociation–recombination mechanism (path B). In general, the former process is of lower activation energy and predominates as the product-determining path; however, higher temperatures[3] and structural changes[4] can facilitate path B. Since the orbital symmetry relationships, implicit in the interconversion (A), must apply to carbanions (I; X = C–) as well as to the neutral ylides –N–, *etc.*) we have examined the possibility of the as yet unknown rearrangement in an all-carbon system. The 1,2-carbanion rearrangement, *e.g.* (II) to (III), often described as the Zimmermann–Grovenstein reaction,[6] is the one known case of path B (X=C–), since concerted rearrangement with retention of orbital symmetry is geometrically impossible, requiring an inversion in the migrating group.[5]

In keeping with this interpretation, there has been obtained some indirect evidence for the presence of radicals in this process.[7] From the above it may therefore be predicted that in a suitable olefinic system path A could be realized. As the simplest case (I; X = C–, R = H) is degenerate, we examined a system (IV) in which substituents would stabilize the product anion and thereby provide driving force for rearrangement. The precursor of anion (IV) was the chloride (V; R = Cl),† obtained by consecutive alkylation of fluorene with 3,3-dimethylallyl bromide and methylene chloride, which was transformed into the lithio-derivative (V; R = Li) by treatment with

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† All new compounds have satisfactory analytical and spectral data.

metallic lithium at −70° in tetrahydrofuran. This carbanion did not rearrange at −70°, as was demonstrated by its carboxylation to the corresponding acid (V; R = CO_2H) (31%), or more efficiently by deuteriation to (V; R = ^2H) (80%). However, on warming up to −20°, rearrangement was complete in 5 hr. The quenching reaction mixture consisted of compounds (VI), (VII), and 9-methylfluorene (VIII), in the proportions shown in the Table, as evaluated from the n.m.r. spectral integral after calibration with authentic mixtures of synthesized samples of (VI)—(VIII). Separation of the product mixture was best achieved through ozonolysis followed by reductive work-up (sodium borohydride) and chromatography over silica gel, whereupon olefins (VI) and (VII) yielded the corresponding alcohols (IX) and (X), respectively, while hydrocarbon (VIII) was unchanged. Similar evaluation of this anion rearrangement at a series of increasing temperatures gave the results shown in the Table. It is evident, as in previous heteroatomic systems,[3,4,8] that increasing temperature favours path B, as reflected in the proportion of products (VII) and (VIII). The production of 9-methylfluorene (VIII) most probably results from further reduction of the intermediate radical anion (XI) by the excess of lithium metal present in these reactions, and in accord with this hypothesis we have demonstrated (g.l.c.) the presence of the cleavage products (XII)—(XIV) in amounts comparable with that of (VIII). Finally the expected reversibility[5] of path (A) was shown by warming a reaction mixture, carried to completion at −20°, up to 25°. After 36 hr. at this temperature the product, after quenching, was almost entirely 9-methylfluorene (VIII) and the hydrocarbons (XII)—(XIV), resulting from reversal of path A followed by an irreversible dissociation and subsequent reduction and coupling to the observed products.

	Composition of product (%)		
Reaction temp.	(VI)	(VII)	(VIII)
−20°	70	20	10
−10°	55	30	15
65°	50	36	14

Demonstration of this new reaction now increases to four the known anion or ylide rearrangements of the general type exemplified by path A, *i.e.* X = N, O, S, C.

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