

SEARCH FOR THE IONIC COPE REARRANGEMENT

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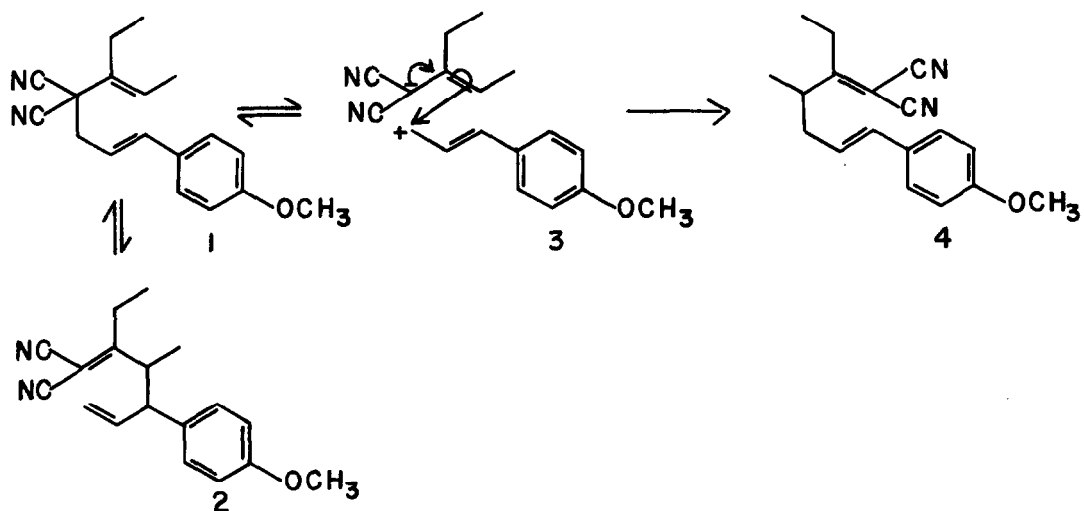
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The Cope Rearrangement has long been considered to be a concerted process¹, although examples have been found which appear to proceed by a second, radical pair mechanism^{2,3,4}. The third possible mechanism, via an ion pair, although considered⁵, and searched for⁶, has never been reported. We now wish to present a reaction, closely related to the Cope Rearrangement, which appears to proceed by an ionic pathway.

In order to observe the ionic mechanism it is clear that one of the main requirements in a potential substrate would be its ability to produce highly stabilized ions. Our earlier work had already revealed that a Cope rearrangement substrate containing a potential simple allyl cation together with a potential malononitrile anion did not rearrange ionically⁶, and accordingly, in the selected substrate, the stability of the potential cation was substantially increased by conjugation with a p-methoxyphenyl group. This substrate, 2-(1-ethyl-1-propenyl)-2-(3-p-methoxyphenylallyl) malononitrile (1), in addition to possessing the ion stability feature, was also designed to give different products according to the mechanism followed, thus permitting rapid mechanistic analysis. This feature is illustrated in the Scheme.



Scheme

The purely concerted mechanism can only interchange **1** and **2**; however, if the ions **3** are produced, and have sufficient lifetime, it is conceivable that they could recombine as shown giving **4**, which being more highly conjugated than either **1** or **2** might well be a significant, if not predominant, product.

2-(1-ethyl-1-propenyl)-2-(3-p-methoxyphenylallyl)malononitrile (**1**) was synthesized by condensation of the anion of 2-(1-ethylpropylidene) malononitrile⁶ with p-methoxycinnamyl chloride⁷. Spectral and analytical data (ν_{\max} 2240 cm^{-1} , weak; λ_{\max} 263 nm, ϵ 28000; δ 1.10 (3H, t, $J = 8\text{Hz}$), 1.65 (3H, d, $J = 6\text{ Hz}$), 2.27 (2H, q, $J = 8\text{Hz}$), 2.77 (2H, d, $J = 8\text{Hz}$), 3.70 (3H, s), 5.7-6.6 (3H, m), and 6.7-7.5 ppm (4H, q). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.17; H, 7.24; N, 9.78) confirm the structure of diene **1**. Pyrolysis of compound **1** caused a remarkably clean reaction: on mild heating (80°), diene **1** was rapidly ($t_{1/2} \approx 2$ hours) and quantitatively converted to a new compound, the spectral and analytical data (ν_{\max} 2220 cm^{-1} , strong; λ_{\max} 263 nm, ϵ 26000; δ 1.22 (3H, d, $J = 7\text{Hz}$), 1.23 (3H, t, $J = 7.5\text{ Hz}$), 2.2-3.6 (5H, m), 3.78 (3H, s), 5.6-6.6 (2H, m), and 6.7-7.5 ppm (4H, q). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.02; H, 7.25; N, 10.04) of which permits the assignment of structure **4**.

Although the conversion of 1 to 4 is the precise reaction predicted if ionic intermediates were involved (vide supra), it is clear that isolation of a product does not constitute proof of mechanism. The crucial point is that only one of the two allyl units has undergone allylic inversion; this point makes a concerted mechanism very improbable. It also raises the question of whether this conversion is in fact a Cope Rearrangement, although it is clearly closely related to it.* The two most probable mechanisms for the rearrangement of 1 to 4 would appear to be the fragmentation-recombination process shown in the scheme, either with ionic intermediates as shown, or with radical intermediates arising from homolytic cleavage. In an effort to evaluate the contribution, if any, of a radical mechanism, the reaction was examined to see if it exhibited chemically induced dynamic nuclear polarization (CIDNP)⁸, a particularly sensitive method for the detection of short-lived free radical intermediates. No such polarization was observed, thus rendering the radical mechanism unlikely. Evidence supporting the ionic mechanism in the conversion of 1 to 4 is presented in the following communication.

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* The definition of the Cope Rearrangement proposed by Hammond and DeBoer³ does, in fact, include this specific type of rearrangement referred to as the process $A=B-C-C'-B'=A' \rightarrow A=B-C-A'-B'=C$.

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