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ARYLCYCLOPROPANE PHOTOCHEMISTRY. AN IONIC MECHANISM FOR THE PHOTOCHEMICAL REARRANGEMENT OF TRANS-2-PHENYLCYCLOPROPYLCARBINYL ACETATE.

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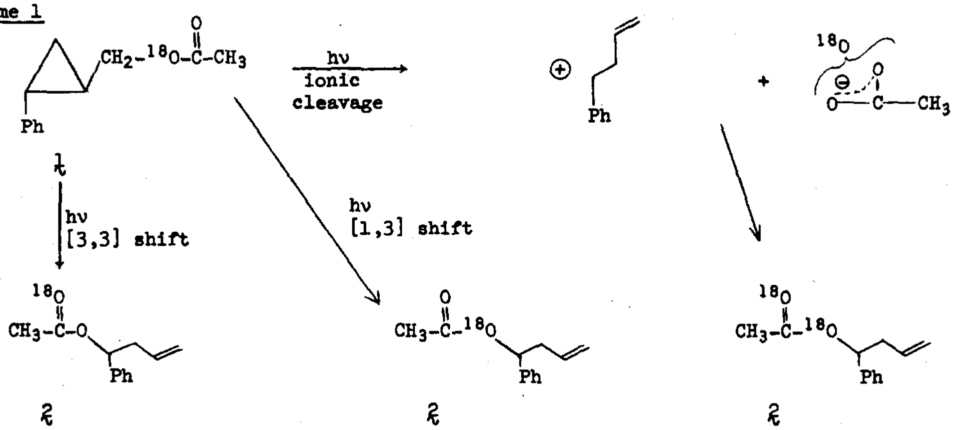
We recently reported that trans-2-phenylcyclopropylcarbinyl acetate (**1**) rearranges photochemically to the homoallyl acetate **2**, and that this process appeared to be general for 2-arylcyclopropylcarbinyl acetates.[1] Our results indicated a free-radical mechanism for rearrangement was very unlikely; however, both ionic and concerted pathways were consistent with the data. Photochemical rearrangements and solvolyses of other systems RX (X = halide or other good leaving group) have been observed, and carbonium ion intermediates frequently have been postulated.[2,3] However, except in certain cases where RX is a benzyl derivative, the intervention of ionic intermediates has not been thoroughly established. In view of the above and our own interest in the nature and behavior of arylcyclopropane excited states, we felt it vital to determine the mechanism of the **1** to **2** transformation.

As shown in Scheme 1, one may distinguish among an ionic, a concerted [1,3] shift, and a concerted [3,3] shift mechanism by irradiating specifically-labeled $[^{18}\text{O}]$-**1**. We therefore prepared $[^{18}\text{O}]$-**1** containing 11.4 ± 0.4 atom % excess ^{18}O with all the label in the ether oxygen. The irradiation[4] of 1.000 g of $[^{18}\text{O}]$-**1** in 180 ml of N_2-purged ether solution was carried out for 28 hr at which point the ratio of **2** to **1** (cis and trans) was 0.12 (gc). The resulting $[^{18}\text{O}]$-**2** was isolated by preparative tlc; a small portion was saved and the rest saponified and re-acetylated. Mass spectral analysis of the $[^{18}\text{O}]$-**2** which had not been saponified showed it to contain 11.3 ± 0.2 atom % excess ^{18}O, i.e., the same total amount of label as starting acetate $[^{18}\text{O}]$-**1**. Similar analysis of the saponified and re-acetylated material indicated the presence of only 5.7 ± 0.2 atom % excess ^{18}O -- one half of that in the unsaponified material. Since we find that, as expected, saponification and re-acetylation of ether labeled $[^{18}\text{O}]$-**2** results in no loss of label, the above results indicate that the ^{18}O which was originally confined to the ether oxygen of $[^{18}\text{O}]$-**1** had become totally scrambled between the ether and carbonyl oxygens in the photoproduct $[^{18}\text{O}]$-**2**.

The recovered $[^{18}\text{O}]$-**1** was saponified and re-acetylated. Mass spectral analysis of this re-acetylated material indicated no ^{18}O scrambling had occurred in the recovered $[^{18}\text{O}]$-**1**. $[^{18}\text{O}]$-**2** containing 8.2 ± 0.3 atom % excess ^{18}O with all the label in the ether oxygen was prepared. A control photolysis of 0.100 g of this material for a time similar to that used in the $[^{18}\text{O}]$-**1**

Scheme 1



photolysis resulted in no detectable scrambling and only a small loss of **2**.[5] These results establish that the ^{18}O scrambling observed in the [^{18}O]-**2** produced from [^{18}O]-**1** must have occurred during its formation. Clearly the concerted [1,3] or [3,3] shift mechanisms (Scheme 1) are eliminated as major contributors to the reaction. Rather, an ionic mechanism is indicated.

The rearrangement of **1** seems best viewed as arising from a radical-like species[6] formed by stretching of an excited singlet state[1] cyclopropane bond. Such a species is expected to have zwitterionic character;[7,8] the loss of acetate ion is thus reasonable. The present finding further illustrates the ionic reaction capability of excited singlet cyclopropanes.[8,9] Both ionic and radical behavior of cyclopropanes in ground state bond cleavage processes have been observed by Cram.[10]

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