Rearrangements of α-Triketones

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THE base-catalyzed rearrangement of diphenyl triketone has been explained[1] as a conventional benzilic acid rearrangement,[2] in which base attack on the central carbonyl is followed by migration of a benzoyl group. In 1961 we demonstrated[3] with ^{14}C-labelling that alloxan is converted by the base into alloxanic acid through a mechanism which involves shift of a nitrogen to an adjacent carbon. The foregoing result was rationalized by presuming base attacks one of the *terminal* carbonyl groups.

Since both diphenyl triketone and alloxan form stable hydrates with the middle carbonyl, we were puzzled about their different behaviour. Further, the earlier mechanism[1] was based entirely on tracer results relating to benzoin and carbon dioxide, in which the benzoin isolated comprised only about

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5% of the total yield. The benzoic and mandelic acids formed were assumed[4] to arise through an intermediate common to all four products.

We now report on the rearrangement, in weakly basic, aqueous media, of phenyl *p*-nitrophenyl triketone monohydrate (I), labelled with ^{14}C in the middle carbonyl. In several experiments we isolated none of the products of benzoyl migration (Path 1, Chart 1), but instead obtained *p*-nitrobenzoic (V) and mandelic (IV) acids in yields of 79 and 66% respectively. The mandelic acid (IV) possessed the same radioactivity as the initial triketone (I), but the *p*-nitrobenzoic acid was non-radioactive. It is, of course, possible to explain these results if we assume that *p*-nitrobenzoyl migrates (Path 2) in preference to benzoyl (Path 1). Because of the greater electrophilicity[5] of *p*-nitrobenzoyl with respect to benzoyl, however, we regard the foregoing explanation as completely untenable and propose instead that hydroxyl ion attacks (I) at the carbonyl adjacent to *p*-nitrophenyl, and that the intermediate (D) so formed undergoes direct cleavage to yield *p*-nitrobenzoic (V) and mandelic (IV) acids (see Chart 2).

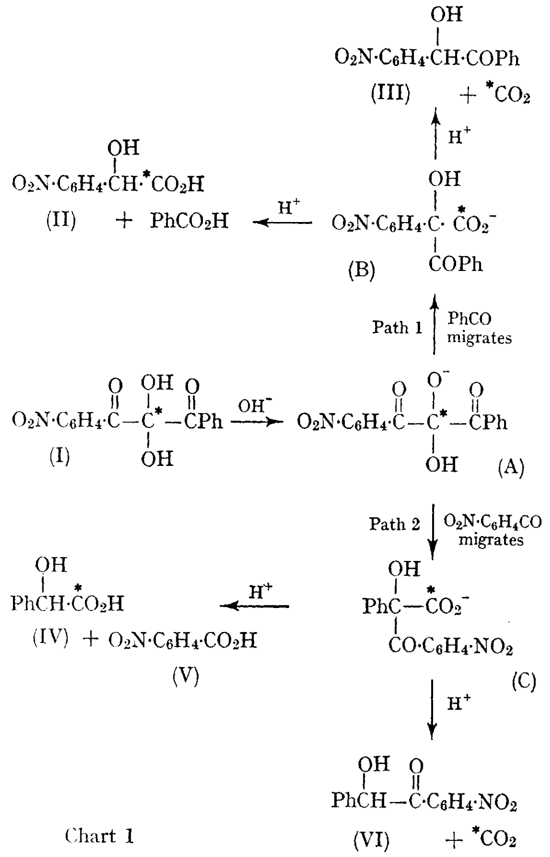

Chart 1

Our present results indicate the base-catalyzed rearrangements of triketones are more complicated than previously[1,3] suspected, and we believe an alternative mechanism for the rearrangement of alloxan (Chart III), involving cleavage and recyclization must now be considered. The very small amounts[1,4] of benzoin (*ca.* 5%) isolated in the base-catalyzed rearrangement of diphenyl triketone are, at present, still best represented by the conventional mechanism (Path 1, Chart 1).

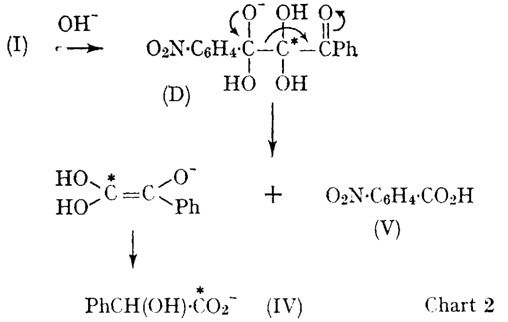

Chart 2

Both labelled diphenyl triketone (IX) and (I), when treated with strong acid, yield products whose nature exclude the *aryl* migration mechanism considered by Schönberg and Azzam.[6] For

$$PhCO\cdot\overset{*}{C}(OH)_2\cdot COPh \qquad (IX)$$

instance, the triketone (IX), when treated with 1 : 1 H_2SO_4–benzene at 20°, yields benzoin (85% yield) containing insignificant amounts of ^{14}C. The triketone (I), however, also forms the cleavage products, unlabelled (V) (34%) and labelled (IV) (41%), alongside of a non-radioactive product (50%) whose composition suggests it could have arisen *via* benzoyl migration.

Our tracer results, therefore, appear to be at variance with expectation based on both the hypothetical acid[6]-and base[1]- catalyzed mechanisms of diaryl triketone rearrangement. We conclude now that the base-catalyzed reaction is predominantly a C–C cleavage resulting from repulsions developed when four hydroxylic functions (or their equivalent) are substituted on the bonded carbons. The acid-catalyzed reaction takes an

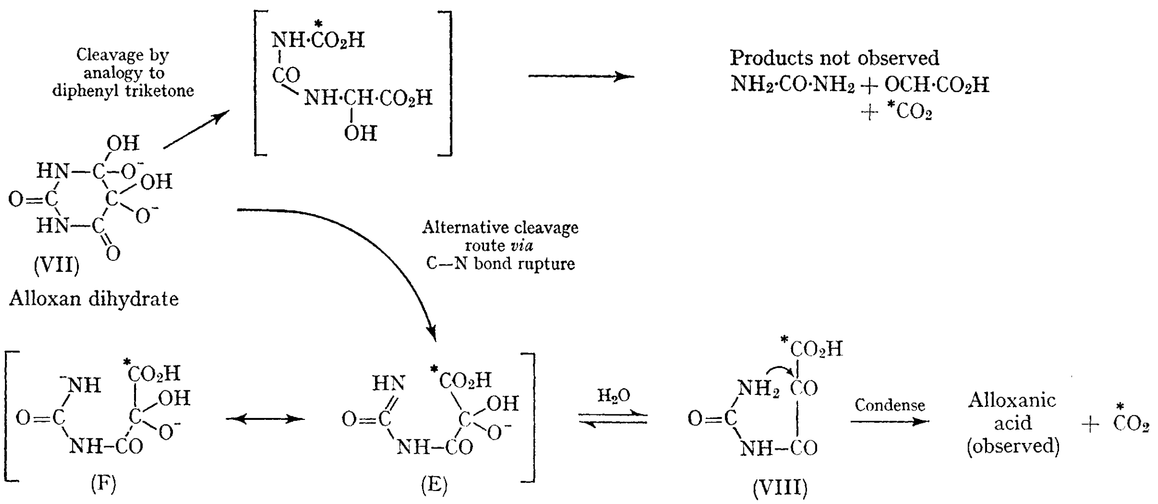

Chart 3

entirely different course than predicted,[6] and, depending on substitution in the aryl moieties, gives products consistent with the occurrence of either or both benzoyl migration and C–C cleavage.

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