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THE KINETICS OF INTRAMOLECULAR MEISENHEIMER COMPLEX CYCLIZATIONS TO BICYCLIC DINITROPROPENIDE ANIONS. A MECHANISM FOR THE REACTION

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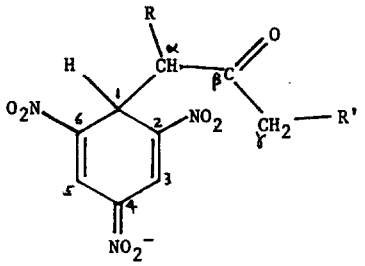
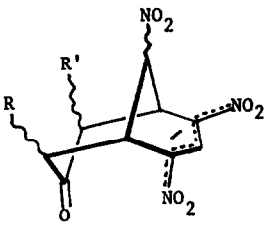
Numerous kinetic studies of Meisenheimer complex formation and decomposition have been reported (1-6) and the thermodynamic and kinetic parameters for such processes are now well known. There has been no report of the kinetics of conversion of Meisenheimer complexes like 1 to the bicyclic complexes 2, however, and the mechanism for such a reaction has been the subject of some speculation (7-11). Such intramolecular cyclizations quite commonly occur in many complexes like 1 in which the exocyclic moiety has potential carbanionic site γ to C-1, i.e., 1-a, 1-b, 1-c (7-12).



1-a (R = R' = H)

1-b (R and/or R' = electron withdrawing or donating groups)

1-c (R = R' = C_6H_5)



2-a (R = R' = H)

2-b (R and/or R' = electron withdrawing or donating groups)

2-c (R = R' = C_6H_5, cis)

The detailed mechanism depends on the nature of R and R', and on the base used to initiate the reaction. We report here a kinetic study and mechanism of cyclization for 1-c, which likely typifies Meisenheimer complex cyclizations when R and/or R' are electron withdrawing or delocalizing.

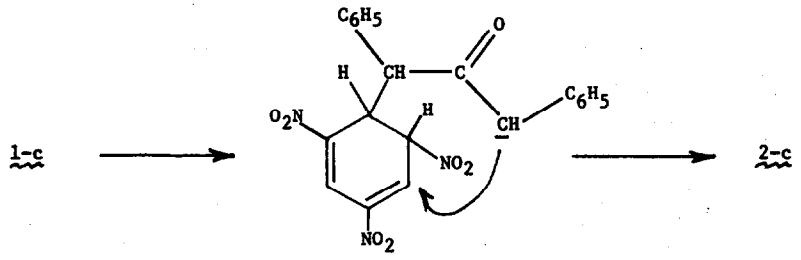
The overall formation of 1-c from sym-trinitrobenzene (TNB), dibenzyl ketone (DBK), and triethylamine (TEA), has been shown to occur in two stages in DMSO (7,8). Both pmr and visible spectra

Stage I
$$TEA + DBK \rightleftharpoons HTEA^{+} + DBK^{-}$$
$$DBK^{-} + TNB \longrightarrow \underset{\sim}{1\text{-}c}$$

Stage II
$$\underset{\sim}{1\text{-}c} \longrightarrow \underset{\sim}{2\text{-}c}$$

(7,8) clearly show initial formation of 1-c, followed rapidly by formation of 2-c with a concomitant decrease in the absorptions of the former. An isosbestic point is formed between the visible absorption maxima of 1-c and 2-c, and the overall rate of stage I and stage II are similar when the concentration of TNB is similar to that of TEA and DBK. In order to study stage II we used TEA and DBK concentrations some 100 to 1000 fold greater than that of TNB. Under these conditions, stage I was complete within a few seconds. This point was checked by extrapolating back to zero time to get the extinction coefficient of 1-c, and confirming that all the TNB was converted to complex. Stage II was followed by measuring the diminishing absorbance of 1-c at 575 nm, where the product 2-c has no absorption. The concentrations of DBK, TEA, and $HTEA^{+}$, as well as the ionic strength were varied, and the effect on rate was noted.

Prior to this study, we had proposed a "least contrived" mechanism, through 3, in which proton transfer was followed by an intramolecular attack.



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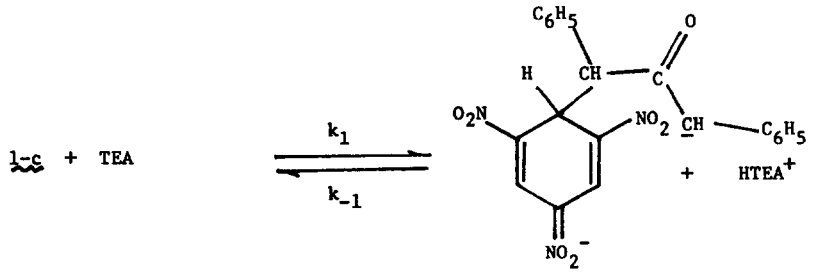
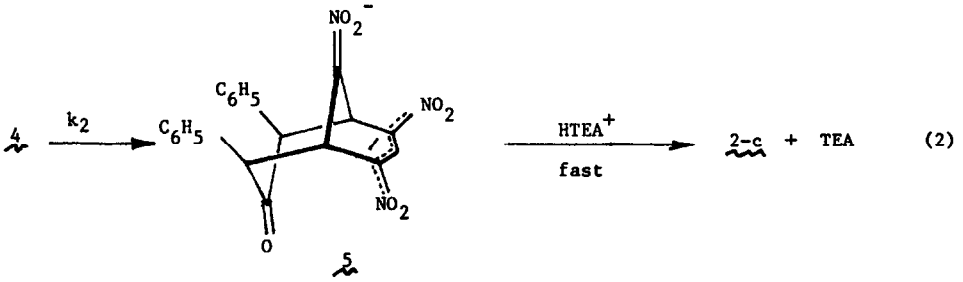
In fact, however, the present study has shown the rate of stage II as: (1) first order in triethylamine, (2) negative nonintegral order (between -1 and zero) in triethylammonium cation, (3) increased by increasing ionic strength, and (4) zero order in dibenzyl ketone. These observations are consistent with the following mechanism for stage II:



(1)



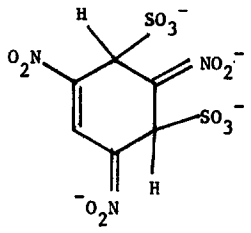
(2)

where,

$$-d[\underset{\sim}{1}\text{-c}]/dt = k_1k_2[TEA][\underset{\sim}{1}\text{-c}]/[k_{-1}[HTEA^+] + k_2]$$

The fact that no intermediate builds up during the reaction (evidenced by the pmr and visible spectra) provides evidence against a mechanism in which step (1) is a rapid pre-equilibrium with a large k_1/k_{-1} ratio, followed by a slow step (2). Even with a very small k_1/k_{-1} ratio, such a pre-equilibrium would not account for the nonintegral order of $HTEA^+$. (A log-log plot of k_{obs} vs $[HTEA^+]$ is nonlinear.)

The short-lived intermediates $\underset{\sim}{4}$ and $\underset{\sim}{5}$ are quite reasonable structures, and are supported by the stable and isolable $\underset{\sim}{7}$ and $\underset{\sim}{8}$ (12,13). In fact, there is good evidence that $\underset{\sim}{2}$-c can be converted to $\underset{\sim}{5}$ in strong base (14). In addition, although triethylamine is ineffective in converting $\underset{\sim}{1}$ to $\underset{\sim}{2}$ when R and R' are electron donating groups (8), very strong base will effect such a conversion, presumably through an intermediate like $\underset{\sim}{4}$ (12).



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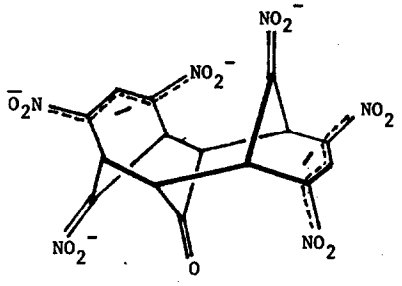

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