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TRAPPING OF REACTIVE INTERMEDIATES IN DIENONE PHOTOCHEMISTRY BY AMINES[1]

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Abstract: Irradiation of 4-methyl-4-trichloromethyl-2,5-cyclohexadienones in amine solvents leads to the formation of the corresponding dichloromethyl cyclohexadienones by a process involving electron transfer from the amines to zwitterion intermediates.

It is generally accepted that the photochemistry of cross-conjugated cyclohexadienones involves the intermediacy of short-lived zwitterions derived from the lowest triplet excited state.[2,3] This reactive ground state species, in certain cases, can be trapped by nucleophiles,[3,4] but more commonly undergoes a [1,4]-sigmatropic rearrangement to give bicyclo [3.1.0]hex-2-en-1-ones (lumiketones).[2,3]

As described in the preceding paper, the extent of conversion of 4-methyl-4-trichloromethyl-2,5-cyclohexadienones 1a-c to phenols 2 on irradiation in amine solvents depends on the ionization potential of the amine, suggesting electron transfer is occurring under these conditions to give dienone radical anions. No lumiketones were formed, but a new type of photoproduct not previously encountered in our extensive studies of these systems was isolated and identified, namely the corresponding dichloromethyl cyclohexadienones 3, in addition to hexachloroethane and the amine hydrochlorides. The following studies were carried out to elucidate the mechanism of conversion of 1 to 3.

Dilution of triethylamine with increasing quantities of methanol resulted in quenching of formation of photoproduct 3b on irradiation of 1b, but no quenching of formation of 2b was observed (see Fig. 1). A methanol adduct 4b was formed, analogous to products of trapping by nucleophiles of intermediate zwitterions found previously in our studies of 1a and 1b.[3-5] A plot (not shown) of the reciprocal of the quantum yield for formation of 4b vs. $[\mathrm{MeOH}]^{-1}$ was linear (r = 0.991), indicating that the kinetics of formation of 4b are linearly dependent on the methanol concentration. These data indicate that reaction intermediates leading to 2 are not intercepted by methanol, and that dienone 3b and methanol adduct 4b arise from a common precursor, most likely a zwitterion. Thus, it appears that the formation of dienones 3 is the direct consequence of trapping of intermediate zwitterions by triethylamine.

This hypothesis was tested by using the amine as a quencher of a process known to involve zwitterion intermediates, namely the photorearrangement of dienones 1 to lumiketones.[4] The relative quantum efficiency for formation of lumiketone 5b in benzene and in isopropyl alcohol was measured as a function of triethylamine concentration, and the results are shown in Fig. 2.

Figure 1

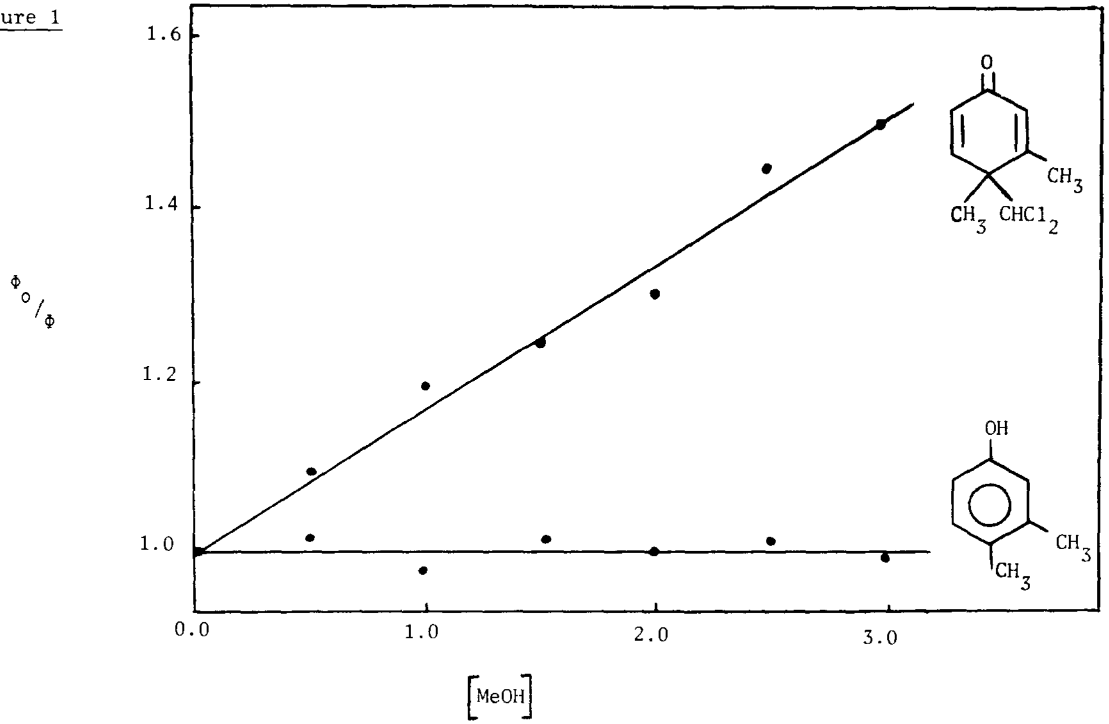
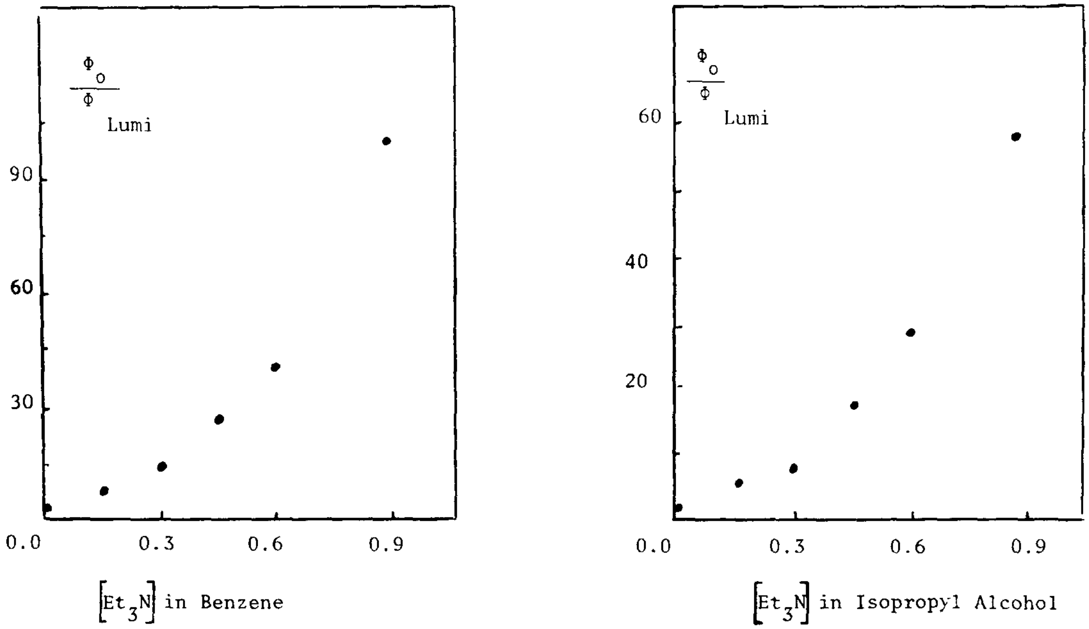
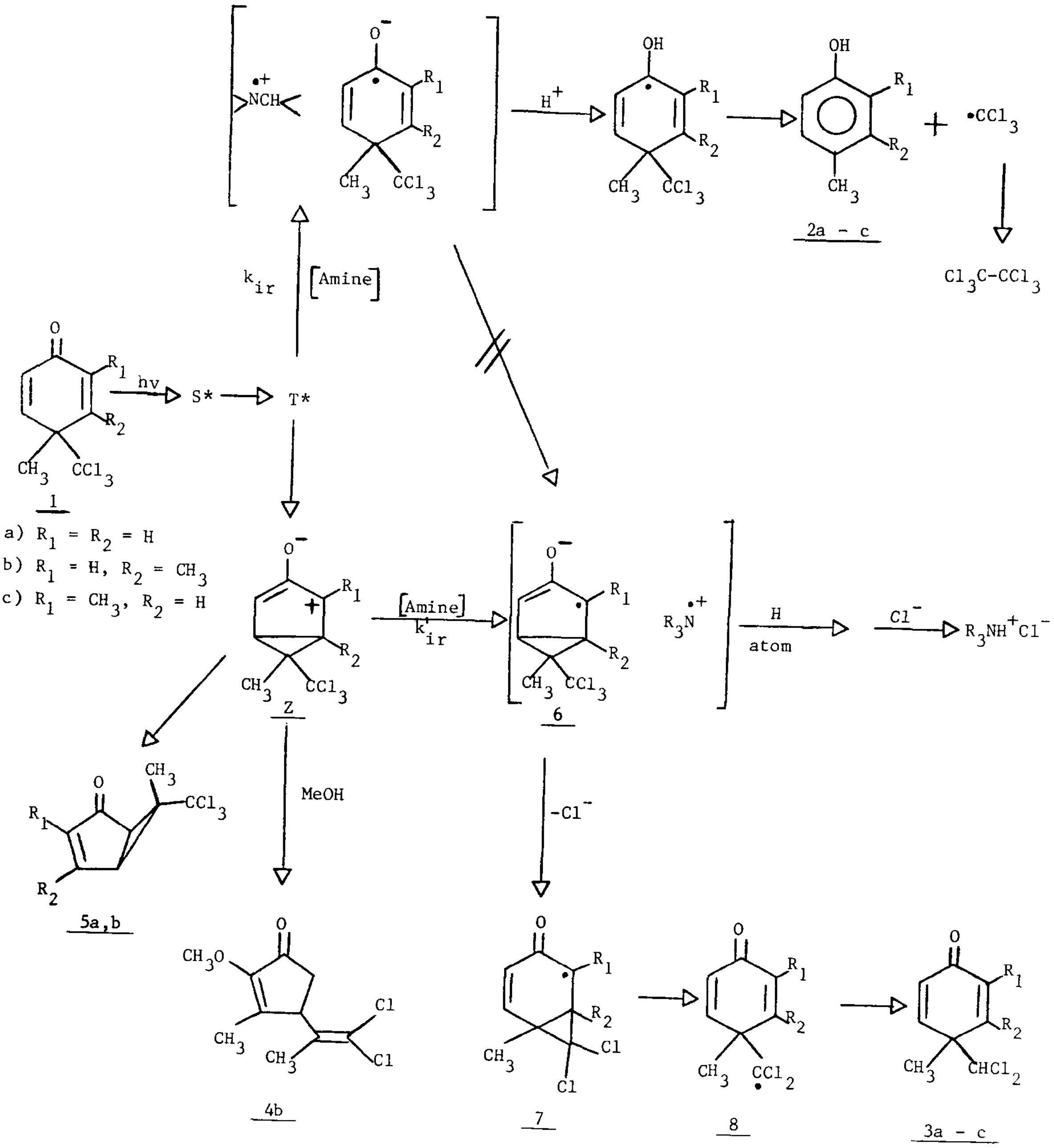


Figure 2



Scheme 1



a) $R_1 = R_2 = H$
b) $R_1 = H$, $R_2 = CH_3$
c) $R_1 = CH_3$, $R_2 = H$

Non-linear quenching with a quadratic dependence on amine concentration was seen in both solvents, concomitant with increasing yields of dienone 3b. This is consistent with the reaction mechanism outlined in Scheme I, in which the amine is proposed to intercept two reaction intermediates, the triplet excited state of the dienone as well as the ground state zwitterion 7.

The proposed route to dienone 3b involves electron transfer from the amine to the zwitterion to give a bridged radical anion 6, which then fragments by cleavage of the internal cyclopropane bond and expulsion of chloride ion, followed by ring opening of cyclopropylcarbinyl radical 7 to give the bishomoallyl radical 8,[6] which finally abstracts a hydrogen atom from the amine to give the final product 3. The conversion of 6 to 7 in a concerted manner would require an exo orientation of the CCl_3 group at C-6 of the bicyclo[3.1.0]-hexyl ring system of 6, which in fact is the preferred stereochemistry of the intermediate zwitterion as indicated by stereochemical[7] and trapping studies.[8] The amine hydrochloride is presumably formed from the amine radical cation by abstraction of a hydrogen atom followed by addition of chloride ion.

Thus, it appears that on ultraviolet irradiation of these dienones in amine solvents electron donation takes place from the amine to both electronically excited and ground state intermediates derived from the cyclohexadienones, affording unbridged and bridged radical anions, respectively, which proceed to different products. The linearity of the plot in Fig. 1 suggests that the dienone radical anion does not cyclize to the corresponding bridged species 6.

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