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CYCLOREVERSION OF CIS-1,2-DINAPHTHYLCYCLOBUTANE VIA EXCIPLEX WITH TRIETHYLAMINE. SOLVENT EFFECT ON THE MODE OF CYCLOREVERSION

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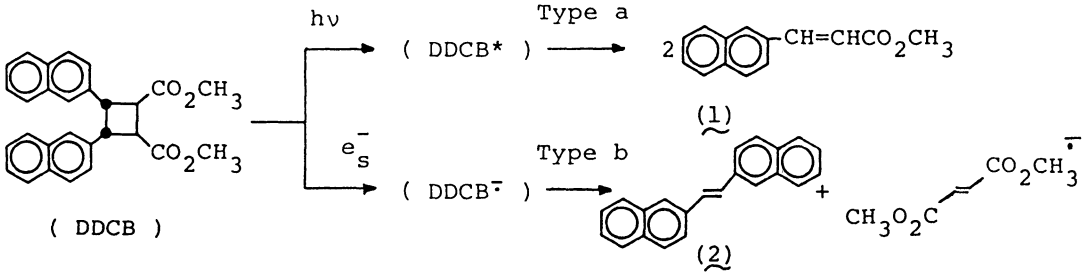
t-3, t-4-Di(2-naphthyl)-r-1,c-2-dimethoxycarbonylcyclobutane (DDCB), when irradiated in the presence of triethylamine, undergoes cycloreversion via the exciplex and/or the ion-pair. The mode of cycloreversion changes with the solvent polarity, reflecting the electronic structure of the intermediates.

We recently reported that one-electron reduction by solvated electrons induces cycloreversion of various arylcyclobutanes via the radical anions.$^{1)}$ As a unique example, t-3, t-4-di(2-naphthyl)-r-1,c-2-dimethoxycarbonylcyclobutane(DDCB) was observed to undergo extremely different mode of cycloreversion between the electronically excited state$^{2)}$ and the radical anion$^{3)}$ as shown in Scheme I.

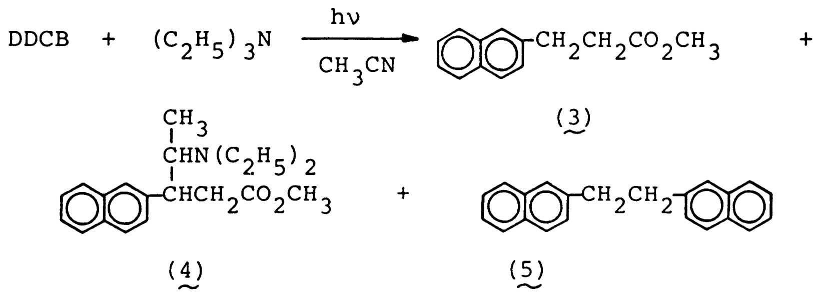
Scheme I



Upon direct photo-irradiation, DDCB results in the formation of cis and trans isomers of methyl 3-(2-naphthyl)propenoate(1), [type a], while the radical anion of DDCB formed by an attachment of solvated electrons gives trans-1,2-di(2-naphthyl)-ethylene(2), [type b]. These observations prompted us to apply the specific reactivity of DDCB as a probe for the charge-transfer character of an exciplex system.

We now report that an exciplex of DDCB with triethylamine(TEA) undergoes cycloreversion of DDCB in competition with the exciplex fluorescence and the mode of the cycloreversion(type a and b) changes with the solvent polarity, reflecting the electronic structure of the exciplex.

Irradiation of an acetonitrile solution of DDCB(0.01 M ; 1 M = 1 mol dm^{-3}) results in the formation of cis- and trans-1 with a quantum yield of 0.05(as DDCB reacted).[4)] The yield was decreased by the addition of oxygen($\phi(O_2)/\phi(N_2)$ = 0.39). Upon the addition of TEA(0.1 M) to an acetonitrile solution of DDCB(0.01 M), the reaction products changed to methyl 3-(2-naphthyl)propanoate(3), methyl 3-(2-naphthyl)-4-diethylaminopentanoate(4), and 1,2-di(2-naphthyl)ethane(5), along with a small amount of TEA dimer.



The structural assignments of these products were satisfactorily carried out on the basis of the spectral data. The formation of these products suggests that two types of cycloreversion of DDCB(type a and b in Scheme I) occur when irradiated in the presence of TEA, and the products initially formed, 1 and 2, undergo further reactions with TEA. Analogous reactions of aromatic olefins with TEA in acetonitrile have been extensively investigated by Cookson et al.,[5)] and Salisbury et al.,[6)] for styrenes, and by Lewis and Ho[7,8)] for stilbene.

The effect of TEA concentration on the quantum yields of these products is shown in Figure 1. The yield of 1 decreases with increasing TEA concentration up to 5×10^{-3} M and further addition of TEA leads to the formation of new products, 3, 4, and 5. The most reasonable explanation of the effect is a quenching of an excited DDCB by TEA, possibly leading to the formation of an exciplex and/or ion-pair. These active speices may induce the new product formation. Indeed, the flu-

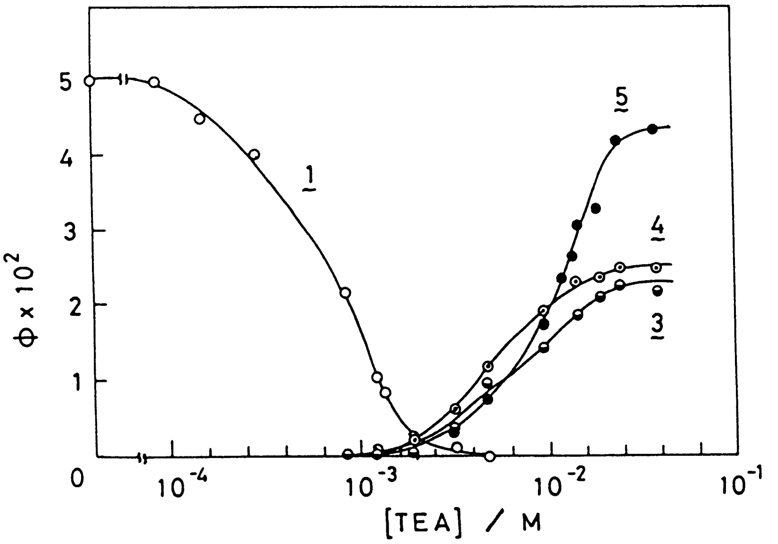


Figure 1. Quantum yields for the formation of products, 1, 3, 4, and 5 vs. [TEA]. DDCB : 0.01 M in acetonitrile : Quantum yields are based on the DDCB reacted.

orescence quenching of DDCB with TEA in acetonitrile was observed in this concentration region of TEA. Plot of I_f°/I_f vs. [TEA] is linear, providing the $K^{SV} = 55\ M^{-1}$. In cyclohexane, a slightly lower value of K^{SV}, $42\ M^{-1}$ was obtained along with a broad and structureless exciplex fluorescence with a maximum at 425 nm.

Of particular interest is the mode of cycloreversion of the exciplex and the ion-pair in connection with the electronic structure of these reactive intermediates. The effect of solvent polarity upon the quantum yields of type a and b products was investigated. The results are presented in Figure 2. The total quantum yield for the type a products indicates a minimum at ε=12 and then increases with increasing solvent polarity, while the type b products increase monotonously but sharply with solvent polarity. The most attractive interpretation of the striking feature of the reactivity is that the mode of the cycloreversion is controlled by the electronic structure of the intermediates. In nonpolar solvent, the selective type a cycloreversion takes place. In the present reaction conditions, 80% of an excited singlet of DDCB is quenched by TEA. Therefore, it is clear that the exciplex itself undergoes the type a cycloreversion in nonpolar solvent, probably owing to the contribution of the locally excited configuration. However, in highly nonpolar solvent($\varepsilon <$ 6), the yield of the type a cycloreversion decreases as shown in Figure 2 because an alternative decay channel of the exciplex, an exciplex emission, becomes predominant.

It has been pointed out that a charge-transfer quenching of fluorescence is associated with a production of triplet states of one of the component molecule by Ottolenghi.[9)] However, in the present case, the possibility that the cycloreversion occurs via a triplet state of DDCB which might be formed by the charge-transfer quenching is excluded because the cycloreversion was not reduced by the addition of oxygen.

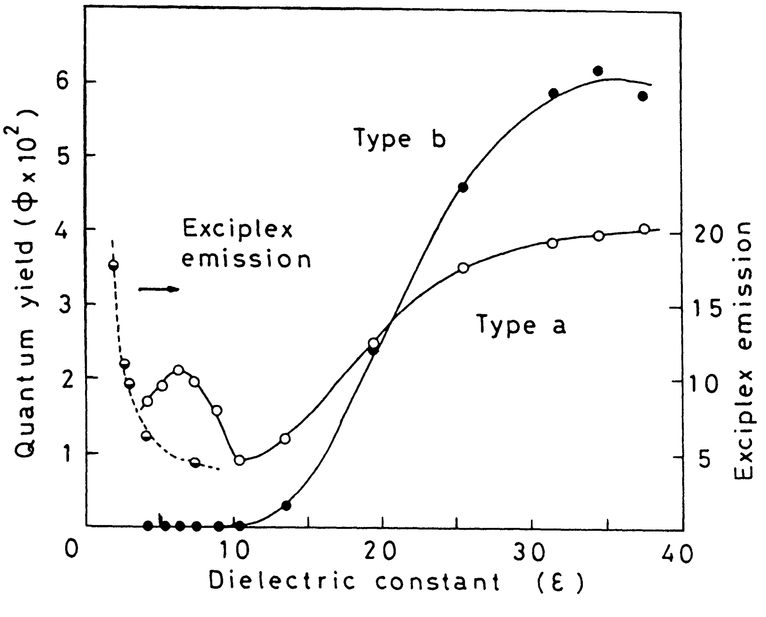


Figure 2. Quantum yields of the formation of type a products and type b products in the cycloreversion of DDCB in the presence of TEA vs. the solvent dielectric constant in cyclohexane-tetrahydrofuran and tetrahydrofuran-acetonitrile mixed solvents. DDCB: 0.01 M, TEA: 0.08 M.

In highly polar solvents, the type b cycloreversion becomes predominant. The fact seems to correspond to the increased charge-transfer character of the intermediates because the free radical anion of DDCB is shown to undergo preferentially the type b cycloreversion by an one-electron reduction with solvated electrons.3) The explanationisinaccord with the pronounced effect of solvent polarity on the extent of the charge transfer in a naphthalene-tertiary amine exciplex.10)

At present we cannot decide whether the type a cycloreversion in moderately to highly polar solvents proceeds via a nonrelaxed exciplex or via the ion-pair itself. In the latter case, the different reactivity of the ion-pair from that of the free radical anion cannot be reasonably explained. Anyhow, it is worthwhile to note that even in highly polar solvent, the cycloreversion reflecting the electronically excited state occurs in competition with the reaction reflecting the charge-transfer state.

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