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ENERGY LOCALIZATION AND PHOTOCHEMICAL REACTIVITY. THE PHOTOCHEMISTRY OF ETHYL 4-(1-NAPHTHYL)-4,4-DIMETHYLBUTENOATE.

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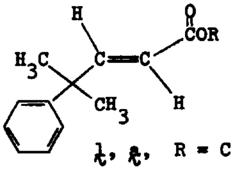
In our study of excited state migration reactions[1] we have turned to an examination of the influence of excitation energy localization on the course of reaction of bichromophoric systems. In a series of compounds $X-(CR_2)_n-Y$ in which X is an aromatic ring, Y is a substituted vinyl group, and $(CR_2)_n$ is a saturated carbon insulator, we are interested in learing how the photochemical reactivity is affected as the difference in excitation energy of chromophores X and Y (when isolated) is varied. Hammond et al.[2] recently reported the photochemistry of some polychromophoric esters of this type (**1a**-**c**). We wish to report some of our work on the photochemistry of the related naphthyl ester **5**. Our findings (eq 2), particularly when compared with the results found for the phenyl analog **1a** of **5** (eq 1),[2] add considerable dimension to the results and conclusions obtained by Hammond et al. and provide an interesting example of how one may alter photochemical reactivity by subtle changes in excitation energy localization.

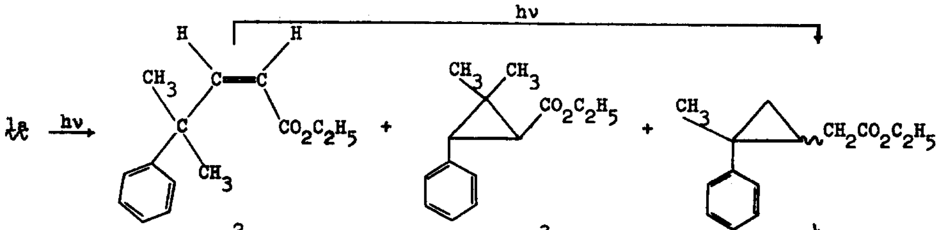


1, **a**, R = C_2H_5

b, R = $CH_2CH_2N(CH_3)_2$

c, R = $CH_2CH_2N(CH_3)Ph$

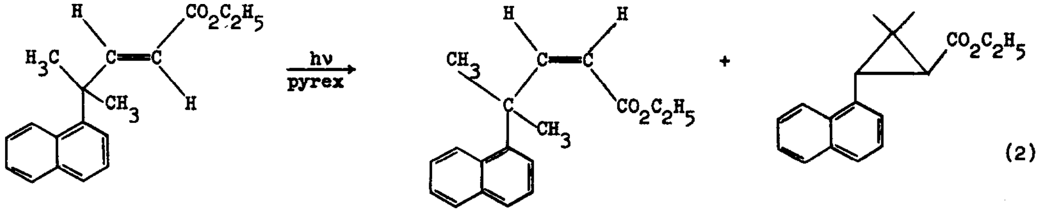
trans-Ester **5** was readily prepared by condensation of α-naphthyldimethylacetaldehyde[3] with the anion of diethyl carbethoxymethylphosphonate.[4] Direct irradiation of 0.470 g of **5** in 110 ml of cyclohexane solution with Pyrex-filtered light[5] resulted in the formation of two compounds, **6**



2 3 4

(1)

and 7, with approximately equal efficiencies. Continued irradiation led to a gradual increase in the relative amount of 7. After 312 min the photolysis was terminated and the products separated by silica gel chromatography



5 6 7

(2)

The nmr spectrum of 6 (0.063 g, 13%) indicated it to be the <u>cis</u>-isomer of 5: nmr ($CDCl_3$) δ 0.90 (t,3, $-CH_2C\underline{H}_3$), 1.60 (s,6,<u>gem</u>-CH_3), 3.60 (q,2,$-C\underline{H}_2CH_3$), 5.62 (d,1, vinyl H, J=16.0 Hz), 7.53 (d,1,vinyl H, J=16.0 Hz), 7.22-8.22 (m,7,arom). Product 7 (0.160 g, 34%) proved to be the <u>trans</u>-cyclopropane shown: nmr ($CDCl_3$) δ 0.19 (s,3,$-CH_3$), 1.30 (t,3,$-CH_2C\underline{H}_3$), 1.58 (s,3,$-CH_3$), 2.10 (d,1, cyclopropyl H, J=6.0 Hz), 3.05 (d,1,cyclopropyl H, J=6.0 Hz), 4.25 (q,2,$-C\underline{H}_2CH_3$), 7.10-8.50 (m,7,arom); ir (neat) 1720, 1190, 790, 760 cm^{-1}. In addition, 0.061 g (13%) of starting ester 5 was recovered. Only minute traces of other volatile products could be detected.

Most interestingly, triplet sensitization of 5 (0.475 g) with xanthone (0.347 g) in 110 ml benzene solution[6] led to very efficient formation of cyclopropane 7. Only small amounts of <u>cis</u>-ester 6 were formed. After 150 min of irradiation the amounts isolated were: recovered 5, 0.164 g (34%); <u>cis</u>-isomer 6, 0.012 g (2%); cyclopropane 7, 0.254 g (53%).

The formation of cyclopropane 7 upon direct irradiation of olefin 5 would appear to be a typical di-π-methane reaction of an acyclic di-π-methane system[7] similar to the 1a→3 transformation observed by Hammond <u>et al</u>.[2] What is striking and unusual, however, is the facility with which the triplet-sensitized photolysis of 5 also leads to 7. This reactivity of the triplet state of **5** is in marked contrast to that of the triplet state of phenyl analog **1a** which was observed to undergo solely cis-trans isomerization; only the singlet state of **1a** was transformed to **3**. In fact, these observations for **1a** are the ones typically found in acyclic di-π-methane systems where, in general, only the singlet states undergo migration, the triplets being deactivated by facile cis-trans isomerization - the "free rotor effect".[7,8] We add that at the moment it is not possible to say whether or not the singlet state of **5** also rearranges to **7** or whether the migration observed on direct irradiation of **5** occurs via prior intersystem crossing to the triplet state.

It has been pointed out before that in di-π-methane systems containing a potential free-rotor whether or not one observes a triplet state migration depends on the relative rates of migration and cis-trans isomerization, the latter usually but not always being the faster process.[7] In the present case we note that the observed difference in migration : cis-trans isomerization rate ratios between the triplets of **1a** and **5** is consistent with expectations based on considerations of initial excitation energy localization; and that the location of initial excitation energy is therefore apparently important in determining the extent to which the various possible triplet reaction pathways are taken. In **1a**, the triplet excitation energy is heavily weighted in the α,β-unsaturated ester group.[10] The process observed - cis,trans isomerization - is typical of acyclic α,β-unsaturated ester triplets.[12] In contrast, in **5** the triplet energy should be essentially localized in the naphthalene ring.[10] Correspondingly, we see here that reaction occurs to a large extent by naphthyl migration; rapid triplet deactivation by double bond rotation no longer eliminates triplet migratory reactivity.

Studies of molecules $X-(CR_2)_n-Y$, $n>1$, are in progress.

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(8) However, there are cases[9] where a potential "free rotor" does not eliminate triplet state di-π-methane reactivity.

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(10) The triplet energy of a simple α,β-unsaturated ester is almost certainly higher than that of most α,β-unsaturated ketones (66-74 kcal/mole)[11a] and of diethyl fumarate (61-67 kcal/mole)[11b] but lower than that of ethylene (≤ 82 kcal/mole)[11c]. Therefore, the unsaturated ester triplet is of higher energy than that of naphthalene (60.8 kcal/mole)[11d] and lower than that of benzene (84 kcal/mole)[11e].

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