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(10) Irradiation of **3** in the presence of methanol afforded a rather complex mixture of photoproducts. The photoreaction was found to be remarkably clean, however, when a small amount of sodium methoxide was added to the methanolic soluton. Control experiments showed that chromanone **3** was stable to these basic conditions in the dark.
(11) A control experiment clearly demonstrated that dihydrocoumarin **5** was stable to extended irradiation, both in benzene and acetonitrile.
(12) For ring opening reactions of cyclopropanols see C. H. Depuy, *Accounts Chem. Res.*, **1**, 33 (1968).
(13) Control experiments show that when trace amounts of sodium methoxide were added to a methanolic solution of **5** in the dark, diester **4** was formed in quantitative yield.
(14) To date, all attempts to detect cyclopropanone **10** by infrared spectroscopy at room temperature have failed. This may be due to the low concentration of this tautomer or to a ring opening reaction which occurs during our experimental manipulations.
(15) Cyclopropanones are known to lose carbon monoxide on exposure to ultraviolet light, see N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965).
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(19) 3-Acetoxy-4-carbomethoxychromene (**14**), mp 72–73°, was conveniently prepared by treating **3** with acetic anhydride; nmr τ 7.82 (s, 3 H), 6.22 (s, 3 H), 5.38 (s, 2 H), and 2.7–3.4 (m, 4 H).
(20) Complete spectroscopic details of all new compounds will be given in our full manuscript.

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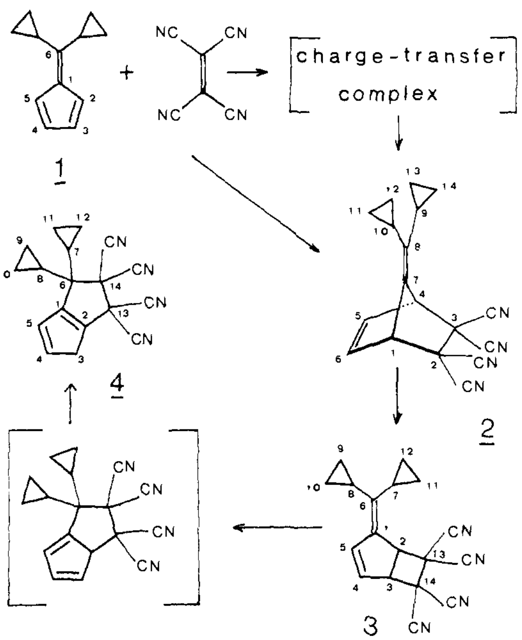
A Reactional Cascade. Addition of Tetracyanoethylene to Dicyclopropylfulvene[1]

Sir:

Fulvenes[2] confront the prospective 2π addend with a multifarious choice: [2 + 2] cycloaddition on the exocyclic 1,6 double bond or [2 + 2] with one of the endocyclic double bonds, [2 + 4] with the whole cyclopentadiene moiety or yet [2 + 6] encompassing atoms 2 and 6 at the termini of the (formally) π system.[3] With dicyclopropylfulvene[4] (**1**), the difficulty of predicting theoretically the outcome of an addition is compounded by the near-degeneracy of the a_2 (A) and b_1 (S) which are the two highest occupied molecular orbitals.[3] We have discovered that **1** adds to tetracyanoethylene with consecutive formation of [2 + 4], [2 + 2], and [2 + 6]cycloadducts (Scheme I). They interconvert through zwitterionic intermediates, the evidence for which will now be delineated.

Reaction of **1** (10 mmol) with TCNE (10 mmol) in ether solution, at 0°, gave the expected[2] [4 + 2] Diels–Alder cycloadduct[5] in nearly quantitative yield. As gauged by the cmr shifts,[5] the exocyclic double bond is electron-depleted *both* by the homoconjugative interaction with the endocyclic 5,6 double bond and by attachment of the cyclopropane rings at C-8; its polarization is weak compared to other 7-methylene norbornenes.[6] The activation energy for this first step is not high. This cycloaddition is either concerted, with the predominant interaction connecting the LUMO of TCNE with the a_2 MO of **1**, both antisymmetric, or proceeding *via* an intermediate; the experimental evidence currently available does not allow us to settle this point.

Scheme I



At slightly higher temperatures, **2** decays by clean first-order kinetics into the [2 + 2] adduct **3**.[7] The rate constant determined by nmr for the transformation of **2** into **3** displays pronounced solvent dependence (Figure 1), with an activation energy $\Delta G^*_{273} = 20.7$ kcal mol^{-1} in pure acetone. The extensive evidence by Huisgen, *et al.*,[9,10] has provided elegant proof for the intermediacy of a zwitterion in the [2 + 2] cycloadditions between TCNE and enol ethers. The analogous zwitterion formed by heterolytic cleavage of the 1,2 bond in **2** is strongly resonance stabilized. A plot of ln k_1 against the dielectric function $(\epsilon - 1)/(2\epsilon + 1)$[9] is linear (Figure 1; $\rho > 0.98$), and indicates an increase in the dipole moment by *ca.* 12 D in going from **2** to the more polar transition state. Observation of a strong dependence of the reaction rate upon the solvent polarity also serves to rule out a 1,3 sigmatropy for the **2** → **3** process.[11]

That is not the end of the story! The [2 + 2] cyclobutane derivative **3** has considerable strain, as implied, *e.g.*, by the

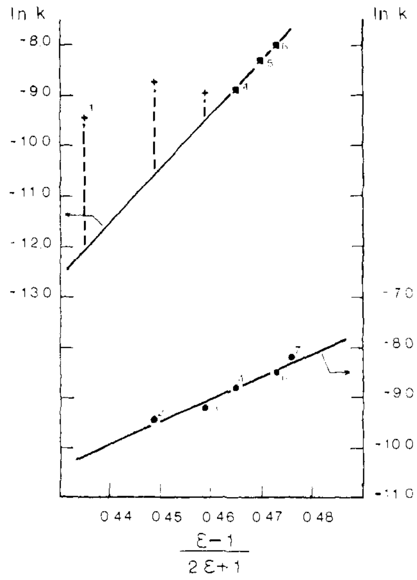


Figure 1. Plots of ln k_{obsd} for decomposition of **2** at 0° (bottom) and of **3** at 50° (top) against the dielectric function $(\epsilon - 1)/(2\epsilon + 1)$. Numbers refer to the solvent systems used (v/v): 1, diethyl ether 60:acetone 40; 2, diethyl ether 40:acetone 60; 3, diethyl ether 20:acetone 80; 4, acetone; 5, acetone 80:acetonitrile 20; 6, acetone 60:acetonitrile 40; 7, acetone 40:acetonitrile 60. The significantly greater slope for the top solid line implies a larger dipole moment for the second zwitterionic intermediate (see text). The dashed segments have lengths approximately proportional to the diethyl ether concentration.

enhanced values of the ^{13}C-H coupling constants at positions 2 and 3.[7] It opens up,[12] probably to re-form a similar zwitterion. The activation energy goes up to $\Delta G^*_{323} = 24.6$ kcal mol^{-1} (acetone) in line with the reduced strain in the [2 + 2] adduct, thermodynamically more stable than the [4 + 2] adduct. Again, an increase in the solvent polarity boosts the rate of decomposition of **3** to form irreversibly another $C_{18}H_{14}N_4$ isomer **4**.[13] Superimposed upon the effect of solvent polarity, the effect of solvent nucleophilicity[15] is now conspicuous (Figure 1). To our knowledge, such a nucleophilic solvent effect is unprecedented for these types of reaction. At the lower solvent polarities, a bimolecular pathway k_2 [ether] sets itself in competition against the unimolecular k_1 decomposition *via* the zwitterionic intermediate. Like its predecessor, this [2 + 2] → [2 + 6] step shuns orbital concert.[16] Indeed, rarely are fulvenes accessible to [2 + 6] concerted cycloadditions.[17]

The [2 + 6] adduct proper cannot be isolated. It rearranges smoothly (Scheme I) into the more stable isomeric cyclopentadiene **4**, a process for which now the most likely mechanism is 1,5-hydrogen sigmatropy.[18,19] The corresponding *ca.* 24.3 kcal mol^{-1} energy barrier[19] is easy to overcome without equilibration back to the [2 + 2] adduct; release of the cyclobutane strain in **3** ensures that the **3** → **4** conversion be highly exothermic.

In summary, one witnesses successive changes in the relative orientation of dicyclopropylfulvene and tetracyanoethylene. The TCNE residue moves from its initial position above the face of the fulvene, allowing for maximum overlap and thus producing the fastest rate, to its final resting position in the nodal plane of the fulvene, where strain has been reduced to a minimum. It is rather remarkable that **2** does not transform itself *directly* into **4** *via* a zwitterion stabilized at the negative pole by the cyano substituents and at the positive pole by the resonance inherent both to the pentadienyl cation and to the cyclopropylcarbinyl cation. The full electronic and nuclear reorganizations do not have enough time to be completed before the intermediate zwitterion collapses to the intermediate structure **3**. It is only then, after **3** opens to another, better delocalized, zwitterion that access is gained to the C-6 terminus. In other words, and to quote a referee, both **2** and **3** rearrange *via* formally the same intermediate, yet the mode of generation of the intermediate determines its fate!

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(5) Nmr, ^1H (acetone-d_6) δ 6.9 and 5.2, AA'XX'system, 4H, $\frac{1}{2}|J_{AX} + J_{A'X}|$ = 2 Hz, olefinic and bridgehead; 1.7–1.2, 1.0–0.5 (m), cyclopropyl, 8H; ^{13}C (toluene-d_8, ppm) 139.3 (C-5,C-6), 138.5 and 133.3 (C-7 and C-8), 113.3 and 112.8 (CN), 54.7 (C-1, C-4), 47.5 (C-2, C-3) 12.5 (C-9, C-10), 5.6 and 5.3 (C-11, C-12, C-13, and C-14).

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(7) Nmr, ^1H (acetone-d_6, $-22°$) δ 7.27 (H-5), 6.21 (H-4), 4.96 (H-2), 4.52 (H-3) 1.5–1.0 (H-7, H-8), 0.9–0.4 (H-9, H-10, H-11, H-12); coupling constants (INDOR, ±0.1 Hz), $J_{23} = +7.3$, $J_{34} = +2.9$, $J_{35} = -1.35$, and $J_{45} = +5.45$ Hz;[8] ^{13}C (acetone-d_6, $-20°$, ppm) 141.7 (C-6), 139.0 (C-5), 138.5 (C-1), 130.2 (C-4), 112.95, 110.7 and 109.7 (CN), 52.9 and 47.4 (C-2 and C-3), 41.6 and 40.8 (C-13 and C-14), 16.2 and 12.6 (C-7 and C-8), 7.8 and 5.9 × 3 (C-9, C-10, C-11, and C-12); $^1J_{CH}$ (±5 Hz), 165 (C-5), 172 (C-4),[8] 157 and 167 (C-2 and C-3).

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(11) If this were an orbitally concerted step, it would have to be of the 1a, 3s type.

(12) By breaking the 3–14 bond, rather than by opening the 2–13 bond, the latter heterolysis would lead to a less stable cross-conjugated zwitterion, whose only forward reaction—bridgehead olefin formation—is prohibited.

(13) Mp 130–133°; mass spec *m/e* 286 ($M\cdot^+$); (M + 1)/M = 22.45% and (M + 2)/M = 2.31% = in accord with a $C_{18}H_{14}N_4$ formula: nmr, ^1H ($CDCl_3$) δ 6.78 (H-4), 6.31 (H-5), 3.25 (H-3) 1.4–1.0 (H-7, H-8); 0.9–0.4 (H-9, H-10, H-11, H-12), coupling constants[8,14] (INDOR, ±0.1 Hz) $J_{45} = +5.45$, $J_{34} = +1.3$, $J_{35} = -1.5$ Hz; ^{13}C ($CDCl_3$, ppm) 156.8 (C-2), 143.2 (C-4), 134.5 (C-1), 127.4 (C-5), 110.4 and 110.6 (CN), 62.1 and 60.9 (C-13 and C-14), 46.6 (C-6), 36.6 (C-3), 16.2 (C-7, C-8), 3.7 and 3.3 (C-9, C-10, C-11, and C-12).

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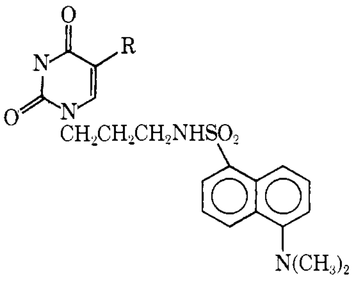
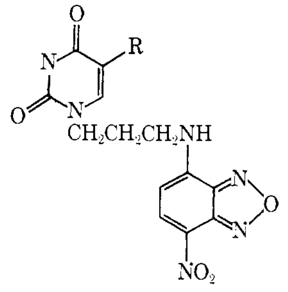
Energy Transfer in Fluorescent Derivatives of Uracil and Thymine

Sir:

We wish to report that light energy (270 nm) absorbed in the uracil or thymine part of the molecules, I–IV, is efficiently transferred to the fluorescent NBD (4-nitrobenzo[2.1.3]oxadiazole) or dansyl (5-dimethylaminonaphthalene-1-sulfonyl) part. The efficiency of transfer is 94% for III, 60% for IV, 38% for I, and 31% for II. The preparation of these compounds is described elsewhere;[1] their identities and purities are confirmed by tlc, pmr, and elementary analysis. Energy transfer was measured (Perkin-Elmer MPF-3 fluorescence spectrometer) by comparison of corrected excitation spectra with absorption spectra (Hitachi 124 spectrometer). Solutions were 3 × 10^{-6} *M* in 20% v/v ethanol-water; Pontachrome Blue Black-R was



I, R = CH_3 (APT-Dansyl)
II, R = H (APU-Dansyl)



III, R = CH_3 (APT-NBD)
IV, R = H (APU-NBD)