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Photochemistry of 1,1-dicyano-1-alkenes The olefin-to-cyclopropane rearrangement

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Abstract

1,1-Dicyano-1-alkenes (DCNA) that lack further unsaturation undergo formation of 1,1-dicyano-cyclopropanes via 1,2-migration of either hydrogen or methyl/alkyl from C-3 to C-2 in their lowest exited singlet state. Quantum yields for this "olefin-to-cyclopropane photorearrangement" (OCPR) were found to span a wide range ($\leq$0.1) and to depend characteristically on alkyl substituents on C-3 and C-2. OCPR occurs preferentially via such 1,2-migration that leaves behind the more alkylated C-3 atom. 1,2-Migration was found to occur suprafacially (i.e. to follow maximum orbital overlap), but to be rather tolerant towards unfavorable orientation of the migrant in the starting DCNA. The ring-closure that completed OCPR was found to be devoid of any intrinsic stereoselectivity; thus, in cyclohexane, each of the two epimeric 2-[(2-methyl-cyclohexyl)-methylene]-malononitriles (**3** and **4**) yielded the same approximately 1:1 mixture of the two epimeric 4-methyl-spiro[2.5]octane-1,1-dicarbonitriles (**28** and **29**). OCPR proceeded via an intermediate that also led to isomeric DCNA and to 1,1-dicyano-3-alkenes as minor by-products. Some deprotonation at C-3 of the photoexcited DCNA was noticeable in methanol, but not in hexane. Supplementary experiments included preparative and kinetic investigations of thermolyses of 1,1-dicyano-cyclopropanes. The combined evidence allowed the deduction of the following reaction path for OCPR. In their lowest excited singlet state, a $\pi\pi^*$ state, DCNA exhibit cationic reactivity of their C-2 atoms (presumably in the perpendicular conformation of C-2 relative to C-1, according to Salem's seminal concept). This reactivity triggers the 1,2 (Wagner–Meerwein type) migration to yield, still on the excited hypersurface, a 1,3 dipole. This 1,3-dipole achieves an almost complete conformational equilibration in cyclohexane (though less so in more polar solvents) before it decays to the electronic ground-state thereby becoming a 1,3-diradical. This 1,3-diradical undergoes three competing terminating reactions: ring closure to cyclopropane (the major path); 1,2-back migration of hydrogen to form starting or isomeric DCNA; 1,4-hydrogen shift to produce 1,1-dicyano-3-alkenes. The 1,3-dipole is too short-lived to undergo a potentially favorable Wagner–Meerwein rearrangement. Like the reactive excited DCNA singlet state, the 1,3-dipole is not trapped to any significant extent by nucleophilic addition of the solvents *tert*-butanol or methanol to its cationic center. The reason for this failure appears to be the excited-state nature of this species, which bars the formation of a ground-state adduct in an adiabatic reaction.

Keywords: Photoisomerisation; 1,2-Shift; Cyclopropane; Electron-deficient olefin; Excited singlet state

1. Introduction

1-Phenyl- [1–3], 1,1-diphenyl- [4], and 1-cyano-1-phenyl-1-alkenes [5,6] that are not conjugated to further double bonds are known to undergo the photorearrangement shown in Scheme 1 (R, R = Ar, H or Ar, Ar or Ar, CN; R^1, R^2, R^3, R^4 = H or alkyl) on direct excitation. This "olefin-to-cyclopropane photorearrangement" (OCPR) has also been observed with 4,4-dialkyl-cyclohex-2-enones [7,8] and with 1-cyano-cyclohexenes [9–11]; these latter two systems (R, R = carbonyl, H or alkyl, CN), however, are peculiar in that they require the incorporation of the reactive double bond in a cyclohexene ring for OCPR to occur. 1-Cyano-1-phenyl-1-alkenes undergo OCPR quite cleanly while in the other non-carbonyl cases alternative photoreactions via intermediate carbenes have been found to compete with OCPR [9–13]. Formally, the well-known di-π-methane [14] and oxa-di-π-methane [15,16] photorearrangements (Scheme 1, R^2 = substituted vinyl/aryl or carbonyl, respectively) are special cases of OCPR, but involving the active participation of an additional double bond, they must be mechanistically different [14].

The title compounds, 1-alkene-1,1-dicarbonitriles (1,1-dicyano-1-alkenes = DCNA), are readily accessible in high yields by Knoevenagel condensation of aldehydes or ketones with malononitrile. In course of an investigation of their photochemistry [17] we found that, with R^1, R^2, R^3, R^4 = alkyl or H (Scheme 1; R, R = CN, CN), many of these compounds underwent OCPR in good chemical

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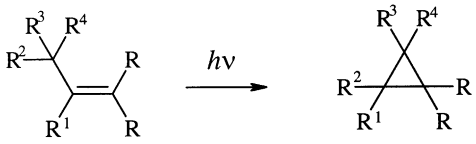


Scheme 1.

yields. In the following, we report a detailed investigation into the mechanism of this reaction, involving steady-state photolyses, end-product analyses, quantum yield determinations, and thermolyses.

2. Experimental

2.1. General

The preparation of the DCNA and of their irradiation products has been described in the accompanying paper; general experimental procedures are as reported there [17].

2.2. Analytic irradiations, quantum yields

The quantum yields for OCPR of **1**, **10**, and **23** at 254 nm were determined using an electronically integrating actinometer [18]. The quantum yield for OCPR of **1** was independently determined using conventional ferrioxalate actinometry. For all other DCNA, the quantum yields were determined relative to these three DCNA as follows: 45 ml of a solution of DCNA (0.05 M) and *n*-hexadecane (0.01 M; internal analytical standard) in cyclohexane or *tert*-butanol was distributed into three equal 15 ml quartz tubes of 15 mm diameter; these tubes were thoroughly bubbled with argon and closed with ground glass stoppers. This was done for three to four different DCNA at a time. The resulting 9–12 quartz tubes were placed together in the interior of a 120 W Rayonet reactor equipped with eight low-pressure mercury lamps; they were randomly distributed in the interior space. The concentrations and $\epsilon_{253.7\,nm}$ values for the DCNA [17] and the tube diameters result in total absorption of the incident 253.7 nm light by the DCNA substrates. After irradiation for (typically) 1, 2, 4, and 6 units of time, corresponding to partial conversion, samples were drawn from each tube and analyzed by quantitative capillary GLC using *n*-hexadecane as the internal standard. For each DCNA, this procedure was repeated with different combinations of other DCNA. For a given DCNA, photochemical conversions in the three quartz tubes were found to be the same within 10%, irrespective of where the tubes had been placed inside the Rayonet reactor. For the majority of DCNA, conversions were found to be proportional to irradiation time if kept below 40%. Some DCNA, particularly those showing prevailing 3,4-bond cleavage, however, strongly deviated from this proportionality and required extrapolation to zero conversion. From the analyses, the relative quantum yields among the different DCNA were obtained.

The relative rates for OCPR and for cyclohexane addition to the non-deuteriated and the three deuteriated forms of **5** (1-mono-, 2,2-di, and 1,2,2-tri-deuteriopropylidene malononitrile) were determined as above. The relative rates of the various H- and D-migrations during OCPR of one particular deuteriated form were determined on solutions of this form in dichloro-dideuterio-methane placed in quartz NMR tubes, using 400 MHz ^{1}H NMR spectroscopy with careful integration and signal multiplicity analysis. These determinations included the isotopic impurities (2-mono- and 1,2-dideuterio forms, respectively) present at 20% in the cases of the 2,2-di- and 1,2,2-tri-deuterio forms and yielded the values given in Scheme 5.

2.3. Preparative thermolyses

2.3.1. Thermolysis of *26*

12 mg (0.1 mmol) **26** were placed in one 2 l glass bulb which was evacuated to 0.02 mbar at room temperature, sealed by the flame, and placed in a drying oven kept at 310 °C for 3 h (see Scheme 4). After cooling, the contents of the bulb were taken up in 0.5 ml $CDCl_3$ and the ^{1}H NMR spectrum was obtained. It revealed the presence of **52** (71%), **1** (25%), and **26** (4%), and no other components, in agreement with capillary GLC analysis. Continuing the thermolysis for another 8 h led to the disappearance of **26**, but to no change in the proportions of the other substances—2-(2-methyl-allyl)-malononitrile (**52**). ^{1}H NMR ($CDCl_3$): δ = 1.79 (s, 3H), 2.67 (d, J = 8.0 Hz, 2H), 3.86 (t, $J = 2 \times 8.0$ Hz, 1H), 4.96 (bs, 1H), 5.07 (bs, 1H). For an independent synthesis of **52**, see the accompanying paper [17].

2.3.2. Thermolysis of *28*

Three 2 l glass bulbs were charged with 100 mg **28** each (total 1.85 mmol), evacuated to 0.02 mbar at room temperature, sealed by the flame, and kept in a drying oven kept at 260 °C for 24 h. After cooling, the bulbs were opened and rinsed with dichloromethane. From the resulting combined solution, the solvent was removed and the residue was chromatographed over 100 g silica gel with pentane to furnish, consecutively, 9.3 mg containing 10% **3** and 45% **4**, 5.3 mg pure **4**, followed by strongly overlapping fractions of, consecutively, 57.7 mg **28**, 84.3 mg **56**, and 60.9 mg **57**, and a final fraction of 75.6 mg pure **57** (liquid).—2-(2-methyl-cyclohex-1-enylmethyl)-malononitrile (**56**). ^{1}H NMR ($CDCl_3$): δ = 1.52–1.65 (m, 4H), 1.71 (s, 3H), 1.93–2.05 (m, 4H), 2.74 (d, J = 7.8 Hz, 2H), 3.74 (t, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ = 19.5 (CH_3), 21.3 (CH), 22.6, 22.8, 29.1, 31.8, 34.6 (each a CH_2), 112.8 (CN), 122.2 (C), 134.9 (C)—2-(6-methyl-cyclohex-1-enylmethyl)-malononitrile (**57**). ^{1}H NMR ($CDCl_3$): δ = 1.03 (d, J = 7.0 Hz, 3H), 1.30–1.80 (m, 4H), 2.04 (m, 2H), 2.14 (bq, $J = 3 \times 7.0$ Hz, 1H), 2.60

(dd, $J = 14.3$, 8.8 Hz, 1H), 2.73 (dd, $J = 14.3$, 6.3 Hz, 1H), 3.75 (dd, $J = 8.8$, 6.3 Hz, 1H), 5.70 (td, $J = 2 \times 3.3$, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 18.9$ (CH_2), 19.4 (CH_3), 22.2 (CH), 25.5 (CH_2), 30.8 (CH), 30.9 (CH_2), 36.1 (CH_2), 112.4 (CN), 112.8 (CN), 128.9 (CH), 134.3 (C).

2.4. Analytic thermolyses

Six 2 l glass bulbs were used. Three bulbs were charged with 5 mg each and the other three bulbs with 10 mg each of one particular cyclopropane. The bulbs were evacuated at room temperature to 0.02 mbar, sealed by the flame, and placed in a drying oven kept at 260 ± 1 °C for a defined reaction time. After cooling, each bulb was opened and its contents taken up in altogether 20 ml dichloromethane. The procedure was repeated for different reaction times. The dichloromethane solutions thus obtained were analysed by quantitative capillary GLC. With **41** and **42** as the substrates, reaction times were 24 h and 48 h. Conversions after 48 h were about 66% of **41** and 44% of **42**. With **26** as the substrate, reaction times were 2, 4, and 6 h. Conversions after 6 h were about 22% of **26**.

3. Results and discussion

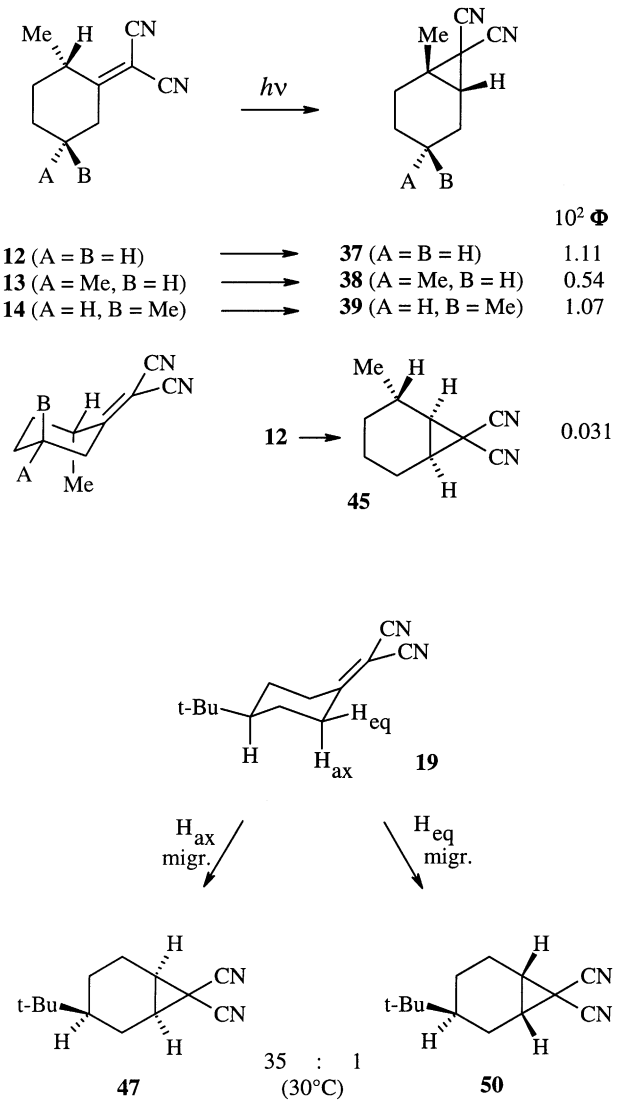
3.1. Quantum yields and regiochemistry of OCPR

Table 1 displays the quantum yields of OCPR of DCNA as obtained in cyclohexane. Quantum yields in dichloromethane, acetonitrile, methanol, or *tert*-butanol were found to be quite similar to those in cyclohexane. OCPR of a few DCNA have not been included in Table 1 since they belong to none of the structure types represented in Table 1; these missing DCNA will receive particular attention later in this paper. Table 1 shows that within any given OCPR structure type the OCPR quantum yields are quite comparable (the reasons for the exceptions **2**, **7**, and **8** are given in the accompanying paper [17], for **15** and **20** in the present paper), but they vary strongly among different structure types. The observed OCPR regioselectivities are implicitly contained in Table 1; as a basic rule, OCPR occurs preferentially via such 1,2-migration that leaves behind the more alkylated C-3 atom.

3.2. Stereochemistrty of OCPR

3.2.1. The 1,2-migration

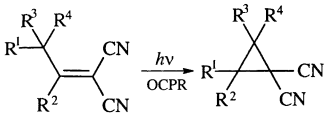
The DCNA, **12**–**14**, rearrange selectively to **37**–**39**, respectively (Scheme 2). Apart from reaction with solvent, only very minor isomeric by-products are formed, such as **45** which is formed as a by-product of **37**. However, no **39** is formed from **13**, and no **38** is formed from **14**. Thus, the hydrogen 1,2-migration is highly stereoselective. **12**–**14** have been shown to be present in the conformation shown in Scheme 2, viz. a cyclohexane chair with the 2-methyl



Scheme 2.

group being axial and the migrating 2-hydrogen atom being equatorial [20]. According to a MM3 force field calculation [21–23], the 2-hydrogen atom in this conformation is positioned almost coplanar with the olefinic plane, being located "above" that plane by a torsional angle of only −7°. MM3 calculations further show that the open-chain DCNA, **10**, too, which like **12**–**14** belongs to structure type 4 (Table 1), in its most stable conformation has its migrating hydrogen atom *syn* coplanar with the olefinic bond. Remarkably, the photorearrangements actually do occur out of these conformations in spite of their unfavorable orientation of the migrating hydrogen atom. This follows from the comparable magnitudes of the OCPR quantum yields for these four DCNA: had the photorearrangements occurred from less stable conformations featuring more favorable (e.g. axial) orientations of the migrating hydrogen atoms, strongly different (by up to two orders of magnitude) quantum yields would have been expected since the quantum yields would

Table 1
Quantum yield (cylohexane, 25 °C; error limits ±15%) for OCPR and for formation of cylohexane adducts. For structures of OCPR products and DCNA see Schemes 1 and 3 of the accompanying paper [17]



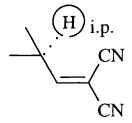
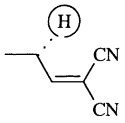
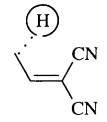
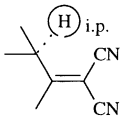
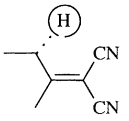
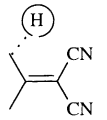
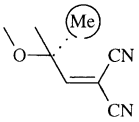
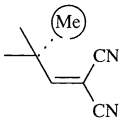
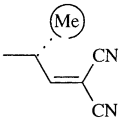
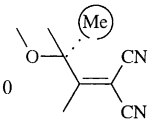
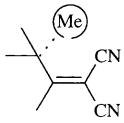
	OCPR: type of molecular structure[a]	DCNA	R^1	R^2	R^3	R^4	OCPR product	$10^2 \times \Phi_{OCPR}$	$10^2 \times \Phi_{Cyh}$
1		**1**	H	H	Me	Me	**26**	10.3	0.6
		2	H	H	Me	*t*Bu	**27**	4.6	0.04
		3	H	H	[b]		**28 + 29**	9.6	
		4	H	H	[b]		**28 + 29**	7.7	
2		**5**	H	H	H	Me	**30**	6.5	1.2
		6	H	H	H	*i*Pr	**31**	4.0	0.3
		7	H	H	H	*t*Bu	**32**	3.4	0.2
		8	H	H	H	Allyl	**33**	4.3	
3		**9**	H	H	H	H	**34**	0.35[c]	
4		**10**	H	Me	Me	Me	**35**	1.43	0.35
		11	H	Me	$(CH_2)_5$		**36**	1.38	0.2
		12	H	$(CH_2)_4$		Me	**37**	1.11	0.55[d]
		13	H	[e]		Me	**38**	0.54	0.5[d]
		14	H	[e]		Me	**39**	1.07	0.22[d]
		15	H	[f]		[e]	**40**	0.18	0.5[d]
5		**16**	H	Me	Me	H	**41 + 42**	0.035	0.35
		17	H	$(CH_2)_3$		H	**43**	0.044	0.5
		18	H	$(CH_2)_4$		H	**44**	0.033	0.65
		12	H	[e]		H	**45**[g]	0.031	0.55
		15	H	[f]		H	**46**[g]	0.046	0.5[d]
		19	H	[e]		H	**47**	0.07	0.65[d]
		20	H	[h]		H	**48**	0.0026	0.29
6		**21**	H	Me	H	H	**30**	$<10^{-3}$	
7		**22**	Me	H	Me	OMe	[i]	62.0[i]	
8		**23**	Me	H	Me	Me	**35**	4.3	0.16
9		**1**[g]	Me	H	Me	H	**41 + 42 + 16**	0.9	

Table 1 (*Continued*)

OCPR: type of molecular structure[a]	DCNA	R^1	R^2	R^3	R^4	OCPR product	$10^2 \times \Phi_{OCPR}$	$10^2 \times \Phi_{Cyh}$
10 	**24**	Me	$(CH_2)_2O$		Me	[i]	9.9[i]	
11 	**25**	Me	Me	Me	Me	**49**	0.58	0.12

[a] Migrating group are highlighted by circle; "i.p." designates migrating hydrogen atom that lies in the olefinic plane of the starting DCNA molecule, *syn* to one CN group. The other migrating group lie above the olefinic plane.
[b] See Scheme 3.
[c] In acetonitrile.
[d] Sum of two epimericcyclohexane adducts.
[e] See Scheme 2.
[f] See Scheme 9.
[g] Minor of two OCPR paths.
[h] See Scheme 10.
[i] Corrected quantum yields of decomposed OCPR products [19] in cyclohexane.

then reflect the strongly different relative energies of the requisite less stable conformations. Not surprisingly, such hydrogen migration out of the unfavorable orientation requires activation energy: as follows from the temperature dependence of the yield of **37** relative to that of **45** (36.6 at 30 °C and 26.6 at −48 °C), formation of **37** requires about 0.5 kcal/mol more of activation energy than formation of **45** which arises by migration of a favorably positioned axial hydrogen atom. The high stereoselectivity observed in cases **13** and **14** suggests that this activation energy is vibration which "flattens" the cyclohexane ring, thus, increasing the torsional angle from −7° to higher (negative) values.

The case of **19** (Scheme 2) affords an accurate quantitative comparison of the relative migratory aptitudes of axially and equatorially positioned hydrogen atoms. **19** is locked in the conformation displayed in Scheme 2 by the bulky *tert*-butyl group, as could be derived from the complete ^{1}H NMR coupling pattern. Its two OCPR products, **47** and **50**, arise from migrations of H_{ax} and H_{eq}, respectively. While H_{ax} migration requires no activation energy as follows from the observed approximate independence of the quantum yield of **47** from temperature, H_{eq} migration requires 1.54 ± 0.11 kcal/mol as follows from the observed ratios of the quantum yields of **47** and **50**, viz. 34.6 ± 4.0, 50.6 ± 8.8, and 87.3 ± 9.7 ($P = 0.95$) at 30, 0, and −45 °C, respectively.

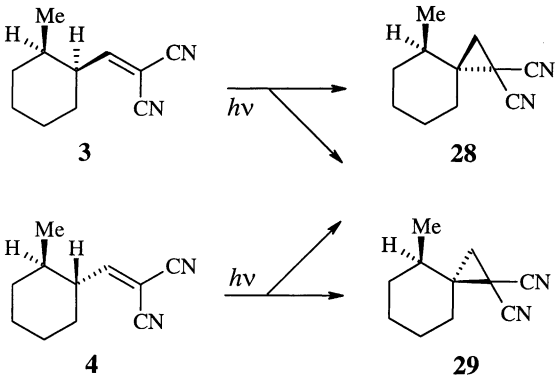
The DCNA of structure type 1 (Table 1), too, feature the same unfavorable orientation of the migrating hydrogen atom like the DCNA of structure type 4 discussed above, as follows both from their ^{1}H NMR data and from MM3 calculations. Nevertheless, their OCPR reactivities rank among the highest. It appears that the higher the OCPR reactivity, the less discrimination exists between favorable and unfavorable hydrogen orientations. This is suggested by a comparison of the quantum yields of **1** (both for hydrogen and methyl migration), **5**, and **23** (Table 1).

3.2.2. The ring closure

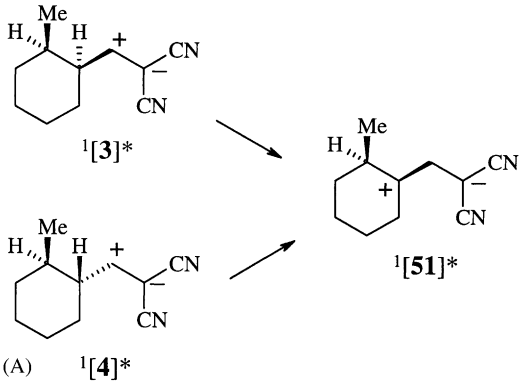
Ring closure in cases **13** and **14** occurs under inversion of configuration on the carbon atom from where the migrating hydrogen atom leaves (see formulae in Scheme 2). This may simply be due to the fact that, given the stereoselective H migration as it is, retention of configuration would lead to a severely strained *trans* fusion of cyclohexane and cyclopropane rings. The question remains as to the intrinsic preference, i.e. the preference in the absence of geometric constraints, for a particular steric course of the ring closure: preferred inversion, preferred retention, or no preference. Scheme 3 shows an epimeric pair, **3** and **4**, that is virtually devoid of geometric constraints imposed on ring closure. **3** and **4** each gives the same pair of products, viz. **28** and **29**. **28** is formed from **3** by ring closure under retention, and from **4** under inversion of configuration; the reverse holds for **29** (see formulae in Scheme 3). Since **28** and **29** are formed in almost equal amounts in either case, the experiment demonstrates the virtually complete absence of an intrinsic preference for retention or inversion on ring closure.

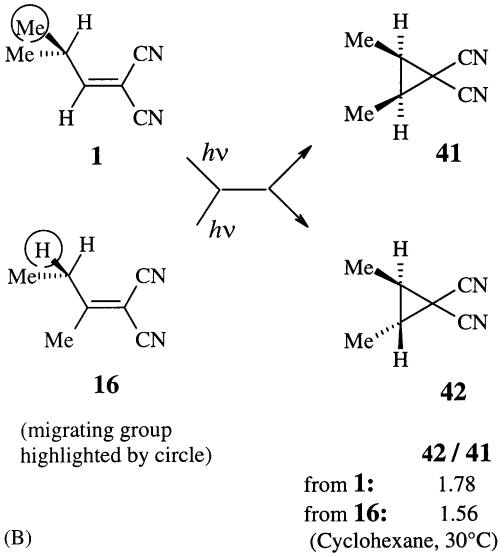
3.3. Mechanism of OCPR

28 and **29** are formed from **3** in almost the same ratio (at least in *n*-hexane) as from **4** (Scheme 3). This indicates that both reactions, that from **3** and that from **4**, share one common intermediate. The structure of this common intermediate is defined by the requirement that the migrating hydrogen must have left its original position since the intermediate obviously has no memory of the steric



		28 / 29
from **3** :	n-Hexane, 50°C	1.29 ± 0.02
	" 30°C	1.27 ± 0.03
	" -10°C	1.27 ± 0.04
	" -44°C	1.27 ± 0.01
	Methanol, 30°C	1.32 ± 0.05
from **4** :	n-Hexane, 50°C	1.16 ± 0.01
	" 30°C	1.18 ± 0.01
	" -10°C	1.19 ± 0.01
	Methanol, 30°C	0.84 ± 0.02





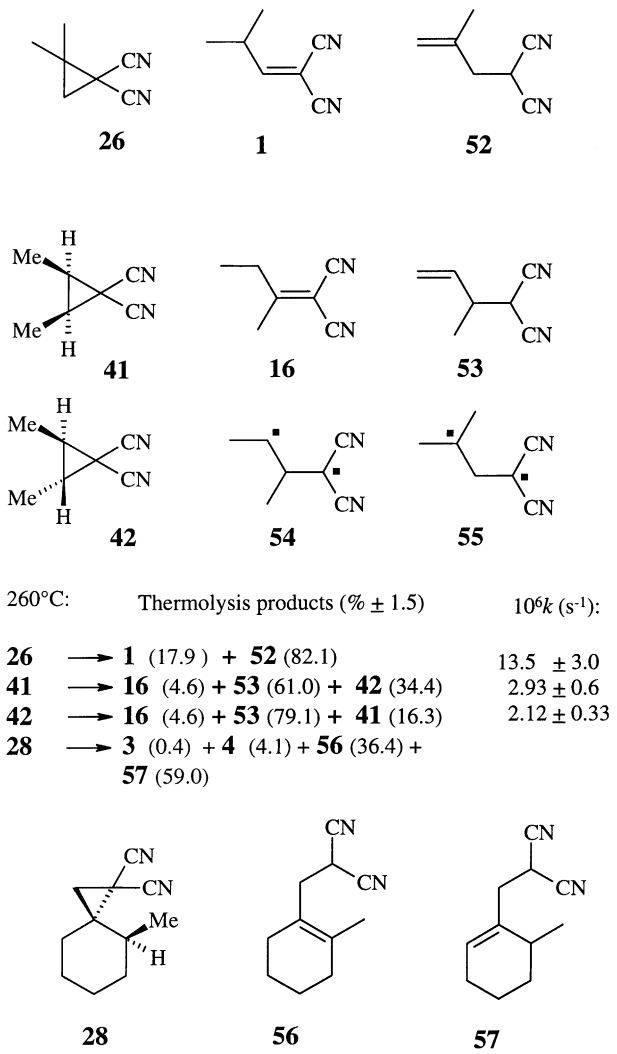
	42 / 41
from **1:**	1.78
from **16:**	1.56
(Cyclohexane, 30°C)	

Scheme 3.

configuration at this position. The only conceivable intermediates to comply with this requirement are the 1,3-diradical and the 1,3-dipoles of structure **51** (Scheme 3 anticipates a 1,3-dipole in the electronically excited-state of **51**, viz. ^{1}[**51**]*, vide infra). An intermediate with structure **51** (diradical or dipole) means that OCPR occurs in two consecutive, well separated, steps, the first one being 1,2-migration and the second one ring-closure to form the cyclopropane ring. The second pair of reactants shown in Scheme 3, viz. **1** and **16**, affords a further demonstration for this mechanism. The 1,2-migration is undergone not only by hydrogen (Table 1; structure types 1–6), but also by methyl (Table 1; structure types 7–11); methyl migration is slower than hydrogen migration by an approximate factor of only 7 [Table 1; structure types 2 (**5**) and 9 (**1**)] and requires only 0.86 ± 0.17 kcal/mol more in activation energy than hydrogen migration (which needs 0 ± 0.2 kcal/mol) as follows from the temperature dependence of the product ratios. An isolated 1,2-migration that is undergone by methyl almost as readily as by hydrogen is well known in electronic ground-state chemistry to occur in cationic systems only [24], where it is termed Wagner–Meerwein rearrangement. In free radical systems, methyl migration is very much less efficient than hydrogen migration, requiring >3.1 kcal/mol more in activation energy [25], and so far has never been observed. We conclude that the first step of OCPR is a Wagner–Meerwein rearrangement leading from an excited singlet state DCNA molecule [17], the electronic configuration of which must therefore be well described by the dipolar formula shown in Scheme 3, to the 1,3-dipole **51** possessing the charge distribution shown in

Scheme 3. Since this Wagner–Meerwein rearrangement occurs on the first excited singlet hypersurface, the conclusion implies that the 1,3-dipolar form of **51** shown in Scheme 3 describes the first excited singlet state of **51**. This in turn implies that, according to the quantum theory of diradicals [26–28], the electronic ground-state of **51** must be the 1,3-diradical.

The last conclusion was tested experimentally as follows. Scheme 4 shows the results of thermolysis (260 °C, gas phase, 1.5–4 hPa) of the cyclopropanes **26**, **41**, **42**, and **28**. From the structures of the observed thermolysis products, one can infer that the thermolysis occurs via the 1,3-diradicals **54** and **55** for cases **41**/**42** and **26**, respectively, or via the corresponding 1,3-dipoles. For the following discussion, we note that in thermal stereomutations of cyclopropanes (as is the mutual conversion of **41** and **42**, Scheme 4) the intermediate 1,3-diradicals/dipoles are either transition states or very shallow energy minima protected by barriers of ≤2.1 kcal/mol [29,30]. The observed order of magnitude for the unimolecular thermolysis constants (Scheme 4) is consistent with 1,3-diradicals as the intermediates, as can be estimated from the rate constants for thermolysis of cyclopropane [31] and the stabilization of radicals by cyano-substituents (5.3 kcal/mol per cyano group [32]). A definite conclusion results from a comparison of the thermolysis rate constant for **26** with those for **41** and **42**. The corresponding intermediate structures, viz. **55** and **54**, differ in that the non-cyano-substituted radical or cationic carbon atom is tertiary in the case of **55** and secondary in the case of **54**. If dipoles, the energy of **55** would therefore be lower than that of **54** by 16.0 kcal/mol [33], if diradicals, the corresponding value would be 3.5 ± 0.6 kcal/mol [34]. The ratio of the rate constants for **26** and **42** indicates that thermolysis of **26** needs 2.0 ± 0.3 kcal/mol less in free energy of activation than thermolysis of **42**, in fair agreement with the mechanism via 1,3-diradicals, but not with the mechanism via 1,3-dipoles. Thus, the above conclusion as to the mechanism of OCPR is confirmed.



Scheme 4.

The mechanism for OCPR as outlined above is consistent with the observed stereoselectivity of the 1,2-migration (in the course of Wagner–Meerwein rearrangements, the three involved bond-forming atomic orbitals are known to combine to a transient three-center bond, leading to a clean suprafacial migration as is observed here). Moreover, the cationic 1,2-migration is reflected in the relative reactivities of the structure types in Table 1: the stability of alkyl carbonium ions in general is known to increase in the sequence, primary, secondary, tertiary, alkoxy-substituted. The more stabilized, according to this sequence, the carbocation generated by the 1,2-migration, the higher the observed OCPR quantum yield according to Table 1. The more stabilized the carbocation saturated by the 1,2-migration, the lower the observed OCPR quantum yield according to Table 1. In this context, structure type 5 deserves attention: in structure type 5, the 1,2-migration transforms a tertiary carbonium ion into a secondary one, which would suggest this migration to be uphill by 16 kcal/mol [33]. However, as indicated above in the case of **19**, OCPR in these systems needs virtually no activation energy (provided, the migrating hydrogen is favorably oriented). This means that the energy of the excited DCNA molecule undergoing the 1,2-migration must actually be higher by >16 kcal/mol than suggested, on the basis of naive group additivity, by the dipolar formulae shown in Scheme 3.

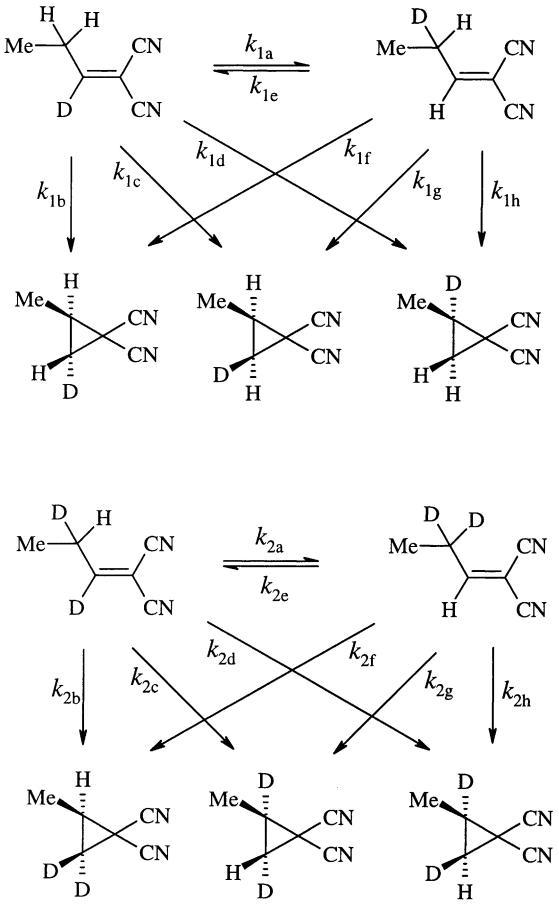
A remarkable implication of the preceding conclusions is that, if OCPR is run in methanol, the dipolar excited DCNA molecule is obviously not trapped by the solvent methanol to give the Michael adduct of one molecule of methanol to one molecule of DCNA; rather, the quantum yield of OCPR in methanol is similar to that in cyclohexane. One cause for this failure may be the short lifetime of the excited DCNA molecule [17]. Another one may be that such addition, leading to a ground-state Michael adduct, would be a non-adiabatic reaction: the first step, viz. the addition

of methanol to C-2 of DCNA, would correlate with the electronically excited-state of the monosubstituted malononitrile anion and hence, would require considerable activation energy.

The question remains as to the geometry of the reactive excited DCNA chromophore; planar like in the electronic ground-state ("spectroscopic" excited species), or perpendicular about C-1 and C-2, or somewhere between. As pointed out by Salem on grounds of quantum mechanical calculations [35], the perpendicular geometry (twist angle 90°) of an olefin in its lowest excited singlet state, which generally is also its energetically most stable geometry, will be fully polarized into a carbanion/carbonium ion pair in the presence of even modest asymmetry, let alone the strong asymmetry caused by the two polar cyano groups. With zero or modest twist angles, by contrast, there will be no polarization. We, conclude that OCPR occurs from the perpendicular geometry.

Above, we have used the fact that in cyclohexane **28** and **29** were formed from **3** in almost the same ratio as from **4** to conclude that they were formed via the same intermediate, viz. ^{1}[**51**]*. The ratios, to be sure, were only approximately the same; there remained a slight bias in favor of retention of configuration (Scheme 3). In the second pair of DCNA displayed in Scheme 3, viz. **1** and **16**, too, the ratios in cyclohexane were only approximately the same; in this case, the slight bias was in favor of inversion of configuration. We conclude that the 1,3-dipolar intermediates like ^{1}[**51**]* are not sufficiently long-lived to allow a perfect equilibration of conformation. In more polar solvents, we observe a significantly stronger bias in favor of retention: thus, in methanol, the two ratios **28**/**29** diverge much more strongly than they do in cyclohexane (Scheme 3). Another example is afforded by the OCPR results obtained in dichloromethane with differently deuteriated forms of **5** and displayed in Scheme 5; in the present context, the ratios **4**–**6** are of interest. Except for secondary H/D isotope effects on ring closure, these ratios should be unity in case of complete conformational equilibration. Taking the geometric mean of ratios **5** and **6** should eliminate the secondary H/D isotope effect; however, this geometric mean (1.35 ± 0.17) still is significantly higher than unity. According to MM3 calculations [21–23], the preferred conformation of **5** is the one pictured in Scheme 5 and featuring an *anti* co-linear arrangement of methyl and C-1 to C-3. On the basis of this conformation, all three ratios, **4**–**6**, show a definite bias in favor of retention of configuration. We speculate that in solvents more polar than cyclohexane, one molecule of solvent coordinates to the developing C-3 carbocation in an SN_2 type arrangement with respect to the leaving hydrogen or methyl group, thus, blocking this face of the carbocation during the lifetimes of the 1,3-dipole and 1,3-diradical (vide infra) intermediates.

Another finding that highlights the short lifetimes of the 1,3-dipolar intermediates is shown in Scheme 6. The DCNA **7** constitutes a special case in that it forms products **9** and **58** besides the OCPR product **32** and addition of



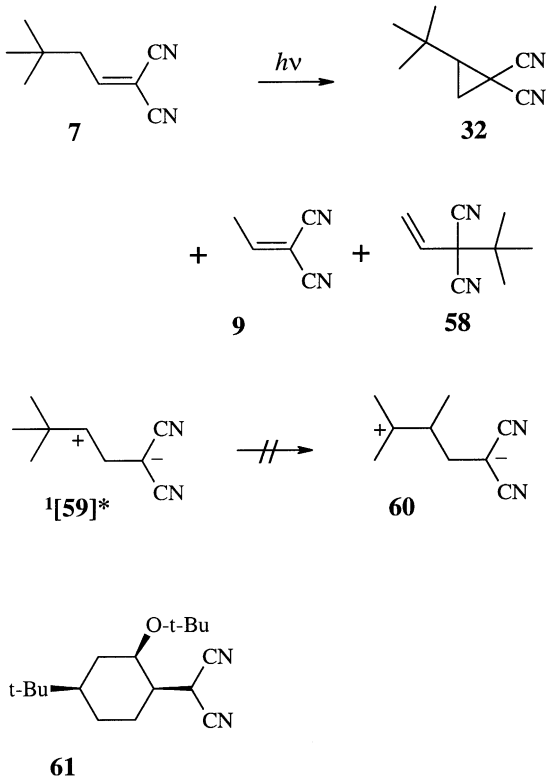
Relative yields in CD_2Cl_2:

1) $k_{1a}/(k_{1b}+k_{1c})$: 0.35 ± 0.03 [a]
2) $k_{2a}/(k_{2c}+k_{2d})$: 0.38 ± 0.03 [a]
3) $k_{2e}/(k_{2g}+k_{2h})$: 0.50 ± 0.01 [a]
4) k_{1g}/k_{1f}: 1.44 ± 0.25
5) k_{2h}/k_{2g}: 1.63 ± 0.13
6) k_{2c}/k_{2d}: 1.11 ± 0.06
7) k_{1d}/k_{1a}: <0.01 [a]

[a] extrapolated to zero conversion

Scheme 5.

solvent (Scheme 6); this matter is discussed in the accompanying paper [17]. For the present context, we note that the only isolated product stemming from the 1,3-dipolar intermediate ^{1}[**59**]* is **32** which is the normal OCPR product. Thus, ^{1}[**59**]* is too short-lived to completely undergo the expected Wagner–Meerwein rearrangement to the energetically more stable (by 16 kcal/mol [33]) **60** even though the free energy of activation for this rearrangement is expected to be below 3.5 kcal/mol [24]; some rearranged product may possibly be contained in mixed fractions that were obtained by preparative GLC, but were not elucidated.



Scheme 6.

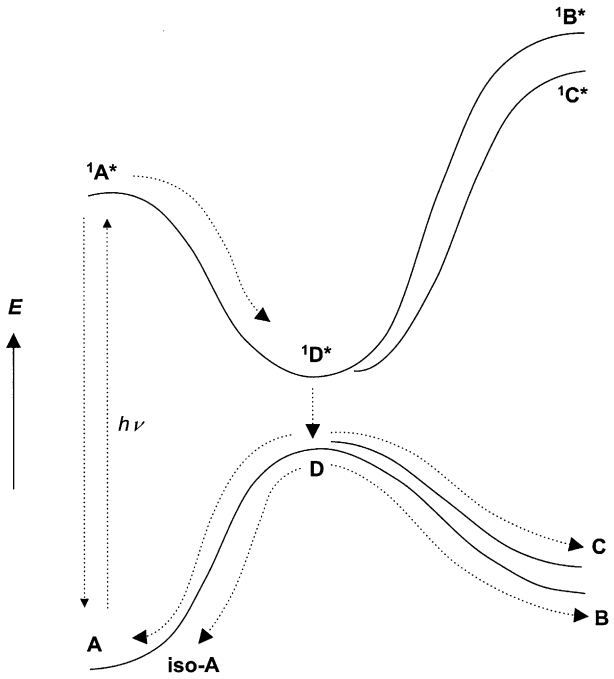
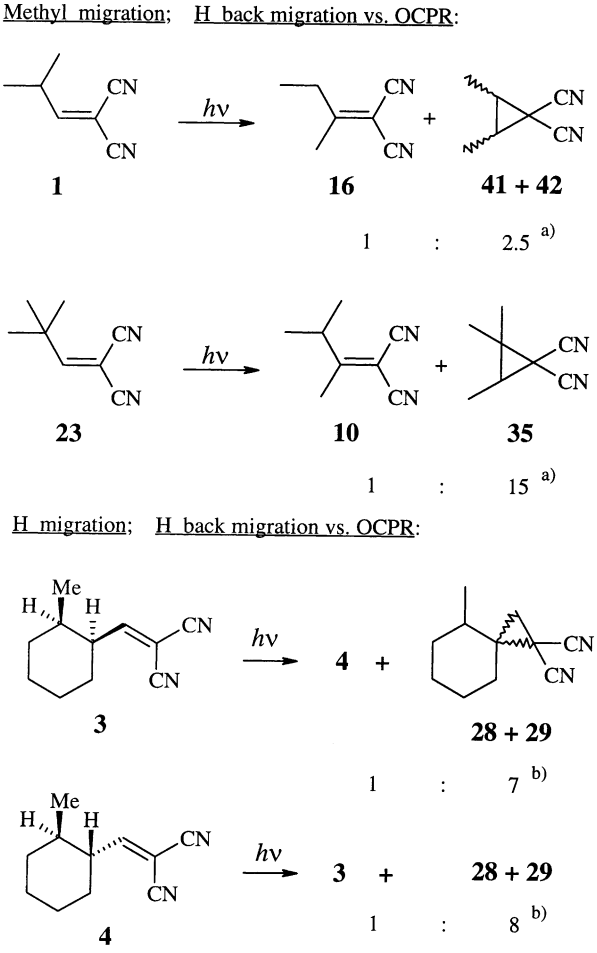


Fig. 1.

Another point is that OCPR can be conducted in methanol or *tert*-butanol which obviously means that the 1,3-dipolar intermediates like ^{1}[**51**]* and ^{1}[**59**]* are not efficiently trapped by these solvents. Again, as with the dipolar excited-state of DCNA (vide supra), one cause for this failure may be associated with ^{1}[**51**]* being an electronically excited-state which renders an adiabatic reaction of ^{1}[**51**]* to the ground-state adduct with ROH impossible. In the case of the irradiation of **19** (Scheme 2) in *tert*-butanol, where we carried out a more careful product analysis, we found 0.3% of **61** (Scheme 6) which is the expected trapping product of the 1,3-dipole en route to **47** by solvent. The observed relative configuration of **61** rules out the possibility that **61** may have arisen by solvolysis of **47**.

Does the second step of OCPR, viz. the ring closure, also proceed on the excited singlet hypersurface like the first one? This is obviously impossible as follows from the UV spectra of the 1,1-dicyano-cyclopropanes (**B**, Scheme 11 and Fig. 1) which exhibit absorption only at much shorter wavelenghts than the DCNA (**A**, Scheme 11 and Fig. 1). In combination with the lower energy of the electronic ground-states of **A** relative to those of **B** (as follows from the thermolysis experiments, vide supra, which can be carried to quantitative conversions of **B** to **A** and other products), the UV evidence indicates that on the lowest excited singlet hypersurface **B** must be much higher energetically than **A** and hence is inaccessible from **A** on this hypersurface. The same holds for the 1,4-hydrogen-shifted photoisomers **52**, **53**, **56**, and **57** (**C**). We conclude that the 1,3-dipole of type ^{1}[**51**]* (^{1}[**D**]*) undergoes internal conversion from the first excited singlet hypersurface to the electronic ground-state hypersurface, to become the 1,3-diradical (**D**). On this hypersurface, **D** decays to cyclopropanes **B** and to **C**, as already documented in Scheme 4 (since **D** on this hypersurface is a family of shallow energy minima and transition states rather than one single deep energy minimum (vide supra) there is no surprise if product ratios obtained in thermolysis differ from those obtained via internal conversion from the excited hypersurface). We conclude that the two steps of OCPR occur on different hypersurfaces.

Besides 1,4-hydrogen shift, there is another side-reaction of OCPR, viz. formation of isomeric DCNA, as exemplified by the formation of **16** from **1** [17] (Scheme 7). These isomeric DCNA appear to form from the same 1,3-dipole and 1,3-diradical intermediates like the cyclopropanes, e.g. **16** originates from the same intermediate (generated from **1** by methyl migration) like **41** and **42**, by a "back" 1,2-migration of hydrogen. The ratio (**41** + **42**)/**16** depended only slightly on temperature, but more strongly on solvent: 2.5 (cyclohexane), 1.6 (dichloromethane, *tert*-butanol), 1.2 (methanol) (extrapolated to zero conversion, 30 °C). Scheme 7 collects the back migration reactions that we detected in the present work, and gives their amount relative to the OCPR ring closure reactions that compete with them. Of course, there will be many back reactions that we did not detect since they led back to starting material. As documented by Scheme 4, the back migrations can occur from the 1,3-diradical on the ground-state hypersurface, in competition to ring-closure and 1,4-hydrogen shift. Still, we



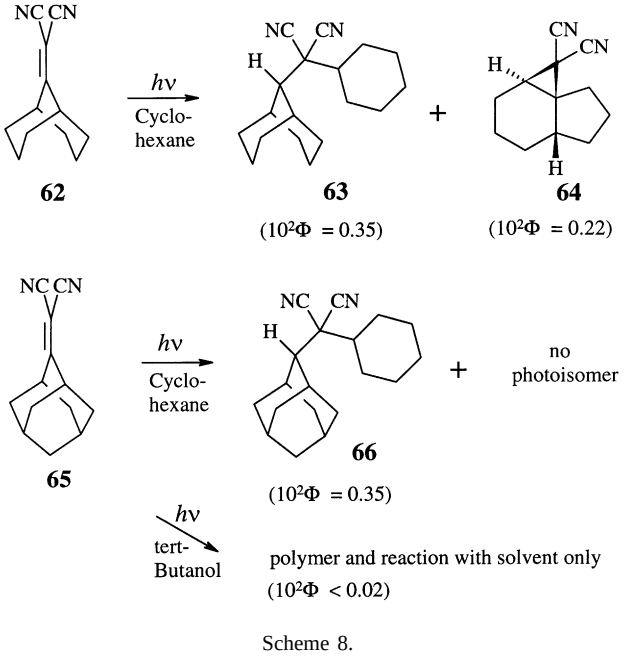
Scheme 7.

have to exclude the possibility of a back migration on the excited hypersurface. This possibility is excluded by ratio 7 in Scheme 5 which, in combination with the quantum yield for **5** → **30** given in Table 1, shows that k_{1a} does not lead to the excited-state of 3-deuterio-**5**. Independently, the possibility is excluded by primary H/D isotope effects. Very low (<2) primary H/D isotope effects for isolated hydrogen shifts are observed only when these shifts are highly exothermic [36–38]. The reciprocals of the values 0.77 and 0.60 in Scheme 5 of the accompanying paper [17] (1.32 and 1.67, respectively) represent primary H/D isotope effects for OCPR of **5**, that is, essentially for the first step of OCPR. The value1.32 includes a counteracting secondary H/D isotope effect whereas for the value 1.67 two secondary H/D isotope effects cancel approximately. A similar primary H/D isotope effect (1.7 ± 0.1) was observed for 3-deuterio-**1**. These low (1.3–1.7) primary H/D isotope effects indicate a strong exothermicity of the 1,2-migration which is the first step of OCPR. For the 1,2-back migration, a comparison (see Scheme 5 of the present paper) of ratios 1 and 2 on one hand, with ratio 3 on the other yields a primary H/D isotope effect of 1.3–1.6, which demonstrates that this step, too, must be strongly exothermic. If a reaction and its back reaction are both strongly exothermic, they must occur on different hypersurfaces. Hence, the 1,2-back migration must occur on the electronic ground-state hypersurface. Since on this hypersurface the 1,2 back migration is a radical rearrangement (vide supra) it is not surprising (vide supra) that we found only hydrogen, but no methyl, back migration.

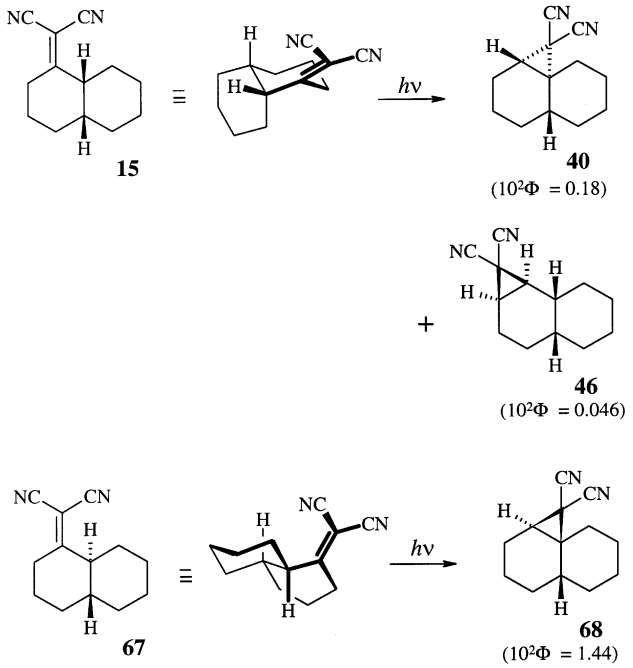
The experimentally found "back migration" in some cases, such as the formation of **4** and **3** from **3** and **4**, respectively (Scheme 7), besides the true back migration includes two further reactions: (a) the isomerization of primarily formed (Δ1 to Δ2)-deconjugated DCNA isomers back to DCNA, and (b) a deprotonation of excited DCNA followed by reprotonation. The low values for "back migration" found for **3** and **4** (Scheme 7) indicate that neither of these two reactions can be a more than a minor reaction besides OCPR in hexane; the values translate into a $10^2 \times \Phi$ value of about 2 for the sum of the three reactions in either case, **3** and **4** (including a factor of 2 to take care of the fact that only one half of the "back migration" is visible). In methanol (in place of hexane), this value roughly triples; we take this to mean that in the ionizing solvent methanol the $10^2 \times \Phi$ value for deprotonation is about 4 whereas in the non-polar hexane it is 0.

3.4. OCPR: special cases due to effects of steric strain

The behavior of two structurally very similar DCNA, viz. **62** and **65**, on irradiation with 253.7 nm light is shown in Scheme 8. They both show very similar quantum yields for cyclohexane addition that are within the usual range; hence, their photophysics appears to be the same. Yet, their reactivity towards OCPR differs dramatically even though the only difference between their molecular structures is an additional methylene bridge in **65** which is quite distant from the chromophore. To be sure, the additional methylene bridge could prevent the ring-closure of the intermediate 1,3-diradical derived from **65**; the cyclopropane resulting from this ring-closure, in contrast to **64**, would be prohibitively strained. No alternative rearrangement products were observed; apart from reaction with solvent and very slow polymer formation, **65** appeared to be photostable. Thus, lacking viable exit channels, this intermediate 1,3-diradical, if formed, should be fairly long-lived and,



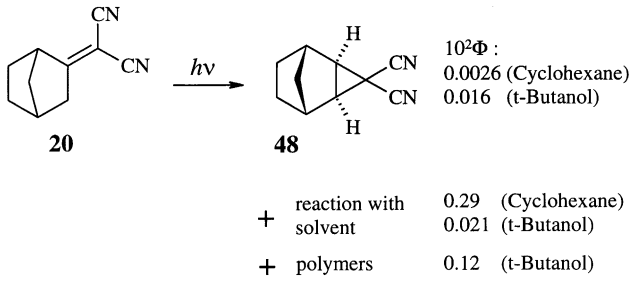
Scheme 8.



Scheme 9.

hence, be prone to be trapped by atmospheric oxygen. Prolonged irradiation of **65** in *tert*-butanol under an oxygen atmosphere, however, gave a result similar to that under argon, slowly leading to polymers and reaction with solvent. Hence, it is the first step of OCPR, viz. the 1,2-migration, that seems to be inefficient in the case of **65**, but not in the case of **62**. Looking for an explanation for this reactivity difference, we note that the quantum yield for formation of the OCPR product **64** ($10^2 \times \Phi = 0.22$) is much higher than naively predicted from the values typical for the related structure type 5 (0.022–0.046, Table 1). The cause for this effect is the strong steric repulsion between the two opposing distal methylene groups in **62** which is absent in the compounds listed under structure type 5 in Table 1 and which is also absent in **65**. In course of the first step of OCPR, viz. the 1,2 alkyl migration, this strong repulsion is entirely eliminated, which constitutes an extra driving force for OCPR in the case of **62** (an alternative conformation of **62**, having one of the two methylene groups flipped upwards to eliminate this repulsion, not only is expected to be less photoreactive, but also is higher in free energy and in heat of formation by 0.2 and 1.2 kcal/mol, respectively, according to MM3 calculations [21–23], and hence is unimportant in the present context). OCPR of **65** does not benefit from this bonus. On the contrary, the 1,2-migration would build up both angle strain and torsional strain with respect to the ideal strainless structure of **65**, whereas it would not create strain in the structures listed under structure type 5 in Table 1. As a consequence, the quantum yield value for OCPR of **65** may well drop far below the values for structure type 5, in agreement with observation.

The two epimeric DCNA **15** and **67** possess the conformations shown in Scheme 9 [20]. The decalin structure is made up of two cyclohexane chairs in the case of **15** and of one chair for the saturated cyclohexane ring and one twist boat for the methylene cyclohexane ring in the case of **67**. The formation of **40** from **15** classifies as structure type 4 in Table 1; the quantum yield for this reaction ($10^2 \times \Phi = 0.18$), however is conspicuously below the usual values for this structure type (Table 1). The formation of **46** from **15**, on the other hand, is a normal structure type 5 case according to its quantum yield. Obviously, the reason for the exceptionally low quantum yield for formation of **40** must be associated with the additional fused saturated cyclohexane ring which is absent in the other structure type 4 cases. The tertiary carbonium ion left behind after departure of the tertiary hydrogen atom en route to **40** claims a planar geometry [39] which imposes strain on the additional cyclohexane ring. This strain readily explains the low quantum yield for the hydrogen migration. There would have been no strain if the migrating hydrogen had left behind a tertiary radical rather than a carbonium ion; tertiary radicals, in contrast to carbonium ions, are about as stable in a pyramidal geometry as in a planar one [40–42]. Thus, the exceptionally low quantum yield of **40** constitutes evidence for the primary formation of a 1,3-dipole, rather than a 1,3-diradical, by the 1,2-migration which is the first step of OCPR, and thus, rules out the possibility that this 1,2-migration, though being a Wagner–Meerwein rearrangement, might lead directly to the 1,3-diradical by internal conversion to the electronic ground-state hypersurface already in its course. **67** is the only DCNA encountered in the present work that has a migrating hydrogen atom that is both tertiary and not located in the olefinic plane, but favorably placed above/below it in



Scheme 10.

the most stable DCNA conformation; it thus classifies under none of the structure types in Table 1. In spite of this particularly favorable situation, the observed OCPR quantum yield (1.44) is only insignificantly higher than the values for structure type 4. Again, the reason is in the strain imposed on the additional cyclohexane ring by the planarity of the carbonium ion generated by the 1,2-migration.

The quantum yield for OCPR of **20** to form **48** (Scheme 10) in cyclohexane ($10^2 \times \Phi = 0.0026$; Table 1) is exceptionally low as compared to the other structure type 5 quantum yields while the quantum yield for cyclohexane addition to **20** ($10^2 \times \Phi = 0.29$) is normal. Moreover, in contrast to the general observation of OCPR quantum yields not depending strongly on solvent, the OCPR quantum yield in this case increased six-fold on passing from cyclohexane to *tert*-butanol. No other rearrangement products of **20** were isolated. We believe that the excited **20**, containing a 2-norbornyl cation moiety notorious for extremely facile Wagner–Meerwein rearrangements involving carbon migration in preference to hydrogen migration [43] does give carbon 1,2-migration in preference to hydrogen 1,2-migration. The resulting OCPR product, however is an extremely strained structure which conceivably may readily rearrange back to **20** at ambient temperature.

3.5. Comparison with other OCPR producing systems reported in the literature

For 1-phenyl- and 1,1-diphenyl-1-alkenes, which give OCPR like DCNA albeit at lower quantum yields, Hixson has arrived at mechanistic conclusions quite analogous to those arrived at in the present work [1–4]. 1-Phenyl- and 1,1-diphenyl-1-alkenes differ markedly from DCNA in that their lowest excited singlet state features an avoided crossing giving rise to an energy barrier of several kcal/mol between its planar (spectroscopic) and perpendicular C-1 to C-2 conformers [44], as a consequence, these compounds show efficient fluorescence [2–4,44] whereas lone DCNA do not fluoresce. The avoided crossing means that for these compounds the electron configuration of the planar conformer of their lowest excited singlet state must be quite different both from that of the perpendicular one and from that of the corresponding planar excited DCNA conformer; according to theoretical calculations this electron configuration corresponds to a local excitation of the phenyl groups [45]. The fact that, in spite of this difference, these compounds undergo OCPR with the same characteristics like DCNA, confirms the conclusion, reached above on theoretical grounds [35], that OCPR occurs from the perpendicular conformations in both cases [46]. [1]

For 1-cyano-1-phenyl-1-alkenes, which give efficient OCPR with similar characteristics like DCNA [5,6], we propose the same mechanism as outlined in the present work even though the authors [5,6] preferred a different one. In the light of our mechanism, one particularly interesting experiment carried out by the authors [5,6] was a comparison of the OCPR quantum yields for two *E*/*Z* isomer pairs of their substrates. For one *E*/*Z* pair, the two quantum yields were virtually the same (ratio 1.08), as required by the mechanism via perpendicular conformers. The second pair differed from the first one in that one, but not the other, of the two members of the second pair was highly sterically strained. On electronic excitation and passage to the perpendicular conformation, this strain energy would be liberated as excess vibrational energy of the perpendicular conformation derived from that one member. The fact that for this pair the OCPR quantum yields were not the same (ratio 2.4) shows that the perpendicular conformations did not become thermalized before reaction and this again emphasises their short lifetimes.

Open-chain phenyl-free 1-cyano-1-alkenes appeared to be OCPR-unreactive in our hands. For 1-cyano-cyclohexenes, which do show OCPR [9,10], the same statements like for 2-en-1-ones appear to hold.

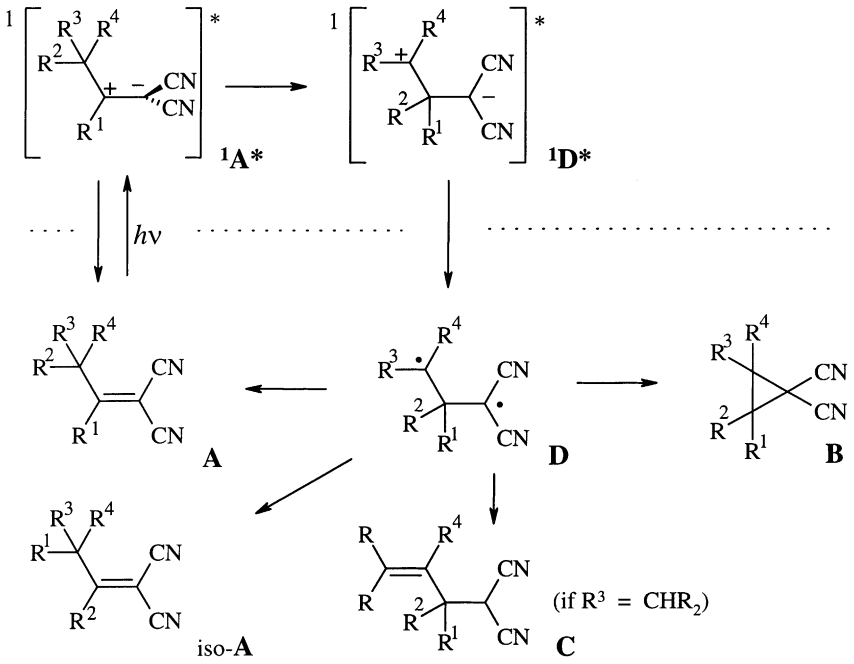
The 2-En-1-ones differ fundamentally from all forementioned systems in that their longest wavelength UV absorption is $n\pi^*$ rather than $\pi\pi^*$, which diverts their photochemistry into triplet-based reactions [7]. Not surprisingly then, open-chain 2-en-1-ones are OCPR-unreactive. 4,4-Dialkyl-cyclohex-2-en-1-ones, however, do show OCPR; this reaction has been intensively investigated, particularly by Schuster [7,8]. Up to a certain time, the accumulated evidence persuasively suggested a concerted (though not synchronous) symmetry-allowed [$_\pi 2_s + _\sigma 2_a$] pericyclic reaction of the highly strained (and therefore, extremely short-lived) electronic ground-state of the *trans* double-bond isomer of the substrate (a *trans*-cyclohexenone). OCPR in these systems would thus occur by a mechanism entirely different from that in the other systems discussed in the present paper. However, attempts in more recent time to detect the ground-state *trans*-cyclohexenone afforded no evidence for its existence [47], apparently successful trapping reactions of it turned out to be spurious [48,49].

[1] In the kinetic treatments in his earlier papers [2–4] which appeared before Salem's seminal paper [35], Hixson had implicitly assumed OCPR to occur from the spectroscopic rather than from the perpendicular singlet. The k_r values given there are thus not true OCPR reaction rates.

4. Conclusion

DCNA lacking additional unsaturation, in their lowest excited singlet state (a $\pi\pi^*$ state) undergo OCPR with structure-dependent quantum yields presented in Table 1. The course of OCPR is concluded to be as follows. The C-2 atom is cationic in the perpendicular conformation (C-2 relative to C-1) of the reactive $\pi\pi^*$ singlet state. It triggers a hydrogen or an alkyl 1,2-migration from C-3 to C-2, thus, generating a 1,3-dipole which is still in the first excited singlet state. This 1,3-dipole decays by internal conversion to the electronic ground-state thereby becoming a singlet 1,3-diradical. This 1,3-diradical, which represents a family of transition states rather than an energy minimum, decays by three channels: ring closure to cyclopropane, thus completing OCPR, which is the main channel; back 1,2-migration of hydrogen to generate the original or an isomeric DCNA; a 1,4-hydrogen shift from C-4 to C-1 to generate a 1,1-dicyano-3-alkene (Scheme 11 and Fig. 1). Further details along this course are the following. The reactive DCNA excited singlet state is short-lived with respect to diffusional movements (as deduced in the accompanying paper [17]). Though a dipolar formula (a carbonium ion attached to a malononitrile anion) would describe the OCPR reactivity of the excited species, this formula would underestimate (on the naive basis of group increments) its energy by at least 16 kcal/mol. The 1,2-migration occurs suprafacially (i.e. follows maximum orbital overlap); unfavourably oriented migrants (i.e. those lying in the olefinic plane) need modest activation energy (<1.6 kcal/mol) to lift them sufficiently out of the plane. Apart from that, the 1,2-migration of hydrogen needs virtually no activation energy throughout (methyl migration has been found to need 0.86 ± 0.17 kcal/mol), even though its efficiency varies strongly (Table 1) in the expected way with the degree of stabilization, by alkyl and alkoxy substituents, of carbocations at the two involved positions, C-2 and C-3. One explanation for this peculiarity may be that the effect of stabilizing or destabilizing substituents on C-2 and C-3 is to vary, along the reaction coordinate for 1,2-migration, the "steepness" and/or the "onset" of the energetic downhill slope leading to the 1,3-dipole. This in turn will vary the time that the migrant, exploring the barrierless hypersurface, will need to reach a "point of no return" after which the species can no longer return to electronic ground-state DCNA by internal conversion. The 1,3-dipole, too, is very short-lived. It does achieve approximate conformational equilibration in cyclohexane, though less so in more polar solvents. It however has no time to undergo a Wagner–Meerwein rearrangement at its cationic center, even though this would be highly exothermic and would require an activation energy of presumably less than 3.5 kcal/mol. All the 1,3-dipole appears to do is decay to the electronic ground-state.

Neither intermediate dipolar species, DCNA excited singlet state and 1,3-dipole, are trapped by solvent to any significant extent if the photoreactions are run in alcohols such as methanol or *tert*-butanol as the solvents. One might have anticipated trapping by nucleophilic attack of the alcohol oxygen atom at the cationic center resulting in an overall addition of the alcohol across the dipole. The reason why this does not occur is seen in the electronically excited nature of these dipoles which bars this nucleophilic attack from leading to the electronically ground-state adduct in an adiabatic reaction.



Scheme 11.

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