1564 (bipy), 1246, 1144 (CF), 975 (HC=CH *E*). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.99 (tt, $^3J_{H2'',H3''}$ = $^3J_{H2'',H1''}$ = 7 Hz, 4 H, $(H_2C)_{2''}$), 2.31-2.52 (m, 4 H, $(H_2C)_{3''}$), 4.41 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, $(H_2C)_{1''}$), 5.51-5.90 (m, 2 H, $HCCF_2$), 6.40-6.59 (m, 2 H, HC=$CHCF_2$), 7.85 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.5 Hz, 2 H, $H_{5,5'}$), 8.82 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$), 8.94 (br s, 2 H, $H_{3,3'}$). ^{19}F NMR (188.8 MHz, $CDCl_3$): δ -81.6 (3 F), -107.3, -111.8 (2 F, CF_2CH=, (*Z*/*E* 14:86), -122.0 (2 F), -123.8 (2 F), -124.2 (2 F), -126.6 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 27.2, 28.6 (both s, $(CH_2)_{2'',3''}$), 64.8 (s, $(CH_2)_{1''}$), 118.6 (t, $^2J_{C,F}$ = 23 Hz, =$CHCF_2$), 120.6 (s, $C_{3,3'}$), 123.3 (s, $C_{5,5'}$), 138.8 (s, $C_{4,4'}$), 141.7 (t, $^3J_{C,F}$ = 9 Hz, CH=$CHCF_2$), 150.2 (s, $C_{6,6'}$), 156.6 (s, $C_{2,2'}$), 165.1 (s, C=O). Anal. Calcd for $C_{34}H_{22}F_{26}N_2O_4$: C, 40.17; H, 2.18; F, 48.59; N, 2.76. Found: C, 40.08; H, 2.13; F, 48.38; N, 2.69.

Synthesis of 4,4'-Bis[12''-(*F*-octyl)-11''-iodododecyl]-2,2'-bipyridine (5). **3a** (740 mg, 2.04 mmol), *F*-octyl iodide (2.98 g, ~3 equiv) and α,α'-azobisisobutyronitrile AIBN (25 mg, 0.02 equiv) were heated at 80 °C under oxygen-free argon for 12 h. Then, the crude product was extracted with methylene dichloride and washed with water before filtration, evaporation, chromatography on SiO_2 with methylene dichloride/methanol 0.5% as eluents, and recrystallization from methylene dichloride to give the expected compound **5** as white crystals (2.29 g, 1.47 mmol, 71% yield). ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.45 (br s, 32 H, $(H_2C)_{2''-8''}$), 1.70-2.05 (m, 8 H, $(H_2C)_{10'',12''}$), 2.71 (t, $^3J_{H,H}$ = 7 Hz, 4 H, $(H_2C)_{1''}$), 4.35 (tt, $^3J_{H,H}$ = 7.5 Hz, 2 H, $(HCI)_{11''}$), 7.12 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 2 Hz, 2 H, $H_{5,5'}$), 8.27 (d, $^4J_{meta}$ = 2 Hz, 2 H, $H_{3,3'}$), 8.58 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$).

Acknowledgements are made to ATTA, FEGEFLUC, and the Centre National de la Recherche Scientifique for support of this research.

Registry No. 1, 1134-35-6; **3a**, 140464-50-2; **3b**, 140464-51-3; (*E*)-**4a**, 140464-53-5; (*Z*)-**4a**, 140464-52-4; (*E*)-**4b**, 140464-55-7; (*Z*)-**4b**, 140464-54-6; (*E*)-**4c**, 140464-57-9; (*Z*)-**4c**, 140464-56-8; (*E*)-**4d**, 140464-58-0; (*Z*)-**4d**, 140605-03-4; **5**, 140464-66-0; **7**, 6813-38-3; **7** dimethyl ester, 71071-46-0; **8a**, 140464-59-1; **8b**, 140464-60-4; **8c**, 140464-61-5; (*E*)-**8d**, 140464-63-7; (*Z*)-**8d**, 140464-62-6; (*E*)-**8e**, 140464-65-9; (*Z*)-**8e**, 140464-64-8; 10-undecenyl tosylate, 51148-67-5; 4-pentenyl tosylate, 19300-54-0; perfluorooctyl iodide, 507-63-1; perfluorobutyl iodide, 423-39-2; 11-(perfluorooctyl)undecanol, 1512-02-3; 2-(perfluorohexyl)ethanol, 647-42-7; 5-(perfluorohexyl)pentanol, 134052-02-1; (*Z*)-11-(perfluorooctyl)-10-undecenol, 135131-74-7; (*E*)-11-(perfluorooctyl)-10-undecenol, 135131-50-9; (*Z*)-5-(perfluorohexyl)-4-pentenol, 135131-75-8; (*E*)-5-(perfluorohexyl)-4-pentenol, 135131-51-0; 11-iodo-1-undecene, 7766-49-6; 5-iodo-1-pentene, 7766-48-5.

Electron Transfer Photoinduced Cleavage of Acetals. A Mild Preparation of Alkyl Radicals[1]

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Electron transfer from 2-alkyl- and 2,2-dialkyldioxolanes as well as from open-chain ketals to singlet excited benzene-1,2,4,5-tetracarbonitrile (TCNB) is followed by fragmentation of the donors radical cation to yield alkyl radicals and dialkoxy carbocations. The first species are trapped by TCNB to yield alkylbenzenetricarbonitriles (substitution of a second cyano group can be obtained sequentially) and in a minor path are reduced to alkanes, while the latter ones react with nucleophiles to give ortho acid derivatives. In view of the results of radical clock experiments, it is assumed that part of the process is a concerted (radical cation cleavage–addition to the aromatic) reaction, while another part involves the free-radical cation. On the other hand, intersystem crossing from the singlet radical ion pair to the triplet manifold causes cleavage of the acetal to the corresponding carbonyl derivative. This reaction offers a mild method for the preparation of alkyl radicals via C-C bond cleavage.

Photoinduced electron transfer reactions have been extensively investigated in recent years and the condition for the efficiency of such processes is prevailence of chemical reactions over energy-wasting back electron transfer within the primary radical ion pair.[2] An important class of such reactions is the fragmentation of a radical cation, $X-Y^{\bullet+}$ (arising from electron transfer to the excited acceptor A*). Such a reaction may lead to an

$$A^* + XY \rightarrow A^{\bullet-} + XY^{\bullet+} \quad (1)$$

$$XY^{\bullet+} \rightarrow X^{\bullet} + Y^+ \quad (2)$$

efficient global process since one of the radical ions is rapidly subtracted from the equilibrium. Indeed, of the species formed from the cleavage of $XY^{\bullet+}$, the cation is trapped by a nucleophile Nu^-, and the neutral radical is

$$Y^+ + Nu^- \rightarrow Y-Nu \quad (3)$$

either reduced by the radical anion (thus completing the sensitizing cycle and regenerating ground state A, eq. 4), and then e.g. protonated (eq 5), or alternatively is trapped by a radical trap Rad (eq 6, A and $A^{\bullet-}$ obviously present in solution are expected to act in this role, and other traps may purposedly be added). Observed reactions involve,

$$X^{\bullet} + A^{\bullet-} \rightarrow X^- + A \quad (4)$$

$$X^- + H^+ \rightarrow XH \quad (5)$$

$$X^{\bullet} + Rad \rightarrow products \quad (6)$$

besides deprotonation,[3] cleavage of carbon–carbon,[3a-d,5]

(1) This is contribution no. 100 from the Photochemical Unit, The University of Pavia, and is dedicated to the memory of Prof. S. Pietra (deceased January 1990), who founded it in 1971.

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Scheme I

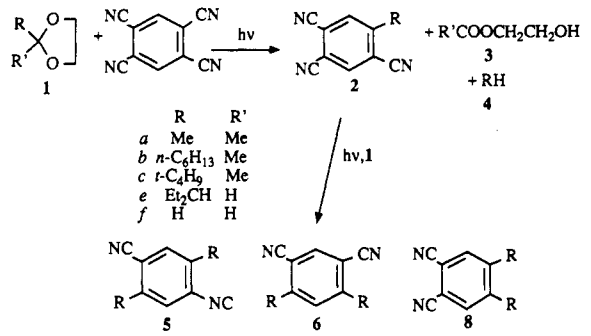


Table I. Isolated Products from the Irradiation of TCNB in the Presence of Acetals 1 and 10 in Acetonitrile

acetal	irradiation time, h	products (% yield[a])
1a	1	**2a** (65), **3a**
1b	1	**2b** (70), **3a**, **4b**
1c	1	**2c** (70), **3a**, **5c** (8), **6c** (15)
1c	2	**2c** (22), **3a**, **5c** (19), **6c** (50)
1d	3	**2g** (40), **7h**
1d	6[b]	**2h** (25), **7h**, **5h** (10), **6h** (25), **8h** (7)
1e	2.5	**2e** (61)
1f	6	**9** (77)
1i	15 min[c]	**2i** (35), **13** (34), **3i**
1j	20 min[d]	**2j** (41), **14** (29), **3a**, **15**
10a	1.5[d]	**2a** (60)
10c	1.5[d]	**2c** (70)

[a] Yield of the products from aromatic substitution, calculated on reacted TCNB. Conversion ≥80% when noted. [b] After the irradiation, the product mixture is transesterified to the corresponding methyl esters. [c] 45% TCNB conversion. [d] 30% TCNB conversion.

carbon–heteroatom,[3c,6] or heteroatom–heteroatom bonds.[7] Formation of alkyl radicals by C–C fragmentation is a process of potential synthetic usefulness, but except for the case of strained rings,[8] known examples are limited to benzyl derivatives.

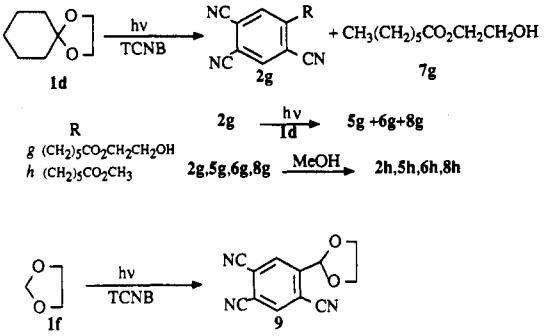
$$ArCHRY^{\bullet+} \rightarrow ArCHR^{\bullet} + Y^{+} \quad (7)$$

We are therefore looking for related preparations of aliphatic radicals, and presently report the photosensitized (electron transfer) fragmentation of ketals and acetals.

Results

The 1,3-dioxolanes 1 remained unchanged when irradiated in the presence of 1,4-benzenedicarbonitrile in degassed acetonitrile; however, when 1,2,4,5-benzenetetracarbonitrile (TCNB) was used both the aromatic nitrile (which absorbed the light) and the acetals were consumed (Scheme I). The reaction with 2,2-dimethyl-1,3-dioxolane (**1a**) gave 5-methyl-1,2,4-benzenetricarbonitrile (**2a**) and 2-hydroxyethyl acetate (**3a**) as the only detected products

Scheme II



at 70% TCNB conversion (yields, Table I). Further transformation led to a complex mixture, more deeply investigated with the other alkyl analogues (see below). When 2-hexyl-2-methyl-1,3-dioxolane (**1b**) was used, only 5-hexyl-1,2,4-benzenetricarbonitrile (**2b**) and 2-hydroxyethyl acetate (**3a**) along with some hexane (**4b**) were obtained, while the alternative products **2a** and **3b** were not present.

Likewise from 2-*tert*-butyl-2-methyl-1,3-dioxolane (**1c**) were formed 5-*tert*-butyl-1,2,4-benzenetricarbonitrile (**2c**) and 2-hydroxyethyl acetate (**3a**) rather than products **2a** and **3c**. Prolonged irradiation (even after all TCNB had been consumed) led to a more complex mixture from which two dialkylbenzenedicarbonitriles were isolated. The position of the substituents was determined on the basis of the correspondence of the ^{13}C NMR resonances with those predicted by literature correlations and of other spectroscopic characteristics (a single aromatic ^{1}H NMR absorption, fluorescence spectrum similar to that of 1,4-benzenedicarbonitrile for the former, and two well-differentiated aromatic signals for the latter). Thus, the products are 2,5-di-*tert*-butyl-1,4-benzenedicarbonitrile (**5c**) and 4,6-di-*tert*-butyl)-1,3-benzenedicarbonitrile (**6c**). Check experiments showed that, while **2c** is photostable in neat acetonitrile, irradiation of this compound in the presence of **1c** gives products **5c** and **6c** (as well as **3c**) at about the same rate as when they are formed starting directly from TCNB (Table I).

When the spirodioxolane **1d** was used, the products were a compound resulting, as in the previous cases, from alkyl substitution on the arene (compound **2g**, containing the 2-hydroxyethyl carboxyl ester function and easily transesterified to the corresponding methyl ester **2h**), and an open-chain aliphatic ester, 2-hydroxyethyl hexanoate (**7g**), identified by trans esterification to the methyl ester **7h**.

Prolonged irradiation gave in this case three dialkylated derivatives, viz. **5g**, **6g**, and **8g** (converted to the methyl esters **5h**, **6h**, and **8h** and distinguished as above on the basis of the ^{13}C spectra and by showing, respectively: one aromatic ^{1}H NMR signal and a relatively long wavelength fluorescence, similar to 1,4-benzenedicarbonitrile; two aromatic hydrogens; one aromatic hydrogen and a short-wavelength fluorescence, similar to 1,2-benzenedicarbonitrile). Check experiments using preformed **2g** in the presence of **1d** gave the three products of dialkylation as well as some **7g** (Scheme II, Table I).

The reaction of 2-(1-ethylpropyl)-1,3-dioxolane (**1e**) gave a single product, viz. 5-(1-ethylpropyl)-1,2,4-tricyanobenzene (**2e**). With parent 1,3-dioxolane (**1f**) again an alkylation was observed, but in this case the acetal function was conserved and the product was 2-(2,4,5-tricyanophenyl)-1,3-dioxolane (**9**) (Scheme II, Table I).

Reaction with open-chain ketals was equally successful. Thus, compound **2a** was obtained from TCNB and 2,2-dimethoxypropane (**10a**) and compound **2c** from 2,2-di-

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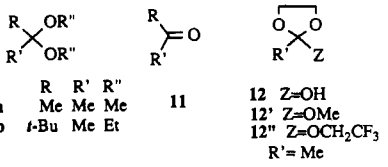
(8) See, e.g.: Gassman, P. G.; Olson, K. D.; Walter, R.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977; **1982**, *104*, 374. Roth, H. D.; Schilling, P. G.; Gasman, P. G.; Smith, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2711. Tsuji, T.; Miura, T.; Segiura, K.; Nishida, S. *J. Am. Chem. Soc.* **1990**, *112*, 1998. Several other examples involve donors containing both a strained ring and aromatic groups.

Scheme III



ethoxy-3,3-dimethylbutane (**10c**). (Scheme III, Table I).

In contrast to the above results with an aromatic nitrile, irradiation of the acetals in the presence of a different light absorber, 2,3,5,6-tetrachlorobenzoquinone (TCBQ) gave the corresponding carbonyl compounds **11**, as tested in the case of compounds **1c** and **10c**.

Effect of the Environment. Further investigations on the reaction were carried out using the dioxolane **1c**, in view of the convenient analysis of the products in this case. Various attempts were made in order to clarify the origin of the products obtained. As for ester **3a**, it was noticed that this compound was not formed when the reaction was carried out in the presence of 0.1 M methanol and was replaced by an equivalent amount of a compound incorporating the additive. This was recognized as the ortho ester **12'** (Z = OMe, R' = Me) by comparison with an authentic sample. When 2,2,2-trifluoroethanol was used instead, both a reduced amount of ester **3c** and a further derivative, the spectroscopic characteristics of which were in accordance with formula **12"** (R' = Me, Z = OCH_2CF_3), were obtained.

Dilution of acetonitrile with water (2 M) slightly slowed down the reaction with some change in the product distribution. Saturation with oxygen decreased the rate of formation of the alkylated tricyanobenzene **2c**, but not that of the ester **3a**.

Addition of small amounts of carbon tetrachloride or of tetrabutylammonium chloride completely changed the course of the reaction, giving 3,3-dimethylbutanone **11c** as the only product.

Radical Clock Experiments. In view of the possible involvement of free radicals in the reaction, two further dioxolanes were considered. 2,2-bis(cyclopropylmethyl)-1,3-dioxolane (**1i**) gave two substitution products, 5-(cyclopropylmethyl)- and 5-(3-butenyl)-1,2,4-tricyanobenzene (**2i** and **13**) as well as the ester **3i**. The **2i** to **13** ratio (evaluated at low conversion in view of the significant photodecomposition of the former compound) was 51 to 49. Likewise 2-(5-hexenyl)-2-methyl-1,3-dioxolane (**1j**) gave both 5-(5-hexenyl)- and 5-(cyclopentylmethyl)-1,2,4-tricyanobenzene (**2j** and **14**, initial ratio 59 to 41) as well as ester **3a** and some methylcyclopentane (**15**), but no 1-hexene (Scheme IV).

Quantitative Measurement. The photoreaction between TCNB and the acetals proceeds regularly, with unchanging products ratio and yield for absorbed dose up to a high (>85%) conversion of the starting material. The second alkylation begins to occur appreciably only when the monoalkyl derivative has accumulated (>75% of the original amount of the starting material). In order to gain a better mechanistic knowledge, quantum yield measurements were carried out in experiments at low conversion for the reaction of TCNB with the dioxolanes **1**, and the open-chain ketals **10** as well as for the reaction of alkyltricyanobenzene **2c** with **1c** (Table II).

As shown in Table II, the quantum yield for TCNB substitution varies from low (0.03) to moderate (0.36) at a 0.1 M donor concentration. In the case of the spirodioxolane **1d**, the yield of the aliphatic ester **7g** is almost 1 order of magnitude lower than that of the aromatic ester **2g**. The second alkylation (on **2c**) takes place at a rate

Scheme IV

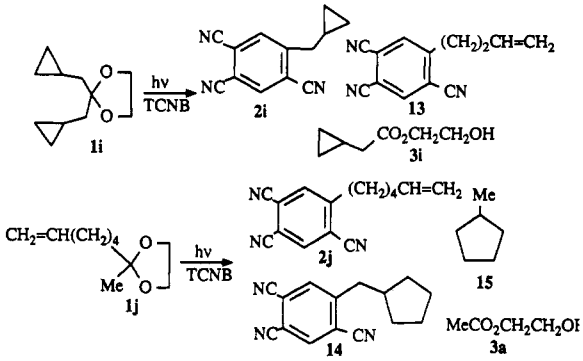


Table II. Steady-State Parameters for the TCNB–Acetal (0.1 M) Photoreaction in Acetonitrile

		Φ_{-TCNB}	products (Φ)	K_{sv}, M^{-1} [a]
1a		0.31	**2a** (0.36), **3a** (0.036)	70
1c		0.28	**2c** (0.32), **3a** (0.635)	84
1d		0.14	**2g** (0.11), **7g** (0.047)	109
1e		0.12	**2e** (0.07)	119
1f		0.018	**9** (0.017)	86
10a		0.07	**2a** (0.03)	40
10c		0.08	**2c** (0.03)	
1c	O_2 [b]	0.06	**2c** (0.046), **3a** (0.034)	
1c	MeOH, 0.1 M	0.18	**2c** (0.16), **12'** (0.036)	
1c	H_2O, 2 M	0.18	**2b** (0.15), **3a** (0.007)	
1c	CF_3CH_2OH, 0.01 M	0.27	**2b** (0.25), **3a** (0.008), **12"** (0.008)	
1c	CCl_4, 0.01 M	0.01	**11c** (0.21)	
1c	Bu_4NCl, 0.05 M	0.01	**11c** (0.32)	
1c	c	0.15	**3a** (0.007), **5c** (0.05), **6c** (0.10)	31

[a] Fluorescence Stern Volmer constants. [b] Oxygen equilibrated solution. [c] Substituting compound **2c** for TCNB.

about 40% lower than the first one (on TCNB). Another noteworthy characteristic is that reaction of the acetal occurs at about the same rate both when it takes the normal course (alkylation of TCNB) and when cleavage to the ketone is rather observed (e.g. in the presence of tetraethylammonium chloride).

Experiments using different starting concentration of the acetal induced a limited change of the **2c**/**3a** ratio. Furthermore, changing the starting TCNB concentration (in the range 5×10^{-4} to 2×10^{-2} M) did not appreciably influenced the quantum yield of reaction.

The chemical studies were supplemented by fluorescence experiments (Table II), evidencing a marked quenching of the TCNB emission by all of the acetals considered.

Discussion

General Mechanistic Scheme. It can be hardly doubted that the present sensitized fragmentation of acetals is an electron-transfer process and adds to the few known reactions of this class involving nonaromatic donors.

The reaction is initiated by electron transfer from the acetal to the nitrile singlet excited state. Thus, positive results are obtained only when the fluorescence of the aromatic is quenched and the free energy change for electron transfer, evaluated by means of the Weller equation, is negative; as an example, 1,4-dicyanobenzene satisfies neither criterion and gives no reaction, while the opposite is true for TCNB (Table III).

Furthermore, intervention of the singlet state is supported by quantum yield measurements. Thus, the double reciprocal plot of quantum yield for formation of both the alkylated derivative **2c** and acetate **3a** vs donor (**1c**) concentration is linear (extrapolated values at infinite donor concentration, 0.32 and 0.046, respectively). The intercept

Table III. Parameters for Electron Transfer

substrate	$E_{1/2}^{red}$,[a,b] V	$E_{1/2}^{ox}$,[a,c] V	E_{exc},[b] eV	ΔG_{et}(1a),[d] eV	ΔG_{et}(1f),[d] eV
p-DCB	−1.62		4.2	0.15	0.51
TCNB	−0.7		3.8	−0.37	−0.01
1a		2.73			
1f		3.09			

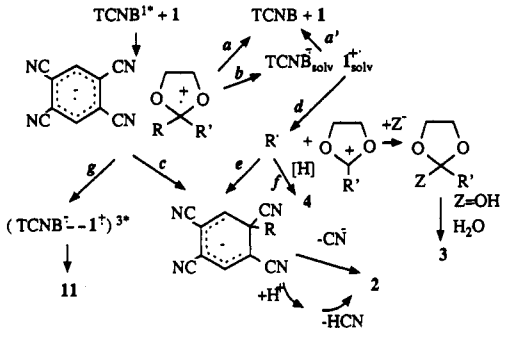
[a] vs SCE. [b] See ref 1d. [c] Evaluated from the ionization potentials (from PES measurements, see: Sweigart, D. A.; Turner, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5599) through the Miller relation (Miller, L. *J. Org. Chem.* **1972**, *37*, 916). [d] Evaluated through the Weller equation (Weller, A.; Rehm, D. *Isr. J. Chem.* **1970**, *8*, 259).

Table IV. Quantum Yield Dependence on Acetal Concentration

acetal	Φ_{lim} (2)[a]	Φ_{lim} (3)[a]	K',[b] M^{-1}
1a	0.36	0.057	93
1c	0.32	0.046	75
10c	0.035		23

[a] Limiting quantum yield at infinite donor concentration, extrapolated from the quantum yield vs donor molarity double reciprocal plot. [b] Intercept–slope ratio from the same plots; compare with the fluorescence Stern Volmer constants in Table II.

Scheme V



vs slope ratio gives an independent measurement of the quenching vs decay rate for TCNB singlet, and this is 75 M^{-1} for the formation of **2c**, a value very near to that obtained by fluorescence quenching measurements. Similar results are observed for other acetals (see Table IV).

The subsequent chemistry is depicted in Scheme V. Thus, the acetal radical cation undergoes efficient cleavage to give an alkyl radical and a dialkoxy carbocation, and these species are trapped respectively by $TCNB^{\bullet-}$ to give the alkylated nitriles (*ipso* substitution of aromatic nitriles by alkyl radicals under similar conditions is largely precedented in literature),[2f,5] and by moisture present in solution to give products of type **12** (such products easily rearrange to the esters **3**), or with other nucleophiles to give the analogues **12′** and **12″**.

When the bicyclic acetal **1d** is used, the cleavage yields a 1,6 radical cation. The nonconjugated radical and cationic sites react independently as above to yield the ω-(tricyanophenyl)hexanoates.

A competing, but minor, pathway observed involves reduction of the radical center, rather than carbon–carbon bond formation, e.g. hexane **4b** from **1b** and the open-chain ester **7g** from **1d**. In the latter case the reaction is formally the hydrolytic cleavage of a cyclic C–C σ bond.

At least two pathways could be considered for this reduction reaction, viz. either electron transfer from $TCNB^{\bullet-}$ to the radical to form the anion and protonation of the latter (eqs 4, 5) or direct hydrogen abstraction. Contrary to what is expected for the first hypothesis, experiments with acetonitrile containing D_2O led to no significant deuteration of the methyl group in compound in **7h**. The possibility that this ester could arise from the cleavage of a primarily formed alkyl dihydro aromatic derivatives was considered, but then again an experiment with D_2O should have given deuteration either of the ester or of recovered TCNB, and this was not the case. Therefore we were forced to conclude that hydrogen abstraction by the radical center takes place. That the hydrogen source was acetonitrile was indicated by experiments in CD_3CN, leading to selective monodeuteration of the methyl group in **7h**.

Chemistry of the Radical Cation. The present reaction is not very sensitive to the environment, e.g. large amounts of protic additives only decrease the quantum yield and saturation of the solution with oxygen quenches only one of the pathways while both conditions completely hinder analogous reactions via radical ion pairs (see e.g. ref 3).

The key factor is fast cleavage of the radical cation successfully competing with back-electron transfer. It is apparent from the data in Table II that this is indeed an efficient process with acetals, limiting quantum yields reaching values as high as 0.4, viz. the rate for bond breaking is two-thirds of the rate for back-electron transfer. Apparently the rigid dioxolane structure favors cleavage, the same process with the analogues **10a,c** being 1 order of magnitude slower.

In the TCNB-sensitized reaction the process observed is exclusively carbon–carbon cleavage α to the acetal function. No competive deprotonation from a position α either to the ether function (position 4 in the dioxolanes) or to the acetal function (position 2 in monosubstituted dioxolanes) takes place, except, obviously, in the case of parent dioxolane **1f**, but then with a much lower quantum yield than in the previous cases. Thus, in the absence of a convenient base, proton transfer is disfavored with respect to generation of delocalized carbocations.

The free energy change for the cleavage of a radical cation according to eq 1 differs from the bond dissociation free energy of the neutral molecule by an amount proportional to the difference in oxidation potential of the radical formed and of the neutral molecule[4b,9]

$$\Delta G(XY^{\bullet+}) = \Delta G(XY) + F[E_{1/2}^{ox}(X^{\bullet}) - E_{1/2}^{ox}(XY)] \quad (8)$$

While thermochemical data for the complete characterization of the process are not available at present, fragmentation of an alkyl radical from the acetal radical cation finds analogy in the mass spectrum of **1c** (see the Experimental Section) as well as in the ESR detection of alkyl radicals by γ-irradiation of some 2-alkyl-1,3-dioxolanes, -1,3-dioxanes, and -1,3,5-trioxanes in CCl_3F at 4.2 and 77 K.[10]

As for the direction of cleavage to give one of the alternative pairs of carbocations and radicals, eq 8 predicts that the carbocation product arises from the radical fragment which has the lower oxidation potential. This has been verified in the case of asymmetric bibenzyl.[4b,11] Recent measurements on the free radicals derived from 1,3-dioxolane evidenced two oxidation waves, the former one (−0.34 V vs SCE) being attributed to the 1,3-dioxolan-4-yl radical, the latter one (0.31 V) to the 2-yl radical.[9a] This would lead to the wrong prediction for the mode of cleavage (compare $E_{1/2}^{ox}$ 0.09 V for the *tert*-butyl radical) while reversing the attribution or at any rate ac-

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cepting the first value for the 2-yl radical is in accordance with the results and better accounts for the facile fragmentation consistently observed under different conditions, as mentioned above, as $E_{1/2}^{ox}(X^{\bullet}) - E_{1/2}^{ox}(XY)$ is then ca. −3.1 V with the dissociation energy of the alkyl group ca 3.5 eV.[10] Finally when different aliphatic radicals can be competitively formed, the preference expected on the basis of the radicals stability is observed (tertiary > primary > methyl).

Chemistry of the Radicals and the Cations. The cations thus formed are rapidly trapped by nucleophiles, though the low isolated yield of products **12** (or of esters **3** arising from them during chromatography) show that further unrecognized processes competitively occur.

The fate of the alkyl radicals differs from that observed with benzyl radicals by Arnold and co-workers.[4b] In that case easily reduced radicals ($E_{1/2}^{red}$ −1.14 to −1.60 V vs SCE)[9a] are formed in the presence of the 1,4-dicyanobenzene radical anion ($E_{1/2}^{red}$ to −1.62 V) and thus reduction followed by protonation leads to alkanes (see eqs 4, 5). In our systems, on the contrary, the reduction path is not available ($E_{1/2}^{red}$ for the *tert*-butyl radical is <−2 V,[9a] while TCNB has −0.7 V), and addition to $TCNB^{\bullet-}$ takes place instead (apparently not to TCNB, in view of the independence of the yield on its concentration). Direct splitting of a cyanide anion or protonation and hydrogen cyanide elimination lead to the observed products. Oxygen interferes with the radicalic process (not with the preceding electron transfer and fragmentation, as shown by the unchanged quantum yield of the cation-derived product) by intercepting the alkyl radical and reoxidizing $TCNB^{\bullet-}$ (the nitrile and oxygen have similar reduction potential).[2d]

In the absence of good hydrogen donors, reduction of the radical to the alkane remains a minor path.

It is interesting that when starting from dioxolanes having no alkyl substituent a dialkoxy radical is formed and reacts analogously (product **9** from **1f**), thus affording a method for introducing a masked formyl group on the ring. However, the quantum yield is much lower, and this is due, as mentioned above, to the lower rate for deprotonation rather than carbon–carbon bond cleavage in these radical cations, since electron transfer quenching of $TCNB^{1*}$ is as effective with **1f** as with **1a–d**.

That the aromatic substitution is repeated, starting from the tricyano derivatives **2**, shows that the singlet excited state of such molecules is again a good oxidizer and is able to initiate a similar electron-transfer sequence. The parallelism with TCNB is confirmed by the comparable quenching rate constant and quantum yield of reaction. Under our conditions (fluorescing lamps centered at 320 nm) the two processes are separated and sequential, probably in view of the somewhat more favorable absorption characteristics of TCNB, and/or to the reoxidation of the tricyanobenzene radical anion by TCNB, until the latter is present in sufficient concentration. At any rate, this fact offers a potentiality for asymmetric dialkylation which is being currently studied. Notice that the most abundant among dialkylated compounds is **5c** from **2c** (and analogously **5g** from **2g**), a fact explained by the greater stability of the intermediate anion since two cyano groups share the charge in these cases.

In Cage vs Out of Cage Radical Cation Cleavage. The experiments with dioxolanes **1i** and **1j** and the establishment of the radical pathways in this reaction allow a deeper understanding of the mechanism of the radical cation cleavage. Thus, substitution on the aromatic ring leads to products containing the rearranged and the unrearranged radicals in about the same ratio starting from both **1i** and **1j**, despite the fact that the cyclopropylmethyl and the 1-hexenyl radical rearrange at a largely different rate (1.3×10^8 vs 1.0×10^5 s^{-1} at 25 °C).[12] Since both compounds are formed in the earliest stage of the reaction, they are primary photoproducts. It appears unlikely that a pair of primary radicals (e.g. cyclopropylmethyl and 3-butenyl) react with the same traps ($TCNB^{\bullet-}$ or a hydrogen donor) at a widely differing rate. Therefore, we rationalize this result as indicating that the radical cation cleavage occurs according to two mechanisms. The first one is a fast process within the originally formed radical ion pair, where splitting of the cation and alkylation of the aromatic ring occurr concertedly and no rearrangement takes place. The latter one, involving the free radical cation and the free radical from it, is accordingly relatively slow since it involves processes which cannot be fast, either on kinetic (addition to $TCNB^{\bullet-}$) or energetic (hydrogen abstraction) grounds, and obviously leads to the rearranged radical (e.g. the (cyclopentylmethyl)tricyanobenzene and methylcyclopentane; notice that no 1-hexene is formed).

While assistance by a nucleophile has been proposed to be required in other cases[13] to overcome a significant barrier to radical cation cleavage, there is no compelling evidence for such a mechanistic pathway in the present reaction, characterized by a relatively high quantum yield, and thus a fast cleavage of the radical cation. However, assistance by $TCNB^{\bullet-}$ may well be determining in the in cage process.

The occurrence of both in cage and out of cage reactions is in part reminescent of what was previously found in the alkylbenzenes–arenenitriles system where, when the radical cation cleavage is fast, both a chemistry of the radical ion pair and a chemistry of the free radical cation are observed.[14]

Summing up the above observations, all processes from the radical ion pair, viz. (a) decay, (b) separation, and (c) direct reaction (Scheme V), occur at a rate in the order of 10^8 s^{-1}, with $k_b \simeq k_c k_d/(k_d + k_{a'})$. The successful quenching experiments are in accordance with this evaluation. Thus diffusion-controlled reaction with 10^{-2} M O_2 quenches both types of alkylation (and thus both the ion pair and $TCNB^{\bullet-}$) and similarly with 10^{-2} M CCl_4 or Cl^- causes complete intersystem crossing of the singlet to the triplet radical ion pair (see below).

Triplet Pathway. When TCBQ is substituted for TCNB, a different reaction course comes in. Electron transfer is less favorable but still possible at least for the dialkyldioxolanes (the reduction potential for triplet TCBQ is 2.72 V vs SCE, and E_T is 2.7 eV). We did not investigate this reaction in detail, but at least two paths can be proposed, viz. (a) hydrogen abstraction (there is precedent for abstraction from position 4 in 2,2-dialkyl-1,3-dioxolanes[15,16]) followed by β-cleavage to yield the ketone or (b) that back-electron transfer is much slower in the triplet radical pair and the long-lived radical cation is hydrolyzed to the ketone (this, however, would require that the C–C cleavage discussed above occurs only through the assistance by $A^{\bullet-}$). [**Note Added in Proof.** Control experiments showed that some acidity is formed under these conditions

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Table V. Main Characteristics of the Alkylbenzenenitriles

compd	mp, °C (solvent)	^{1}H NMR, δ, in $CDCl_3$	analysis, found (calcd) C	H	N
2a	147–148 (EtOH)	8.05 s, 7.85, 2.7 s	71.57 (71.85)	2.81 (3.02)	25.37 (25.14)
2b	oil	8.25 s, 8 s, 3.25 t, 2.1–1.5 m, 1.15 t	76.20 (75.92)	6.41 (6.37)	17.35 (17.71)
2c	195 (EtOH)	8.1 s, 7.95 s, 1.55 s	74.30 (74.62)	5.27 (5.30)	19.82 (20.08)
2e	105–6 (C_6H_6)	8.05 s, 7.65 s, 3.1 m, 0.8 t	75.61 (75.31)	5.93 (5.87)	18.59 (18.82)
2g	oil	8.055, 7.8 s, 4.2 m, 3.8 m, 2.8 t, 2.35 m, 1.6 m	65.9 (65.58)	5.45 (5.50)	13.37 (13.50)
2h	oil	8.05 s, 7.8 s, 3.7 s, 3 t, 2.4 m, 1.6 n	68.51 (68.31)	5.53 (5.38)	14.56 (14.94)
2i	82–5 (C_6H_6)	8.05 s, 8 s, 2.9 d, 1.05 m, 0.72 q, 0.35 q	75.45 (75.34)	4.19 (4.38)	20.20 (20.28)
2j	oil	8.05 s, 7.8 s, 5.75 m, 5.05 dd, 5 dd, 2.95 t, 2.1 q, 1.7 m, 1.55 m	76.80 (76.57)	5.75 (5.97)	17.59 (17.86)
5c	172–4 (EtOH)	7.95 s, 7.7 s, 1.55 s	80.09 (79.95)	8.34 (8.39)	11.80 (11.66)
5g	oil	8.05 s, 7.85 s, 4.2 m, 3.8 m, 2.8 t, 2.35 m, 1.6 m	64.51 (64.86)	7.32 (7.26)	6.1 (6.30)
5h	oil	8.1 s, 7.8 s, 3.7 s, 2.8 t, 2.35 m, 1.6 m	67.9 (68.72)	7.29 (7.34)	7.1 (7.20)
6c	189–90 (EtOH)	7.8 s, 1.55 s	80.00 (79.95)	8.33 (8.39)	11.63 (11.66)
6g	oil	7.57 s, 4.2 m, 3.85 m, 2.8 t, 2.35 m, 1.6 m	64.98 (64.84)	7.30 (7.26)	6.21 (6.30)
6h	83–4 (MeOH)	7.55 s, 3.7 s, 2.8 t, 2.35 m, 1.6 m	68.43 (68.72)	7.31 (7.34)	7.22 (7.29)
8g	oil	7.55 s, 6.2 m, 3.85 m, 2.8 t, 2.35 m, 1.6 m	64.94 (64.84)	7.19 (7.26)	6.35 (6.30)
8h	oil	7.55 s, 3.7 s, 2.8 t, 2.35 m, 1.6 m	68.02 (68.72)	7.21 (7.34)	7.19 (7.29)
9	180 (EtOH)	8.4 s, 8.65 s, 4.2 m, 6.15 s	64.31 (64)	3.25 (3.13)	18.41 (18.66)
13	oil	8.05 s, 7.9 s, 5.8 m, 5.1 dd, 5 dd, 3.1 t, 1.9 d	75.49 (75.34)	4.29 (4.38)	20.35 (20.28)
14	oil	8.05 s, 7.8 s, 3 d, 2.25 m, 1.7 m, 1.3 m	76.72 (76.57)	5.65 (5.57)	17.75 (17.86)

[a] Furthermore, IR spectra (nitrile band at ca 2210 cm^{-1}) and mass spectra are in accord. For representative ^{13}C NMR spectral data, see Table VI.

Table VI. Representative ^{13}C NMR Spectral Data of the Alkylbenzenenitriles[a]

	1-C	2-C	3-C	4-C	5-C	6-C	C≡N	others
2c	119.2	113.5	139	114.2	159.8	132	116.5, 116.3, 114.4	36.7, 29.5
2h	119.2	113.6	137	117.5	152.4	134.5	114.5, 114.2, 114	173.6, 51.5, 34.5, 33.5, 29.8, 28.4, 24.2
2i	119.3	113.7	136.7	117.5	152.2	134.1	114.6, 114.4, 114.2	38.6, 10, 5
5c	114.7	151.6	133.4	114.7	151.6	133.4	119	35.3, 29.8
5h	116.1	145.5	132	116.1	145.5	132	119	173.8, 51.5, 34.5, 33.6, 30, 28.5, 24.4
6c	109.3	141.5	109.3	158.1	124.9	158.1	118	36.5, 29.8
6h	111	136.7	111	151	130.7	151	116	173.9, 51.5, 34.5, 33.6, 30, 28.5, 24.4
8h	113	113	133.9	146.6	146.6	133.9	115.7	174, 51.6, 33.7, 32.3, 30, 28.8, 24.5
13	119.2	113.6	136.8	117.5	151.4	134.2	114.5, 114.3, 114	135, 117.8, 38.6, 34

[a] In δ, measured in $CDCl_3$. In every case the observed ring resonances fit well with the values calculated from tabulated substituent increments, see: Kalinowski, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: Chichester, 1984.

and probably causes the observed deprotection. This does not change the conclusion that C–C cleavage takes place only through a singlet, not a triplet, path.]

For the present purpose, the TCBQ experiments (via unambigous triplet path) serve to support the rationalization of the effect of chlorinated additives as heavy atom induced intersystem crossing from the initial singlet TCNB–donor radical ion pair to the corresponding triplet (path g in Scheme V). The subsequent course of the reaction is not clear for the moment, and the mechanistic hypotheses presented above are currently being examined. Apparently, intersystem crossing is complete under our conditions, and deprotection occurs at the same rate as carbon–carbon cleavage.

Conclusions. In this work it has been shown that under suitable conditions efficient electron-transfer chemistry can be carried out also using relatively poor donors such as acetals (and for the first time the use of a pair of radical clocks gives the timing of radical cation cleavage). We also showed that a relatively high oxidation potential of the donor *favors* cleavage of the radical cation since it lowers the corresponding ΔG value (see eq 8), provided of course that the radical produced is not too hard to oxidize. This condition is easily met, since radicals are often easily oxidized, and thus photoinduced oxidation of poor donors makes the cleavage of strong bonds possible. This observation should stimulate research of new electron transfer photoinduced reactions using aliphatic donors. At any rate, the present findings disclose a new mild method of preparing aliphatic radicals in solution, which should be exploited from the synthetic point of view. In particular, the part of the process which occurs out of cage should offer a large potential for manipulation for synthetic aim.

Experimental Section

General Information. The ^{1}H NMR spectra were recorded on either a Bruker 80 or 300 spectrometer and are reported in parts for million (ppm) downfield from TMS. Mass spectra were obtained on a Finnigan instrument and are reported in m/z (rel intensity). IR spectra were recorded on a Perkin-Elmer 297 spectrometer. Elemental analyses were performed by means of a Carlo Erba Model 1106 instrument. Melting points were determined by using a Büchi "Tottoli" apparatus. Anhydrous acetonitrile was obtained by refluxing and fractional distillation from CaH_2. Solvents for chromatography were distilled before use. Silica gel for flash chromatography was Merck 9385.

Reagents. 1,2,4,5-Benzenetetracarbonitrile was prepared from the acid.[17] An intimate mixture of pyromellitic acid (10 g) and urea (13 g) was heated at 135–40 °C for 6 h. After cooling, the mixture was stirred with 25% aqueous ammonia for 1.5 h. Filtering and washing with aqueous NH_3 and water gave the tetramide (6 g, 60% yield); 10 g (0.04 mol) of this product in DMF (56 g) was heated at 60 °C, 19 g (0.16 mol) of $SOCl_2$ was slowly added, and heating at 60 °C was continued for 7 h. Dilute HCl was added, and the solid was filtered and washed with water until neutral washings were obtained. Repeated extraction of the residue with hot acetic acid and recrystallization of the unsoluble material from nitroethane gave the nitrile, 7.1 g, 40% yield, mp 250 °C.

The acetals **1b–e** and **1i–j** were prepared from the corresponding carbonyl derivatives by azeotropic water elimination from the benzene–ethylene glycol solution in the presence of *p*-toluenesulfonic acid (TSA) and redistillation.[18] Compound

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1a was prepared from dry acetone, ethylene glycol, and TSA at room temperature for 12 h followed by addition of K_2CO_3 and fractional distillation,[19] and compound 10c was prepared from 3,3-dimethyl-2-butanone and triethyl orthoformate in absolute ethanol in the presence of TSA.[20] The acetals 1f and 10a were of commercial origin. TCBQ was a recrystallized commercial sample. Mass spectrum of 1c: 129 (75), 99 (4), 87 (100), 57 (10), 43 (40), 32 (65).

Photochemical Reactions. A solution of TCNB (100 mg, 0.01 M) in 60 mL of MeCN was placed in round quartz tubes and degassed by flushing with purified argon. The amount of acetal required for making the solution 0.05 M was then added, and after brief purging, the serum-capped tubes were irradiated for 0.5–3 h by means of a multilamp apparatus fitted with six 15-W phosphor-coated lamps (emission centered at 320 nm). The solvent was evaporated, and the residue bulb-to-bulb distilled under reduced pressure (50 mmHg) in order to isolate excess acetal and the 2-hydroxyethyl aliphatic esters. The residue was then submitted to flash chromatography in order to separate the alkylated aromatic nitriles by eluting with a cyclohexane–ethyl acetate mixture of increasing polarity. Further thin-layer chromatography was required for the more complicate mixtures. In the case of 1d, a much easier separation was obtained when the esters had been previously trans esterified by brief refluxing in methanol in the presence of hydrochloric acid.

Identification of the Photoproducts. The structures of the alkylbenzenenitriles 2, 5, 6, 8, and 9 were assigned on the basis of elemental analysis and spectroscopic characteristics. The most significant features are reported in Tables V and VI. Each of the hydroxyethyl esters 5g, 6g, and 8g was obtained as an oil not completely free of the other isomers; however, the NMR spectrum of each fraction was sufficiently clean to allow identification. The aliphatic hydroxyalkyl esters 3a and 3d are known compounds and are identical to samples prepared by synthesis;[21,22] 3d was also converted to methyl hexanoate. The ortho ester 12′ was recognized by comparison with a sample prepared through an unambigous synthesis. The imino ester hydrochloride MeC(OMe)=NH·HCl (5 g),[23] ethylene glycol (2.8 mL), and K_2CO_3 (1 g) in anhydrous MeCN (50 mL) were stirred at 40–50 °C for 6 h. The reaction course was followed by VPC. Some K_2CO_3 was added, the salt was filtered, and the liquid distilled under reduced pressure (50 mmHg) to yield the ester 12′ (3.1 g): NMR δ 2.05 s, 3.3 s, 4.1 AB system.

Quantum Yield Determination. Experiments for quantum yield determination were carried out either in quartz tubes placed in a rotating merry-go-round and illuminated by means of a multilamp apparatus as above or in spectrophotometric cuvettes irradiated by means of a focalized Osram 150-W high-pressure mercury arc fitted with an interference filter centered at 313 nm. Reagents consumption and product formation were determined by VPC (after conversion of the 2-hydroxyethyl to methyl ester when appropriate).

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Registry No. 1a, 2916-31-6; 1b, 937-94-0; 1c, 6135-54-2; 1d, 177-10-6; 1e, 17155-64-5; 1f, 646-06-0; 1i, 139071-38-8; 1j, 15144-28-2; 2a, 88830-20-0; 2b, 139071-39-9; 2c, 132381-82-9; 2e, 139071-45-7; 2g, 139071-41-3; 2h, 139071-44-6; 2i, 139071-47-9; 2j, 132381-83-0; 3a, 542-59-6; 3i, 139071-49-1; 4b, 110-54-3; 5c, 139071-40-2; 6c, 139100-52-0; 6h, 139071-43-5; 7h, 106-73-0; 8h, 139071-44-6; 9, 139071-46-8; 10a, 77-76-9; 10c, 52162-28-4; 11a, 67-64-1; 11b, 111-13-7; 11c, 75-97-8; 11e, 97-96-1; 11f, 50-00-0; 11i, 14113-98-5; 11j, 3664-60-6; 13, 139071-48-0; 14, 132381-84-1; 15, 96-37-7; 1,2,4,5-benzenetetracarbonitrile, 712-74-3; pyromellitic acid, 89-05-4; urea, 57-13-6; 1,2,4,5-benzenetetraamide, 6183-35-3; acetone, 67-64-1; 3,3-dimethyl-2-butanone, 75-97-8; triethyl orthoformate, 122-51-0.

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Formation and Reactivity of σ-Radical Cation Intermediates in the C–C Coupling Reaction of Phenyldiazomethanes by One-Electron Oxidation

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One-electron oxidation of phenyldiazomethanes afforded *cis*-stilbene predominantly. The reaction was independent of the oxidation methods, e.g., electrolysis, copper(II), triarylaminium salts, or photosensitized one-electron oxidations. The C–C coupling reaction was retarded by introducing α-substituents on phenyldiazomethane. The ESR spectra of diazoalkane radical cations could be obtained during the electrolysis at low temperature and the resulting spectra revealed their unique electronic structure as σ-radicals for most cases. When a bulky *tert*-butyl group was substituted, the corresponding π-radical cation was observed, but the C–C coupling reaction did not occur. The novel HOMO–LUMO switching by one-electron removal from the HOMO π-orbital of diazomethane is explained by the interaction of phenyl group with the C–N–N σ-radical moiety. The C–C coupling reaction proceeds via facile [4 + 2] cycloaddition between the diazomethane and σ-radical cation, and the preferential formation of *cis*-olefins is based on the secondary orbital interaction between the two phenyl groups. The structure and the stability of radical cation intermediates are rationalized on the basis of ab initio calculations.

Introduction

Dimerizations of diazoalkanes affording olefins or azines are well-known and are mostly explained as carbenoid reactions catalyzed by metallic salts.[1] These reactions are not always useful because of formation of product mixtures involving olefins, azines, glycols, and ketones. An exceptionally clean reaction has been reported for the oxidation of diphenyldiazomethane; the corresponding dimeric olefin was obtained in high yields by the anodic oxidation[2] and

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