Photochemical Reaction of Phthalimides and Dicyanophthalimides with Benzylic Donors

Mauro Freccero, Elisa Fasani, and Angelo Albini*

Department of Organic Chemistry, The University, V. Taramelli 10, Pavia, Italy, and Institute of Organic Chemistry, The University, V. Giuria 7, Torino, Italy

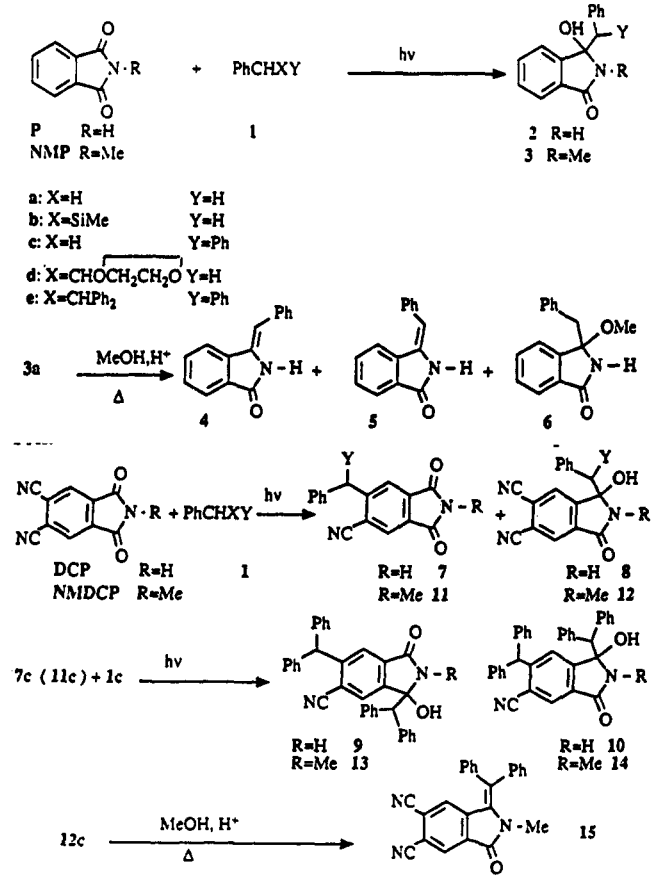
Received June 8, 1992 (Revised Manuscript Received November 30, 1992)

Irradiation of phthalimides in the presence of benzylic donors PhCRHX (R=H, Ph, X=H, $SiMe_3$, $CHPh_2$, $CHOCH_2CH_2O$) proceeds via electron transfer and radical cation cleavage, resulting in benzylation at the carboximide moiety to yield 3-benzyl-3-hydroxyisoindol-1-ones. With 4,5-dicyanophthalimides substitution of benzyl for a cyano group is a competitive, and in some cases predominating, pathway. A rationalization is proposed on the basis of the in cage vs out of cage radical cation cleavage. In the first mechanism, the radical anion of the dicyanophthalimide, where spin and charge are differently located, probably assists the radical cation fragmentation.

The photochemical reactivity of phthalimide and some of its derivatives has been extensively investigated in several laboratories.[1-5] In a typical example, *N*-methylphthalimide (NMP) has been found by Mazzocchi, to react with alkenes according to four modes,[1c] viz. i, reductive addition to the C=O bond, ii, the same, but involving also addition of a nucleophile, iii, insertion into the C-N bond, and iv, cycloaddition onto the C=O bond. The last reaction arises from the triplet state, whereas the other three involve a charge-transfer interaction of the alkene with the NMP singlet. While similar studies with phthalimides have been extended to several groups of donors, alkylbenzenes have been considered only marginally.[2c] On the other hand, the electron-transfer photochemistry of alkylbenzenes in the presence of arenenitriles has also been investigated in several laboratories including our own and usually results in benzylation of the aromatic ring.[6]

Product distribution in the last group of reactions depends on whether the chemistry takes place directly from the initially formed radical ion pair or from the solvent-stabilized free ions, and this in turn depends on the structure of the donor and the acceptor. Therefore, we decided to investigate the photochemistry of various benzylic donors in the presence both of phthalimides and of cyanated phthalimides in order to evaluate the mode of attack, of benzylic radicals on such molecules, in particular with the substituted phthalimides where competition between different sites was expected.

Scheme I



Results

The irradiation of an acetonitrile solution of phthalimide (P) or *N*-methylphthalimide (NMP) and toluene (**1a**), benzyltrimethylsilane (**1b**), and diphenylmethane (**1c**) leads to the expected products, viz. the hydroxyisoindolones **2a,c** from P and **3a,c** from NMP (Scheme I, Table I). As it is already known, in such products the cyclic form predominates over the tautomeric open-chain ketoamide.[7a]

Product **3c** was obtained from NMP and **1c** also by irradiation in methanol, although in this case the imide

(1) (a) Mazzocchi, P. H. *Org. Photochem.* **1981**, *5*, 421. (b) Mazzocchi, P. H.; Wilson, P.; Khachik, F.; Klinger, L.; Minamikawa, S. *J. Org. Chem.* **1983**, *48*, 2981. (c) Mazzocchi, P. H.; Klinger, L. *J. Am. Chem. Soc.* **1984**, *106*, 7567. (d) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *J. Org. Chem.* **1985**, *50*, 2681. (e) Somich, C.; Mazzocchi, P. H.; Edwards, M.; Morgan, T.; Aummon, H. L. *J. Org. Chem.* **1990**, *55*, 2624.

(2) (a) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407. (b) Machida, M.; Takechi, H.; Kanaoka, Y. *Tetrahedron Lett.* **1982**, 4981. (c) Kanaoka, Y.; Sakai, K.; Murata, R.; Hatanaka, Y. *Heterocycles* **1975**, *3*, 719.

(3) (a) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1985**, *50*, 1426. (b) Kubo, Y.; Taniguki, E. Araki, T. *Heterocycles* **1989**, *29*, 1857.

(4) (a) Coyle, J. D. *Pure Appl. Chem.* **1988**, *60*, 941. (b) Coyle, J. D.; Harriman, A.; Newport, G. L. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 799.

(5) Yoon, U. C.; Kim, H. J.; Mariano, P. S. *Heterocycles* **1989**, *29*, 1041.

(6) (a) Albini, A.; Sulpizio, A. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. C, p 88. (b) Sulpizio, A.; Albini, A.; d'Alessandro, N.; Fasani, E.; Pietra, S. *J. Am. Chem. Soc.* **1989**, *111*, 5773. (c) Lewis, F. D.; Petisce, J. R. *Tetrahedron* **1986**, *42*, 6207. (d) Ohashi, M.; Suwa, S.; Osawa, Y.; Tsujimoto, K. *J. Chem. Soc., Perkin Trans 1* **1979**, 2219.

(7) (a) Marsili, A.; Scartoni, V. *Gazz. Chim. Ital.* **1972**, *102*, 507. (b) Marsili, A.; Scartoni, V. *Gazz. Chim. Ital.* **1972**, *102*, 806.

0022-3263/93/1958-1740$04.00/0

Table I. Isolated Yield of the Photoproducts from Preparative Irradiation

imide	donor[a]	condns	irradn time (h)	unreacted imide	products (% yield)[b]
P[c]	1a	d,e	40	64	2a (28)
	1b	d,e	15	43	2a (61)
	1c	d,e	14	64	2c (26)
NMP[c]	1a	d,e	40	56	3a (10)
	1b	d,e	15	35	3a (52)
	1c	e,f	6	65	3c (32)
	1c	f,g	6	35	3c (30)
DCP[h]	1a	d,e	2		7a (49), 8a (tr)
	1b	d,e	0.75	20	7a (61), 8a (25)
	1c	e,f	1	20	7c (16), 8c (70), 9 (2), 10 (1)
NMDCP[h]	1a	d,e	2		11a (50)
	1b	d,e	0.75	20	11a (65), 12a (31)
	1c	e,f	1.75	5	11c (14), 12c (79), 13 (3), 14 (1.5)

[a] 0.1 M. [b] Calculated on the reacted imide. [c] 0.02 M. [d] Irradiation by means of external phosphor-coated lamp, emission maximum at 320 nm. [e] In acetonitrile. [f] Irradiation by means of an internal high-pressure mercury arc, through Pyrex. [g] In methanol. [h] 0.01 M.

Table II. Product Distribution and Limiting Quantum Yields with the Dicyanoimide DCP (2.5×10^{-3} M) in Acetonitrile

donor[a]	$\Phi_{lim}^{(7)}$	$\Phi_{lim}^{(8)}$	$\Phi_{lim}^{(7+8)}$	7/8
1a, $PhCH_3$	0.085	0.015	0.10	5.8
1b, $PhCH_2SiMe_3$	0.16	0.15	0.31	1.1
1c, Ph_2CH_2	0.07	0.29	0.36	0.25
1d, $PhCH_2CHOCH_2CH_2O$	0.14	0.05	0.19	3.0
1e, $Ph_2CHCHPh_2$	0.07	0.32	0.39	0.23

Table III. Quantitative Data in Acetonitrile

substrate	quencher	K_{sv},[a] M^{-1}	k_q, M^{-1} s^{-1}	K',[b] M^{-1}
P	1c			19
DCP[c]	1a	141	1.5×10^{10}	127
	1b	143	1.5×10^{10}	149
	1c	111	1.2×10^{10}	121
	1d	140	1.5×10^{10}	136

[a] From fluorescence quenching. [b] From photochemical quantum yield (see Figure 1). [c] τ = 9.5 ns.

Table IV. Voltammetric and Spectroscopic Data in Acetonitrile

substrate	E^{red} vs SCE, V	E_S, kcal/mol	E_T, kcal/mol	ΔG_{et} (1a)[a] kcal/mol
P	−1.43	80[b]		−1.4
NMP	−1.46	80[b]	68.5[b]	−0.7
DCP	−0.75	89	68	−27.7
NMDCP	−0.75	89	66	−26.0

[a] Free energy change for electron transfer from 1a to the singlet excited state of the acceptor, as calculated by the Weller equation. [b] See: Coyle, I. D.; Newport, G. L.; Harriman, A. *J. Chem. Soc., Perkin Trans. 2* 1978, 133. The low value of E_{S_1} ($n\pi^*$), as proposed by Coyle et al., is related to a low-intensity tail in the UV spectrum extending to ca. 335 nm. No such tailing appears in the spectrum of DCP (S_1 $\pi\pi^*$). Even if the E_s values for P might have been somewhat underestimated, this does not affect the observed trend of ΔG_{et}.

was in part consumed by a reaction with the solvent. When refluxed in acidic methanol, the hydroxyisoindolenone **3a** gave the two isomeric phenylidene derivatives **4** and **5**[7b] as well as a minor amount of the methoxyisoindolenone **6**.

We next turned to 4,5-dicyanophthalimide (DCP), obtained by partial dehydration of pyromellitic amide with thionyl chloride (molar ratio 1:8) at 50–70 °C. Irradiation of an acetonitrile solution containing **1a** gave a single main product, easily recognized from elemental analysis and spectroscopic characteristics as the benzylcyanophthalimide **7a**. This was the main product also when the silane **1b** was used, but there it was accompanied by a significant amount of a second product, obtained in traces with **1a**, viz. the hydroxyindolone **8a**. With diphenylmethane **1c** the analogous hydroxyindolone **8c** was by far the main product and was accompanied by a low amount of the benzhydrylmonocyanoimide **7c**. Furthermore, two additional products were separated and found to contain two benzhydryl groups. Spectroscopic characterization showed that these were compounds **9** and **10**, and separate irradiation of the benzhydrylcyanophthalimide **7c** in the presence of **1c** demonstrated that they were secondary photoproducts from it.

With this imide, the investigation was extended to two further donors, the ethylene acetal of phenylacetaldehyde (**1d**) and 1,1,2,2-tetraphenylethane (**1e**); it turned out that in the first case the yield of **7a** was larger than that of **8a**, while in the latter one **8c** was more abundant than **7c**. With all the donors dimerization to yield diphenylmethane (from **1a**, **1b**, **1d**) or tetraphenylethane (from **1c**) was also observed, but it occurred to a much smaller extent than the alkylation of the imide.

The irradiation of 4,5-dicyano-*N*-methylphthalimide (NMDCP) confirmed the trend, with predominant or exclusive cyano group substitution with the donors **1a** and **1b** (yield of **11a** > **12a**) and predominant attack at the carboximide moiety with **1c** (yield of **12c** > **11c**). In the last case a small amount of the bisalkylated derivatives **13** and **14** resulting from a secondary photoreaction of **11c** was also obtained. Refluxing **12c** in acidic methanol gave the yellow tetrasubstituted alkene **15**.

A series of experiments designed to clarify the mechanism were carried out. Quantum yields for photoproduct formation were measured at different arene concentrations for all substrates (**1a–e**). The results are reported in Figure 1 as the reciprocal plots for the pairs P/**1c** and DCP/**1a–e** (see also Table III). These experiments were carried out at low conversion, and under these conditions the exact ratio for product **7a,c** vs product **8a,c** was free for secondary photoreactions as determined (Table II). One can see that the ratio **7/8** does not change over the concentration range explored and is larger than 1 for the benzylic donors (**1a,b,d**), while it is near 0.25 for the benzhydryl donors (**1c,e**). The room-temperature fluorescence of P and NMP is quite weak, and reliable quenching data were difficult to obtain. However, DCP and NMDCP emitted more strongly, and all the arenes considered quenched their fluorescence in acetonitrile. Representative Stern–Volmer constants are reported in Table III.

The reduction potential of the four phthalimides in acetonitrile was measured by cyclic voltammetry (see Table IV). Previous measurements[8] on the noncyanated derivatives had been carried out in dimethylformamide and had given results quite similar to the present ones, although in that case there is a difference between P and DMP due to the formation of a hydrogen bond with the solvent for the former product.

Discussion

The literature reports examples of both singlet and triplet reactions in the photochemistry of phthalimides.[1-5] The characterization of the lowest excited singlet state is

(8) Leedy, D. W.; Muck, D. L. *J. Am. Chem. Soc.* 1971, *93*, 4284.

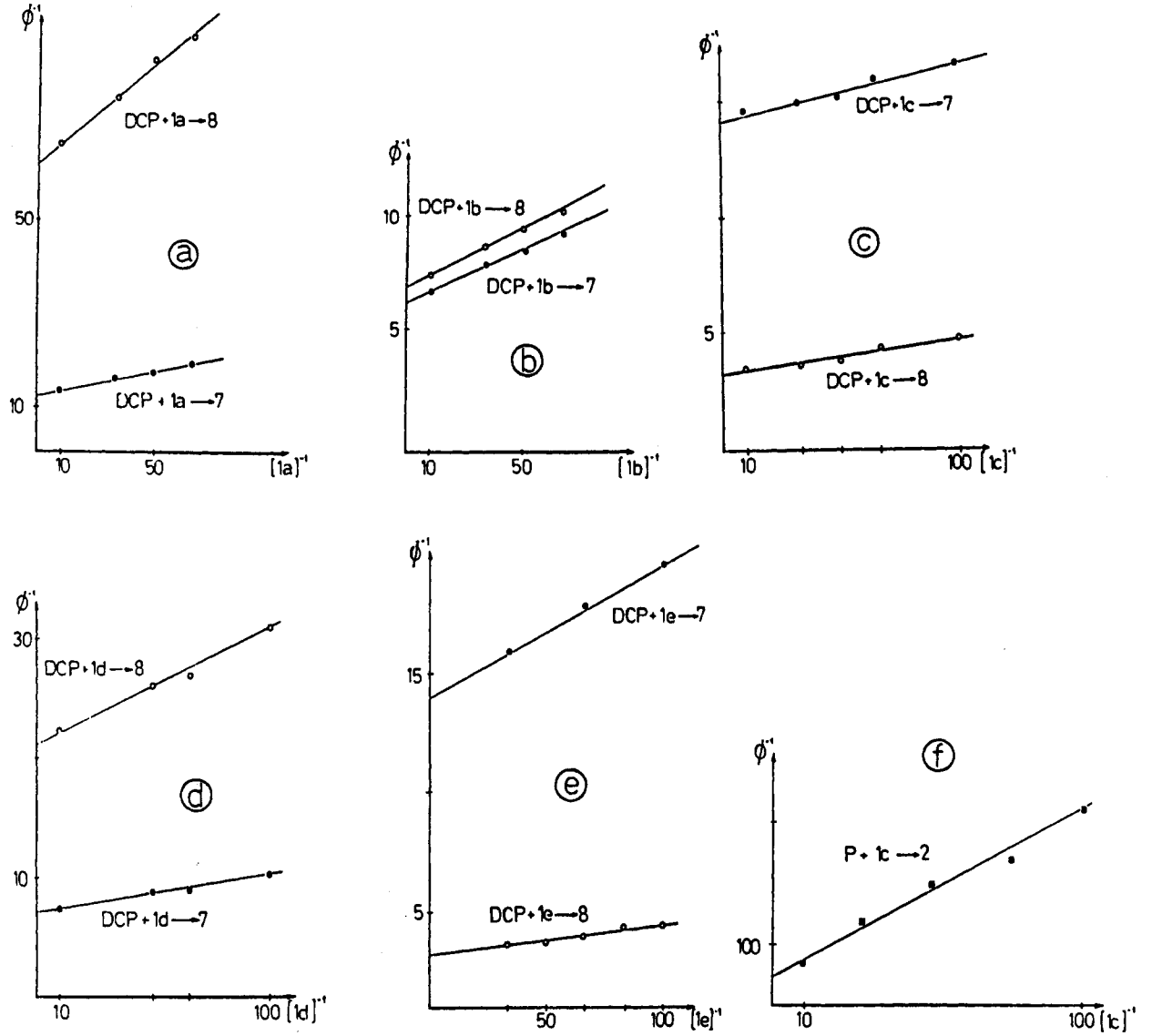


Figure 1. Double reciprocal plot for the reaction quantum yield vs the donor concentration.

not unambigous since phthalimide (P) is only weakly fluorescing and shows a long tail in the absorption spectrum. The hypothesis has been presented that the lowest singlet is a $n\pi^*$ state, while a slightly higher-lying $\pi\pi^*$ state is responsible for emission.[4b] Which is the nature of the reacting excited state has not always been unambigously established, but as mentioned in the introduction, it has been recognized in the case of alkenes that the Paterno–Büchi cycloaddition to the C=O bond is a triplet reaction, while the other ones (reduction, additions to the C=O bond, and insertion into the C–N bond) are singlet processes.[1]

The presently considered cyanated phthalimides DCP and NMDCP fluoresce (and phosphoresce) more strongly than P and NMP. Both emissions are similar in shape and wavelength to what was observed with related benzene nitriles, showing the $\pi\pi^*$ nature of both lowest singlet and triplet states. Fluorescence quenching studies show that the singlet state is efficiently intercepted by the arenes 1. The observed linear relation between the reciprocal of quantum yield and the concentration of 1 allows evaluation of the quenching rate for the reactive excited state. The values obtained (K' = intercept/slope in Figure 1, see Table III) are close to the Stern–Volmer fluorescence quenching, thereby identifying the reacting state of the imides as the excited singlet. The corresponding plot for P gives a parameter K' that is lower by a factor of 8–10. The electrochemical and spectroscopic data in Table IV show that electron transfer from the benzene derivatives 1 to the excited singlet of the cyanoimides is an exergonic process, while it is near to thermoneutral with P and NMP. Thus, there is no doubt that the reaction is initiated by electron transfer to the singlet excited state in the case of DCP and NMDCP. As for P, the simplest rationalization in view of the similarity of the reaction is that the first step is also in this case electron transfer to the singlet, although it occurs at a lower rate due to the less negative ΔG (electron transfer to the triplet is thermodynamically unfeasible).

The following step is fragmentation of the arene radical cations to yield the benzyl (or respectively benzhydryl) radicals according to the scheme

$$\mathrm{PhCHRX}^{\bullet+} \rightarrow \mathrm{PhCHR}^{\bullet} + \mathrm{X}^{+} \quad (\mathrm{R} = \mathrm{H}, \mathrm{Ph})$$

Literature analogy supports this view. In particular, deprotonation of the radical cations of toluene[6] and diphenylmethane[6b] has been observed when such species have been produced by electron transfer to the excited

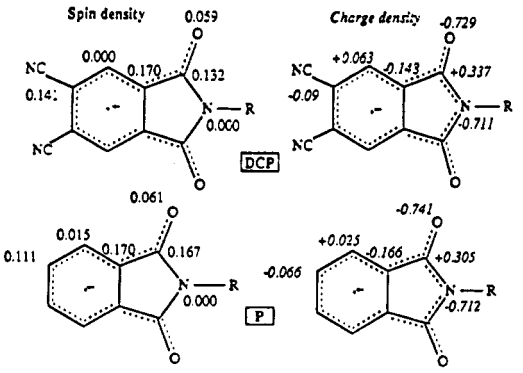


Figure 2. Calculated charge and spin densities for the radical anions of phthalimide and 4,5-dicyanophthalimide.

singlet and various nitriles; carbon–carbon bond cleavage occurs both in $\mathbf{1d}^{\bullet+}$ and in $\mathbf{1e}^{\bullet+}$[6b,9-11] (with the latter compound fragmentation is observed at room temperature when the acceptor is 1,4-dicyanonaphthalene,[6b] but only at 80 °C when it is 1,4-dicyanobenzene),[9b] and desilylation takes place with $\mathbf{1b}^{\bullet+}$.[6b,11] The cleavage occurs in such a way as to generate the cation corresponding to the more easily oxidized radical and the other fragment as the neutral radical[12] (in the present case the benzyl or the benzhydryl radical). The lowering of the bond dissociation energy occurring upon ionization can be evaluated through thermochemical cycles.[12] With some simplificative assumptions, such calculations show that a diminished but still sizeable barrier remains for the fragmentation of $\mathbf{1d}^{\bullet+}$ (ca. 10 kcal/mol)[9a] of $\mathbf{1e}^{\bullet+}$ (9.3 kcal/mol)[9b] and $\mathbf{1b}^{\bullet+}$ (ca. 30 kcal/mol;[11] in this case, however, some of the values used refer to the gas phase, making the result not free from uncertainty), while deprotonation of $\mathbf{1a}^{\bullet+}$ and $\mathbf{1c}^{\bullet+}$ is expected to be exergonic.[6b] In the case of $\mathbf{1b}^{\bullet+}$ there are some indications for its cleavage in solution occurring as a nucleophile-assisted process.[11]

All of the reactions presented here follow a similar course, and this suggests that an electron transfer–radical cation cleavage mechanism is obeyed both with cyanated and with noncyanated imides. However, the mechanism requires further elaboration in order to explain why the efficiency for alkylation with **1b**, the radical cation of which should be the slower to cleave is higher than with **1a** or **1d**, or why the ratio for cyano group substitution vs addition to the carboxyimide group with DCP is larger with benzyl than with benzhydryl donors.

The rationalization we propose is based on the consideration of the spin and charge distribution in the cyanoimides. Figure 2 shows that while spin density is large both on the substituted benzene carbons and on the imide carbons, the charge is localized at the periphery of the molecule, viz. on the oxygen atoms and on the imide nitrogen.[13]

Thus, the reaction can be represented as follows (see Scheme II). With all the donors considered (D–X) the HOMO is a relatively undisturbed benzene HOMO, and the first interaction with the cyanoimides (A–Z) involves a polarized sandwich complex as usual in aromatic photochemistry. Then a σ bond β to the aromatic ring in the radical cation is cleaved. If this step takes place within this initial radical ion pair than a specific donor–acceptor orientation of the complex will be favored, viz. the one in which the developing positive charge will be in front of the negative charge (this would also make nucleophilic assistance to the cleavage easier). Since the following carbon–carbon bond formation will be fast, the regiochemistry of alkylation is determined by the orientation of the initial complex. Apparently, this favors benzylation of the aromatic ring (ipso substitution of a cyano group rather than attack to the C=O bond). Nucleophile assistance to the cleavage can occur either inter- or intramolecularly. The latter path (the cation becomes bonded to the negatively charged oxygen atom) is probably preferred; this would explain the more efficient cleavage of $\mathbf{1b}^{\bullet+}$ (where a strong silicon–oxygen bond is formed) with respect to $\mathbf{1a}^{\bullet+}$ (where a proton is transfered).[15] Thus, the rate of fragmentation under this condition is not simply related to the cleavage of the isolated radical cation in gas phase, but must take into account the bonds formed.

On the other hand, with the more bulky benzhydryl donors reaction from a tight complex is less likely because the complex is destabilized and, besides that, the cleavage yields a more stable (delocalized) radical. Thus, radical ion separation is easier and the benzhydryl radical is generated and reacts out of cage. The alkylation involves the reencounter of the benzyl radical and the imide radical anion and involves predominantly the imide function, both because in this way it encounters less steric hindering and because a more stable anion is formed (aromaticity is conserved in the anionic intermediate and the charge is localized on the oxygen atom). At any rate with both types of donors coupling of the benzyl radicals remains a minor process showing that $DCP^{\bullet-}$ is a good radical trap.

This work shows that benzyl derivatives participate in electron transfer photoreactions with phthalimides as previously shown with other donors. Furthermore, two new acceptors, 4,5-dicyanophthalimide and its *N*-methyl derivative, have been considered. In this case, spin and charge density are localized far apart in the radical anion, and this suggests that radical cations cleave through intramolecular nucleophile assistance, at least when they are not too bulky. If our hypothesis is correct, these cyanated phalimides may be a probe of the in cage vs out of cage course and, in general, of the mechanism of radical cation fragmentation, a problem of current interest.

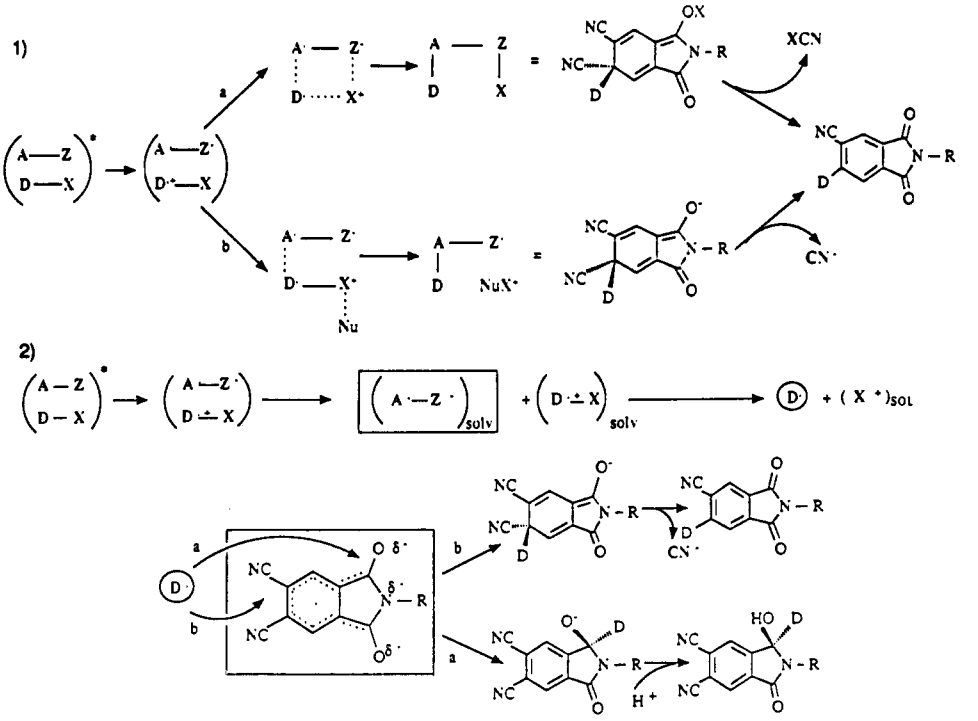
Experimental Section

Phthalimide and the donors **1a–e** were of commercial origin. NMP, **1d**, and **1e** were prepared according to literature methods.

4,5-Dicyanonaphthalimides. An intimate mixture of 1,2,4,5-benzenetetracarboxylic acid (20 g) and urea (24 g) in a round-bottomed flask was heated at 135–40 °C in an oil bath for 6 h. The solid obtained was grounded, suspended in 25% aqueous ammonia (125 mL), and stirred for 12 h. Filtration, washing with 25% ammonia and then with water until the filtrate was

(9) (a) Mella, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1992**, *57*, 3051. (b) Arnold, D. R.; Lamont, L. J. *Can. J. Chem.* **1989**, *67*, 2119.
(10) Mizuno, K.; Terasaka, K.; Yasueda, M.; Otsuij, Y. *Chem. Lett.* **1988**, 145.
(11) Dinnocenzo, J.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973.
(12) (a) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068. (b) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. *Chem. Phys. Lett.* **1986**, *131*, 189.
(13) Spin and charge distribution are calculated according to the method of McLachlan, ref 14a. For the parametization see ref 14b,c.
(14) (a) McLachlan, A. D. *Mol. Phys.* **1958**, *1*, 233. (b) Rieger, P. H.; Fraenkel, G. K. *J. Chem. Phys.* **1962**, *35*, 2795. (c) Sioda, R. E.; Koski, W. S. *J. Am. Chem. Soc.* **1967**, *89*, 475.
(15) That radical anions of suitable structure induce in cage deprotonation of radical cations has been previously noticed (ref 16).
(16) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215.
(17) Lawton, F. A.; McRitchie, D. D. *J. Org. Chem.* **1959**, *24*, 26.

Scheme II. Mechanism for the In Cage (1) and Out of Cage (2) Reactions[a]



[a] In the radical anion $AZ^{\bullet-}$ the spin is delocalized on positions 1, 3a, 5 and the charge is on the oxygen and nitrogen atoms. In the radical cation $DX^{\bullet+}$ both charge and spin are on the ring. In the mechanism 1 fragmentation of the σ bond is assisted by transfer of a X^+ cation either to the phthalimide oxygen or to an external nucleophile; in mechanism 2 fragmentation occurs on the free-radical cation, and the benzyl radical reacts on reencounter with $AZ^{\bullet-}$. In the first case the radical cation has a predetermined orientation and benzylation at position 5 is preferred, in the latter case both possible attacks occur.

neutral, and oven drying gave **1,2,4,5-benzenetetracarboxamide** (14.5 g, 74%, mp 300 °C). Dehydration of the tetramide gave three products (the diimide, the dicyanoimide, and tetracyanobenzene) in different yields according to the conditions.[17] In our hands, the best conditions for the dicyanoimide were as follows. To a vigorously stirred solution of the tetramide (8 g, 32 mmol) in DMF (10 mL) was added 20 mL (36.62 g, 274 mmol) of thionyl chloride at once, and the temperature was maintained at 60–70 °C for 7 h. The cooled solution was poured in a mixture of concd hydrochloric acid and ice, and the light-yellow precipitate was filtered, washed until a neutral filtrate was obtained, oven dried, and extracted with 50 mL and then 3 × 20 mL of hot acetic acid (the diimide is not extracted under these conditions). Part of the product precipitated out on cooling as dark chips and another part on diluting with four parts of water. The reunited solids were recrystallized from nitroethane to give **4,5-dicyanophthalimide** (DCP) as colorless crystals, mp 280 °C, 1.26 g (20%): ^{1}H NMR ($(CD_3)_2CO$) 2.75 (s, 1 H, exch) 8.60 (s, 2 H); IR (KBr) 3220, 2255, 2253, 1780, 1727 cm^{-1}. To a vigorously stirred solution of DCP (1 g, 5 mmol) in methanol (50 mL) was added a solution of KOH (0.3 g, 5.3 mmol) in MeOH (5 mL) dropwise. The voluminous precipitate which slowly separated was filtered, washed with a little methanol, and vacuum dried overnight (the crystal took a violet hue superficially). It weighted 1.15 g (96.6%). A mixture of this salt and methyl iodide (2.2 mL, 5.16 g, 35.3 mmol) was heated in a steel container at 150 °C for 2 h. The solid thus obtained was dissolved in hot nitroethane, and a small amount of unreacted DCP crystallized out on cooling. Evaporation of the solution and recrystallization from ethanol gave **4,5-dicyano-*N*-methylphthalimide** (NMDCP), colorless crystals, mp 228–230 °C (0.64 g, 60%): ^{1}H NMR ($CDCl_3$) 3.25 (s, 3 H), 8.28 (s, 2 H); IR (KBr) 3051, 2242, 1780, 1759, 1715 cm^{-1}. When heated DCP and NMDCP pass through a characteristic sequence of color changes from colorless at room temperature to green on heating above 250 and 215 °C, respectively.

Preparative Irradiation. A solution of P (298 mg, 2 mmol) in 100 mL of acetonitrile containing 0.92 g of toluene (**1a**) was divided in five quartz tubes. These were serum capped, purged with purified argon, and irradiated in a multilamp apparatus fitted with six phosphor-coated lamps (center of emission 320 nm). After 40 h the solution was evaporated and the residue chromatographed on silica gel eluting with cyclohexane–ethyl acetate mixtures to give unreacted P (191 mg, 64%) and 3-hydroxy-3-(phenylmethyl)isoindol-1-one (**2a**), mp 154–5 °C (from MeOH, lit.[7a] 160–1 °C, 48 mg, 28%).

A solution of NMP (326 mg, 2 mmol) and diphenylmethane (1.68 g, 10 mmol) in acetonitrile (100 mL) was refluxed, cooled under argon, and irradiated for 6 h in an immersion well apparatus by means of a high-pressure 125-W mercury arc through Pyrex. Workup as above gave unreacted imide (212 mg) and 3-hydroxy-2-methyl-3-(diphenylmethyl)isoindol-1-one (**3c**, 69 mg, 30%), mp 192–4 °C (MeOH); NMR ($(CD_3)_2CO$) δ 2.75 (s, 3 H), 4.8 (s, 1 H), 5.5 (s, 1 H, exch), 7–7.5 (m, 14 H); IR (KBr) 3260, 1675 cm^{-1}. Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.0; H, 5.8; N, 4.0.

Other products were obtained under the same conditions (see Table I for conditions and yields). 3-Hydroxy-3-(diphenylmethyl)isoindol-1-one (**2c**), mp 156–8 °C: NMR ($(CD_3)_2CO$) δ 2.75 (s, 1 H, exch), 4.5 (s, 1 H), 5.6 (s, 1 H, exch) 7.0–7.5 (m, 10 H), 7.6–7.7 (m, 4 H); IR (KBr) 3310, 3290, 1695 cm^{-1}. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.3; H, 5.5; N, 4.2. 5-Cyano-6-(phenylmethyl)isoindoline-1,3-dione (**7a**): mp 210–11 °C (MeOH); NMR ($CDCl_3$) δ 4.4 (s, 2 H), 7.2–7.3 (m, 5 H), 7.8 (s, 1 H, exch), 7.75 (s, 1 H), 8.1 (s, 1 H); IR (KBr) 3352, 2231, 1783, 1700 cm^{-1}. Anal. Calcd for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.7; H, 3.7; N, 10.3. 5-Cyano-6-(diphenylmethyl)isoindoline-1,3-dione (**7c**): mp 222–3 °C (MeOH); NMR ($CDCl_3$) δ 6.1 (s, 1 H), 7.0–7.5 (m, 10 H), 7.85 (s, 1 H, exch), 7.7 (s, 1 H), 8.15 (s, 1 H); IR (KBr) 3230, 2230, 1770, 1750, 1725 cm^{-1}. Anal. Calcd for $C_{22}H_{14}N_2O_2$: C, 78.09; H, 4.17; N, 8.28. Found: C, 77.7; H, 4.4; N, 8.0. 5,6-Dicyano-3-hydroxy-3-(phenylmethyl)isoindol-1-one (**8a**): mp 156–7 °C (DMSO–H_2O); NMR ($(CD_3)_2CO$) δ 4.35 (s, 2 H), 7.25–7.35 (m, 5 H), 7.75 (s, 1 H), 8 (s, 1 H), 8.15 (s, 2 H, exch); IR (KBr) 3235, 2225, 1690 cm^{-1}. Anal. Calcd for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.53. Found: C, 70.2; H, 3.9; N, 14.2. 5,6-Dicyano-3-hydroxy-3-(diphenylmethyl)isoindol-1-one (**8c**): mp 204–6 °C (DMSO–H_2O); NMR ($(CD_3)_2SO$) δ 4.75 (s, 1 H), 7.0 (s, 1 H, exch), 7.1–7.6 (m, 10 H), 7.9 (s, 1 H), 8.3 (s, 1 H), 9.6 (s, 1 H, exch); IR (KBr) 3270, 2230, 1710 cm^{-1}. Anal. Calcd for $C_{23}H_{15}N_3O_2$: C, 75.60; H,

4.14, N, 11.50. Found: C, 75.3; H, 4.1; N, 11.3. 5-Cyano-3,6-bis(diphenylmethyl)-3-hydroxyisoindol-1-one (**9**): mp 171–4 °C (chromatographically purified); NMR ($CDCl_3$) δ 2.85 (s, 1 H, exch.), 4.25 (s, 1 H), 5.95 (s, 1 H), 6.5 (s, 1 H, exch), 7.05 (s, 1 H), 7.4–7.6 (m, 20 H), 7.55 (s, 1 H); IR (KBr) 3500, 3400, 3300, 2230, 1715 cm^{-1}. Anal. Calcd for $C_{35}H_{26}N_2O_2$: C, 82.98; H, 5.17; N, 5.53. Found: C, 82.8; H, 4.9; N, 5.6. 6-Cyano-3,5-bis(diphenylmethyl)-3-hydroxyisoindol-1-one (**10**): mp 177–8 °C (chromatographically purified); NMR ($CDCl_3$) δ 3.15 (s, 1 H, exch), 4.2 (s, 1 H), 5.9 (s, 1 H), 6.4 (s, 1 H, exch), 6.8 (s, 1 H), 7–7.5 (m, 20 H), 7.85 (s, 1 H); IR (KBr) 3350, 3420, 3300, 2230, 1710 cm^{-1}. Anal. Found: C, 82.6; H, 4.8; N, 5.4. The structure attribution to isomeric **9** and **10** is based on the larger spacing of H_4 and H_7 NMR signals in the latter one, where both carboxyamido and cyano groups are in the ortho position with respect to H_7. 5-Cyano-6-(phenylmethyl)-2-methylisoindoline-1,3-dione (**11a**): mp 195 °C (MeOH); NMR ($CDCl_3$) δ 3.3 (s, 3 H), 4.35 (s, 2 H), 7.25–7.4 (m, 5 H), 7.75 (s, 1 H), 8.1 (s, 1 H); IR 2230, 1775, 1703 cm^{-1}. Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.6; H, 4.4; N, 10.4. 5-Cyano-6-(diphenylmethyl)-2-methylisoindoline-1,3-dione (**11c**): mp 221–3 °C (MeOH); NMR ($CDCl_3$) δ 3.2 (s, 3 H), 6.05 (s, 1 H), 7.0–7.5 (m, 10 H), 7.7 (s, 1 H), 8.15 (s, 3 H); IR (Nujol) 2230, 1775, 1710 cm^{-1}. Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.39; H, 4.58, N, 7.95. Found: C, 78.2; H, 4.5; N, 7.9. 5,6-Dicyano-3-hydroxy-3-(phenylmethyl)-2-methylisoindol-1-one (**12a**): mp 183–6 °C (DMSO–H_2O); NMR ($(CD_3)_2CO$) δ 3.1 (s, 3 H), 3.6 (AB system, J = 14 Hz, 2 H), 5.8 (s, 1 H, exch), 6.8–7.2 (m, 5 H), 8 (s, 1 H), 8.1 (s, 1 H); IR (KBr) 3290, 2230, 1710 cm^{-1}. Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.27; H, 4.32; N, 13.86. Found: C, 70.9; H, 4.5; N, 13.8. 5,6-Dicyano-3-hydroxy-3-(diphenylmethyl)-2-methylisoindol-1-one (**12c**): mp 175–6 °C (DMSO–H_2O); NMR ($(CD_3)_2SO$) δ 3.75 (s, 3 H), 4.8 (s, 1 H), 6.9 (s, 1 H, exch), 7.0–7.5 (m, 11 H), 8.45 (s, 1 H); IR (KBr) 3300, 2235, 1695 cm^{-1}. Anal. Calcd for $C_{24}H_{17}N_3O_2$: C, 75.97; H, 4.52; N, 11.08. Found: C, 75.6; H, 4.5; N, 10.8. 5-Cyano-3,6-bis(diphenylmethyl)-3-hydroxy-2-methylisoindol-1-one (**13**): mp 166–9 °C (chromatographically purified); NMR ($CDCl_3$) δ 2.75 (s, 3 H), 2.8 (s, 1 H, exch), 4.0 (s, 1 H), 6.0 (s, 1 H), 6.75 (s, 1 H), 7.55 (s, 1 H), 7.25–7.35 (m, 10 H); IR (KBr) 3500, 3400, 3300, 2230, 1715 cm^{-1}. Anal. Calcd for $C_{36}H_{28}N_2O_2$: C, 83.05; H, 5.42; N, 5.38. Found: C, 82.8; H, 5.4, N, 5.2. 6-Cyano-3,5-bis(diphenylmethyl)-3-hydroxy-2-methylisoindol-1-one (**14**): mp 170–2 °C (chromatographically purified); NMR ($CDCl_3$) δ 2.7 (s, 3 H), 2.75 (s, 1 H, exch), 4.0 (s, 1 H), 6.0 (s, 1 H), 6.8 (s, 1 H), 8.0 (s, 1 H), 7.25–7.35 (m, 10 H); IR (KBr) 3500, 3410, 3300, 2230, 1710 cm^{-1}. Anal. Found: C, 82.9; H, 5.1; N, 5.2.

Reactions with Acids. A solution of product **3a** (50 mg) in MeOH (5 mL) containing concd aqueous HCl (20 mL) was refluxed for 1 h. Evaporation and chromatography of the residue as above gave (*Z*)-3-(phenylmethylene)-2-methylisoindolin-1-one (**4**, 28 mg, 60%),[7b] the corresponding *E* isomer (**5**, 14 mg, 30%),[7b] and 3-methoxy-3-(phenylmethyl)-2-methylisoindolin-1-one (**6**, 5 mg, 10%), mp 146–8 °C (MeOH): NMR ($(CD_3)_2CO$) δ 2.8 (s, 3 H), 3.0 (s, 3 H), 3.3 (d, 1 H, J = 14 Hz), 3.55 (d, 1 H, J = 14 Hz), 7.0–7.2 (m, 4 H), 7.5–7.6 (m, 5 H); IR (KBr) 1695, 1100 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.0; H, 6.6; N, 5.0.

A solution of product **12c** (50 mg) treated as above gave 5,6-dicyano-3-(diphenylmethylene)-2-methylisoindolin-1-one (**15**, 45 mg, 90%), mp 280 °C (MeOH): NMR ($CDCl_3$) δ 2.9 (s, 3 H), 6.7 (s, 1 H), 8.2 (s, 1 H)), 7.35–7.45 (m, 10 H). Anal. Calcd for $C_{24}H_{15}N_3O$: C, 79.76; H, 4.18, N, 11.63. Found: C, 79.4; H, 4.0; N, 11.6.

Quantum Yield Measurements. Absolute quantum yields were measured using 3-mL aliquots of acetonitrile solution containing the imides (2.5×10^{-3} M) and the donor in spectrophotometric couvettes after several freeze–degas–thaw cycles. The samples were irradiated by means of a focalized super-high mercury arc through an interference filter (λ_{max} = 313 nm). Light flux, determined by ferrioxalate actinometry, was about 5×10^{-7} Einstein min^{-1} cm^{-2}. Chemical analysis of the irradiated solutions was performed by HPLC.

Electroanalytical measurements were made with a Amel Model 472 recorder and EG&G Park Model 303A SDME. Solutions were purged with nitrogen for 10 min. Measurements were made in MeCN (~0.1% H_2O) with NEt_4ClO_4 as supporting electrolyte vs Ag/AgCl.

Acknowledgment. Support of this work by CNR, Rome, is gratefully acknowledged.