Photoinduced Single Electron Transfer Reactions of Bibenzyl and some of its Derivatives

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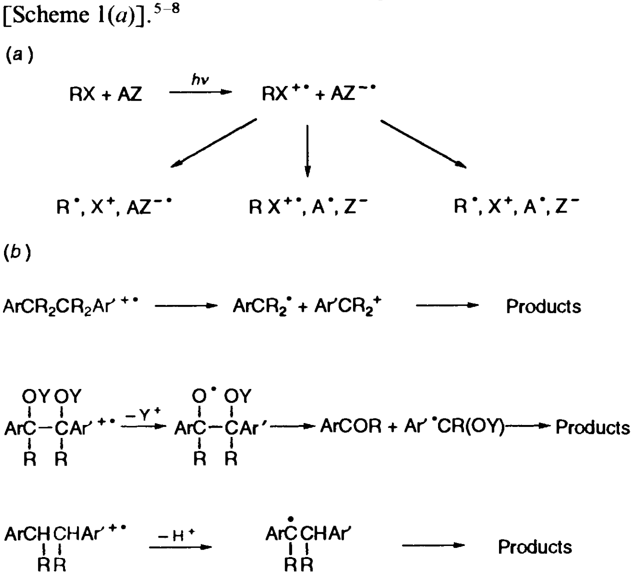
The photochemical reaction of bibenzyl **1**, its 4,4'-dimethoxy derivative **2** and bicumyl **3** with some aromatic nitriles (leading to alkylation of the nitrile) and tetranitromethane (TNM) (leading to ring trinitromethylation or nitration) involve SET fragmentation of the radical cation (either C–H or C–C bond) and, in the case of TNM, also of the radical anion.

Photochemically induced single electron transfer (SET) leads to a radical ion pair.[1,2] Reasonably efficient, and thus preparatively significant, processes based on this principle depend on the competition between chemical reactions of one or both of the radical ions and chemically unproductive back electron transfer. Typical among such processes is fragmentation to yield a radical and an ion.[3,4] According to the process occurring, triads or tetraads of reacting intermediates are formed [Scheme 1(*a*)].[5–8]



Scheme 1

A relevant example is the SET induced fragmentation of the central bond in bibenzyls. This has been extensively investigated [Scheme 1(*b*)], and one can class the reports from the recent literature in three groups according to the primary process in the radical cation.

1. Direct fragmentation of the σ_{C-C} bond. Thus, 4-methoxybicumyl derivatives fragment when irradiated in the presence of tetranitromethane (TNM),[7] the radical anion of which is itself labile and yields NO_2 and the trinitromethyl anion; the end products result from the combination of the radicals and ions formed. The same compounds as well as several 1,1,2,2-tetraarylethanes and 1,1,2-triarylpropanes have been found to cleave on irradiation in the presence of 1,4-dicyanobenzene (DCB).[5,8] The benzylic cations thus formed add a nucleophile while the benzylic radicals are reduced by the stable DCB radical anion to the corresponding anions which in turn are protonated to give the hydrocarbons. In the reaction between 1,4-dicyanonaphthalene (DCN) and bicumyl the cumyl radical adds to the acceptor instead of being reduced.[9]

2. Indirect fragmentation, in the sense that the first process from the radical cation is splitting of some electrofugal group to yield a neutral radical conserving the bibenzyl skeleton, but the C–C bond is then broken at the radical stage. Thus, in arylpinacols and their silyl ethers[10,11] loss of a proton or, respectively, a silyl cation is the primary process, and the resulting alkoxyl radical undergoes C–C fragmentation to yield a ketone and a ketyl radical. The fragmentation of related α-amino alcohols occurs similarly.[12]

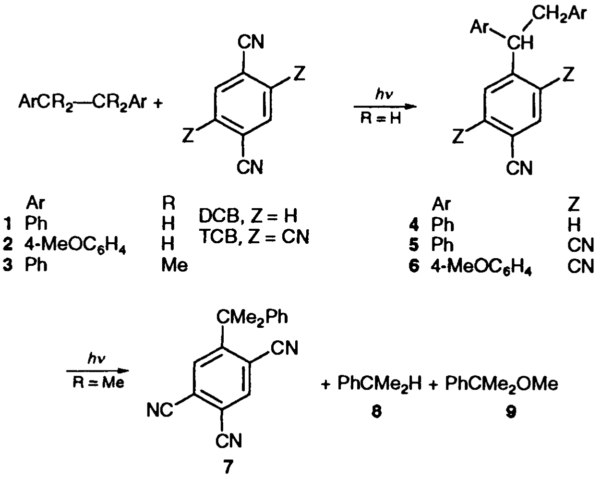
3. No C–C bond fragmentation. Several bibenzyls have been found to be unreactive upon irradiation in the presence of arenenitriles.[5] Alternative paths are possible, however, *e.g.* with some substrates deprotonation at the benzylic position occurs and is followed by addition of the radical to the radical anion of the acceptor to yield an adduct conserving the bibenzyl structure.[9,13,14]

As it appears from the foregoing, the explorative studies carried out up to now with bibenzyls are not exhaustive. For example, studies with fragmentable radical anions ($TNM^{\bullet-}$) have mainly been limited to donors forming ground state electron donor-acceptor complexes with TNM (*viz.* electron-donating substituted bibenzyls), which have been little investigated in their reaction with arenenitriles,[8] and conversely little is known about the reactivity with TNM of the relatively weak donors used in the studies with the nitriles. Therefore, we selected three bibenzyl derivatives, with structural variations meant to favour the different available paths, *viz.* bibenzyl itself, a better donor such as 4,4'-dimethoxybibenzyl and a more easily cleaved derivative such as 2,3-dimethyl-2,3-diphenylbutane, and investigated their photochemistry both in the presence of TNM and in the presence of two arenenitriles, and of DCB (the radical anion of which is expected to reduce a benzyl radical when formed) and of 1,2,4,5-tetracyanobenzene (TCB, for which no such reduction is expected).

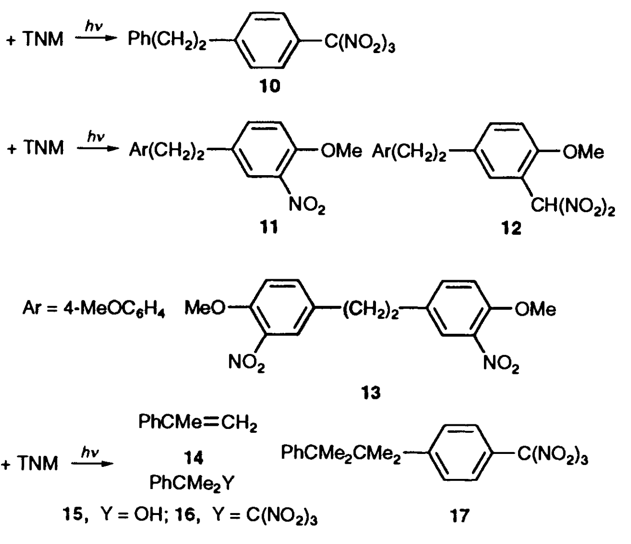
Results

Reactions with Bibenzyl.—Bibenzyl **1** quenched the fluorescence of DCB, and irradiation of an acetonitrile solution of **1** and DCB (light absorbed by the latter) in MeCN led to the formation of a single product, 1-(4-cyanophenyl)-1,2-diphenylethane **4** (Table 1, Scheme 2). A similar result was obtained with TCB, where likewise 1-(2,4,5-tricyanophenyl)-1,2-diphenylethane **5** was formed. Prolonged irradiation caused the formation of products of disubstitution, which were not further investigated.

No new absorption was noticed upon mixing acetonitrile solutions of **1** and TNM. Irradiation at >300 nm (light absorbed by TNM) caused a slow consumption of the hydrocarbon and the formation of several products, the main one



Scheme 2



Scheme 3

being 4-(trinitromethyl)bibenzyl **10** (Scheme 3). The formation of the corresponding 2-(trinitromethyl) isomer in a further reaction was suspected.

Reactions with 4,4′-*Dimethoxybibenzyl*.—4,4′-Dimethoxybibenzyl **2** did not give ground state CT complexes with either DCB or TCB in acetonitrile solution, at least up to 0.1 mol dm^{-3} concentration, while it quenched the fluorescence of both nitriles. Irradiation of MeCN solutions (light absorbed by the nitriles) caused no detectable change in the case of DCB while it gave the expected substitution product **6** in the case of TCB.

A mixture of **2** and TNM in MeCN showed a new absorption tailing to 450 nm. Irradiation both at 320 and 366 nm caused a complex reaction. The products isolated were the 3-nitro **11** and the 3,3′-dinitro **13** derivatives of **2**. When the reaction was carried out in the presence of 10% methanol 3-(dinitromethyl)-4,4′-dimethoxybibenzyl **12** was also obtained.

Reactions with Bicumyl.—Bicumyl **3** quenched the fluorescence of both DCB and TCB. With DCB, the irradiation in acetonitrile containing 5% methanol gave cumene **8** and cumyl methyl ether **9**, while, although some DCB was consumed, no substitution product was detected. In the case of TCB, on the contrary, a substitution product, the cumyltricyanobenzene **7** was obtained along with the ether **9**.

Table 1 Products from the irradiation of the bibenzyl derivatives **1**–**3**

Donor	Acceptor	Solvent	Products (% isolated yield)
1	DCB	MeCN–5%MeOH	**4** (34)
1	TCB	MeCN–5%MeOH	**5** (85)
1	TMN	MeCN–20%MeOH	**10** (36)
2	DCB	MeCN–5%MeOH	No reaction
2	TCB	MeCN–5%MeOH	**6** (50)
2	TMN	MeCN	**11** (24), **13** (5)
2	TMN	MeCN–10%MeOH	**11** (12), **12** (11), **13** (2)
3	DCB	MeCN–5%MeOH	**8** (12), **9** (54)
3	TCB	MeCN–5%MeOH	**7** (87), **9** (50)
3	TMN	MeCN	**14** (2), **15** (24), **16** (10), **17** (5)

With TNM there was no new absorption. The products isolated from the irradiation were styrene **14**, cumyl alcohol **15**, α-trinitromethylcumene **16** and a small amount of 4-trinitromethylbicumene **17**.

Discussion

All of the reactions reported above appear to be initiated by single electron transfer (SET) in the excited state. With the nitriles (singlet excited state) as the acceptors, the free energy change for electron transfer varies from moderately to strongly negative(**1**–DCB, −13,**1**–TCB, −25,**2**–DCB, −28,**2**–TCB, −39 kcal dm^3 mol^{-1},* calculations based on the known voltammetric data),[14] and the observed fluorescence quenching supports the participation of the singlet state. In the case of TNM the mechanism is less straightforward to determine. Two of the bibenzyls considered, **1** and **3**, do not form a ground-state complex, while the better donor **2** does. In the case of the first two donors light is absorbed by TNM, and two possibilities have to be considered, *viz*. (1) that excited TNM fragments and the observed chemistry are due to the trinitromethyl radical, as has indeed been suggested in the literature;[15] or (2) that excited TNM accepts an electron prior to fragmentation. We observe that the same type of chemical reactions take place both with **1** and **3** and with **2**, and further that these processes are closely related to those observed with other aromatic substrates (forming charge-transfer complexes) for which there is literature evidence for the electron transfer path.[5,7] Therefore, we suggest that a similar path is followed not only with **2** but also with **1** and **3**. An excited state of TNM long-lived enough to undergo bimolecular SET is involved [the reduction potential for the ground state TNM is $E^{\frac{1}{2}\mathrm{red}}$ −0.15 V *vs*. saturated calomel electrode (SCE)].[7]

Although the first step following photoexcitation is the same in all cases, chemical reactions occurring with the nitriles (mainly side-chain functionalization) and those occurring with TNM (mainly ring functionalization) are quite different. However, a unified picture of the chemistry of these systems can be obtained with reference to the rate of fragmentation of the radical ions and the competition between the direct reaction of the intermediates thus formed and their diffusion out of the solvent cage.

The radical cation of bibenzyl and its dimethoxy derivative are not subjected to carbon–carbon bond cleavage (the calculated ΔH for the fragmentation of $\sigma_{\mathrm{C-C}}$ bond in the radical cation are 29.3 and 34.6 kcal dm^3 mol^{-1}, respectively, calculated from thermodynamic cycles based on the radical oxidation, see ref. 4); the alternative fragmentation is deprotonation from the

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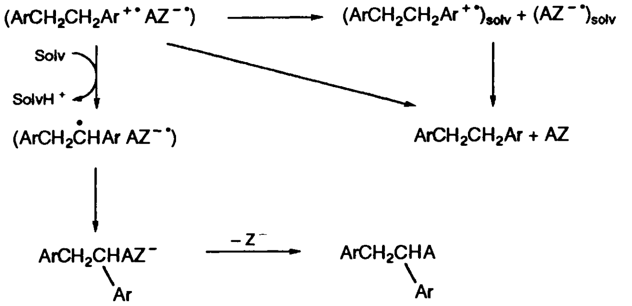
* 1 cal = 4.184 J.

benzylic position. Previous experience shows that although this process is largely favoured from the thermodynamic point of view ($\Delta H < -10$ kcal dm^3 mol^{-1}),[4] it often is too slow to compete with back electron transfer, unless it takes place either in the solvent cage before ion separation, or in the presence of a good nucleophile (which may be the radical anion itself, *e.g.* the oxygen-centred anion arising from a ketone).

In the reaction with the nitriles, the radical anion formed is non-fragmentable and non-basic. The only accessible path requires that the radical ion pair (or strongly polarized exciplex) $\mathbf{1}^{\cdot+}$–DCB$^{\cdot-}$ is stabilized. Thus, deprotonation takes place at this stage, and is followed by carbon–carbon bond formation to give ultimately the alkylated product (Scheme 4). In keeping with this rationalization, with the radical cation of **2**, where the charge is in part localized on the oxygen atoms rather than on the aromatic ring, such stabilization is weaker, and the radical ions diffuse away prior to deprotonation. Thus, alkylation is too slow to be observed. A similar observation had been previously made with naphthalene-1,4-dicarbonitrile;[9] in that case the photochemical SET alkylation with **1** proceeds rather efficiently, while the corresponding reaction with **2** is sluggish. However, the increased delocalization brought about by the two additional cyano groups in the radical anion of TCB is apparently enough to allow a better stabilization of the complex with both radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$, and in that case alkylation is obtained with both donors.



Scheme 4

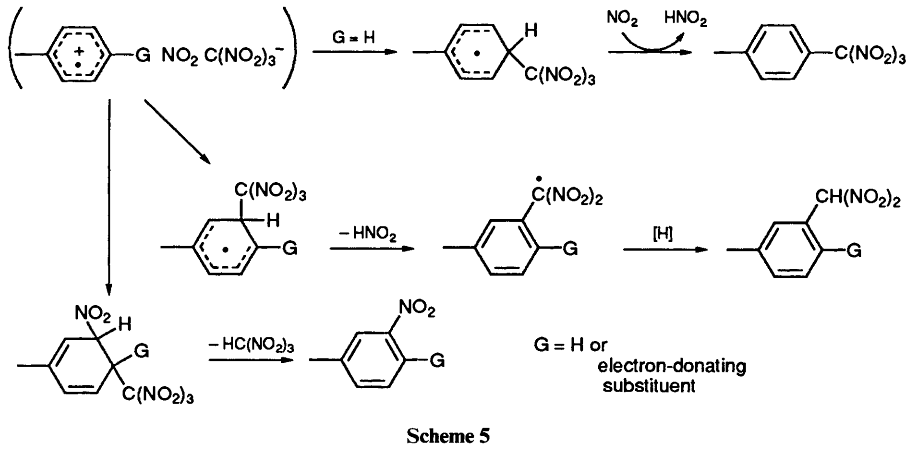
In the reaction with TNM, fragmentation of the radical anion (known to occur within 3 ps)[16] follows electron transfer. Since the trinitromethane anion [$C(NO_2)_3^-$] is again a poor base, no benzylic deprotonation (and thus no side-chain functionalization) occurs. The reaction is again dependent on the radical cation structure (Scheme 5). With bibenzyl, radical cation–anion combination is the fastest process, resulting in ring trinitromethylation, as previously observed by Maslak for non-fragmenting bicumyls.[7] This process is not observed with the methoxylated bibenzyl **2**, possibly because the more stabilized $\mathbf{2}^{\cdot+}$ diffuses out of the solvent cage before addition. However, some dinitromethylation takes place in the presence of methanol, and, following a proposal by Maslak and Chapman,[7] this process can likewise be considered to arise from an in cage ion combination, although at a different solvation stage. Apart from this, the main process with **2** is nitration. It is unlikely that this results from a thermal reaction, although NO_2 is set free from the photocleavage of TNM. Rather, it may be attributed to the addition of both fragments of TNM to **2** (as previously observed *e.g.* with naphthalene derivatives)[17,18] followed by trinitromethane elimination from the intermediate adduct during work-up. The order in which NO_2 and $C(NO_2)_3^-$ add to the hydrocarbon in related reactions has caused controversy in the literature,[17,18] and we have not pursued the point further in our case. At any rate, this reaction occurs only with more reactive substrates, such as naphthalenes and methoxybenzenes, and not with unactivated benzenes such as **1** and **3** (see below).

The central C–C bond is scissible in the radical cation of bicumene (calculated ΔH -3 kcal dm^3 mol^{-1}, see above),[4] and indeed the observed reactions are rationalized in terms of fragmentation to yield a cumyl radical and a cumyl cation. The cation is either trapped by nucleophiles present to yield cumyl alcohol or its methyl ether, or, in the reaction with TNM, α-trinitromethylcumene, or it deprotonates to give α-methylstyrene.

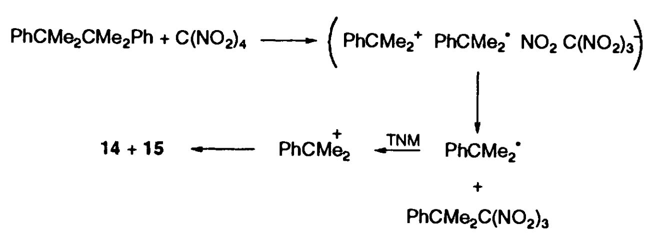
The fate of the radical depends on the acceptor used. DCB has a quite negative reduction potential in the ground state (-1.62 V *vs.* SCE). This is close to the measured E_{red} for the cumyl radical (-1.73 V),[19] and thus the interaction between the radical and the radical anion of the acceptor leads to electron transfer and protonation of the anion to finally yield cumene.[8] The lower yield of cumene with respect to the products from the cation is probably due to diffusion out of the cage of the radicals and coupling to give back **3**. With TCB, which has a less negative E_{red} (-0.7 V), electron transfer is not possible and radical–radical anion addition followed by cyanide elimination leads to the observed product. With TNM, cumyl radicals diffuse and are oxidized (E_{ox} 0.16 V)[18] to the corresponding cations by ground state TNM (E_{red} -0.15 V in CH_2Cl_2) (Scheme 6).[7]

Finally, the isolation of a small amount of the trinitromethyl derivative of **3** in the reaction with TNM is evidence that the fragmentation of the C–C bond in the radical cation is slower than that of the C–N bond in the radical anion, though rather close to it. This is relevant in view of the present interest in establishing the relative rate of detachment of electrofugal or respectively nucleofugal groups from radical ions.

In conclusion, this work shows the similar course and the similar rationalization of two different classes of photochemical



Scheme 5



Scheme 6

SET reactions, with the use of fragmentable and non-fragmentable radical anions, and also shows some important differences, *e.g.* the role that π interaction may have in the stabilization of the radical ion pair when the acceptor is an aromatic molecule. This facilitates reaction before diffusion.

Experimental

IR spectra were measured on a Perkin Elmer 186 spectrophotometer. NMR spectra were determined on a Bruker 300 instrument using tetramethylsilane as an internal standard. Chemical shifts (δ) are reported in ppm. *J* Values are reported in Hz. Fluorescence spectra were measured by means of an Aminco-Bowman spectrofluorimeter. Elemental analyses were performed on a Carlo Erba 1106 instrument. TCB was prepared by dehydration of benzene-1,2,4,5-tetracarboxamide.[20] 4,4'-Dimethoxybibenzyl was prepared from 4-methoxybenzyl chloride[21] and bicumene from cumene.[22] The other reagents and the solvents were commercial products and were used as received. Products **8**, **9**, **14**, **15** were identified by comparison of gas-chromatographic and mass-spectroscopic data with those of authentic samples. The spectroscopic properties of product **16** were compared with those of an authentic sample prepared according to a literature method.[7]

Photochemical Reactions between DCB and the Donors **1**–**3**.—A solution of DCB (80 mg, 0.62 mmol) and bibenzyl **1** (180 mg, 1 mmol) in a mixture of acetonitrile (190 cm^3) and methanol (10 cm^3) was flushed for 15 min with nitrogen and then irradiated for 6 h by means of a 20 W low-pressure mercury arc in an immersion well apparatus. The contents of the tubes were recombined and the solution was examined by vapour phase chromatography (VPC) and then evaporated at reduced pressure. Chromatography of the residue on a silica gel column eluting with cyclohexane–ethyl acetate (9:1) gave unchanged starting material (40 mg) and 1-(*4-cyanophenyl*)-1,2-*diphenylethane* **4** (30 mg, 34%), oil (Found: C, 89.4; H, 6.3; N, 4.6. Calc. for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%); δ_H(CDCl$_3$) 3.25 and 3.37 (2 H, two AB q, J_{AX} 9, J_{BX} 7, CH$_2$), 4.25 (1 H, dd, *J* 7, 9, CH), 6.9–7.25 (10 H, m), 7.21 (2 H, d, *J* 8) and 7.47 (2 H, d, *J* 8); ν/cm^{-1} 2215.

The reactions with compounds **2** and **3** were similarly carried out (see Table 1).

Photochemical Reactions between TCB and the Donors **1**–**3**.—A solution of TCB (75 mg, 0.42 mmol) and bibenzyl **1** (150 mg, 0.82 mmol) in acetonitrile (75 cm^3)–methanol (5 cm^3) was equally divided between three septum-capped quartz tubes, and purged with argon for 15 min. The tubes were then irradiated for 4 h in a multilamp apparatus fitted with six 15 W phosphor-coated lamps, with a centre of emission at 320 nm. The contents of the tubes were recombined and the solution was examined by VPC and then evaporated at reduced pressure. Chromatography of the residue on a silica gel column eluting with cyclohexane–ethyl acetate (9:1) gave unchanged TCB (5 mg) and 1,2-*diphenyl*-1-(2,4,5-*tricyanophenyl*)*ethane* **5** (110 mg, 85%), m.p. 143–145 °C (EtOH) (Found: C, 82.9; H, 4.5; N, 12.5. Calc. for $C_{23}H_{15}N_3$: C, 82.86; H, 4.54; N, 12.61%); δ_H(CDCl$_3$) 3.3 (1 H, dd, *J* 9, 14), 3.55 (1 H, dd, *J* 7, 14), 4.85 (1 H, dd, *J* 7, 9), 7–7.4 (10 H, m), 7.88 (1 H, s) and 7.90 (1 H, s); ν/cm^{-1} 2210.

The reactions with compounds **2** and **3** were carried out analogously (see Table 1).

1,2-*Bis*(4-*methoxyphenyl*)-1-(2,4,5-*tricyanophenyl*)*ethane* **6**, m.p. 69–72 °C (EtOH) (Found: C, 76.5; H, 4.9; N, 10.5. Calc. for $C_{25}H_{19}N_3O_2$: C, 76.32; H, 4.87; N, 10.68%); δ_H(CDCl$_3$) 3.3 and 3.45 (2 H, two AB q, J_{AX} 9, J_{BX} 7, CH$_2$), 3.85 (3 H, s), 3.90 (3 H, s), 4.8 (1 H, dd, *J* 7, 9), 6.7–7.2 (8 H, m), 7.8 (1 H, s) and 7.85 (1 H, s); ν/cm^{-1} 2210 and 1505.

5-(1-*Methyl*-1-*phenylethyl*)*benzene*-1,2,4-*tricarbonitrile* **7**, m.p. 187–189 °C (EtOH) (Found: C, 79.8; H, 4.9; N, 15.3. Calc. for $C_{18}H_{13}N_3$: C, 79.68; 4.83; 15.49%); δ_H(CDCl$_3$) 1.85 (6 H, s), 7–7.4 (5 H, m), 7.95 (1 H, s) and 8.05 (1 H, s); ν/cm^{-1} 2210.

Photochemical Reactions between TNM and the Donors **1**–**3**.—A solution of TNM (2.9 g, 14.8 mmol) and bibenzyl **1** (600 mg, 3.3 mmol) in a mixture of acetonitrile (48 cm^3) and methanol (12 cm^3) was equally divided between three septum-capped quartz tubes and purged with argon for 15 min. The tubes were irradiated for 5 h in a multilamp apparatus fitted with six 15 W phosphor-coated lamps, with the centre of emission at 320 nm. The contents of the tubes were recombined and the solution was diluted with water (25 cm^3) and extracted with dichloromethane (2 × 50 cm^3). The combined organic layers were examined by VPC and then evaporated at reduced presure. The residue was chromatographed on a silica gel column to yield unchanged bibenzyl (422 mg) and 1-*phenyl*-2-(4-*trinitromethylphenyl*)*ethane* **10** (80 mg, 36%), m.p. 44–45 °C (Found: C, 54.1; H, 4.1; N, 12.4. Calc. for $C_{15}H_{13}N_3O_6$: C, 54.38; H, 3.96; N, 12.69%); δ_H(CDCl$_3$) 3.0 (4 H, AA'BB'), 7.1–7.3 (5 H, m), 7.35 (2 H, d, *J* 8) and 7.5 (2 H, d, *J* 8); ν/cm^{-1} 1605 and 1590.

The reactions with compounds **2** and **3** were carried out analogously (see Table 1).

1-(4-*Methoxyphenyl*)-2-(4-*methoxy*-3-*nitrophenyl*)*ethane* **11**, m.p. 79–80 °C (Found: C, 66.7; H, 5.9; N, 4.7. Calc. for $C_{16}H_{17}NO_4$: C, 66.88; H, 5.96; N, 4.88%); *m/z* 287; δ_H(CDCl$_3$) 2.85 (4 H, s), 3.75 (3 H, s), 3.90 (3 H, s), 6.75–7.25 (6 H, m) and 7.65 (1 H, d, *J* 3); ν/cm^{-1} 1600 and 1535.

1,2-*Bis*(4-*methoxy*-3-*nitrophenyl*)*ethane* **13**, decomposes at *ca.* 150 °C (Found: C; 57.8; H, 4.9; N, 8.3. Calc. for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43%); *m/z* 332; δ_H(CDCl$_3$) 2.87 (4 H, s), 3.90 (6 H, s), 6.90 (2 H, d, *J* 9), 7.25 (2 H, dd, *J* 9, 3) and 7.68 (2 H, d, *J* 3); ν/cm^{-1} 1620 and 1525.

1-(3-*Dinitromethyl*-4-*methoxyphenyl*)-2-(4-*methoxyphenyl*)-*ethane* **12**, m.p. 77–80 °C (Found: C, 58.7; H, 5.4; N, 7.9. Calc. for $C_{17}H_{18}N_2O_6$: C, 58.95; H, 5.24; N, 8.09%); δ_H[(CD$_3$)$_2$CO] 2.85 (4 H, AA'BB'), 3.8 (3 H, s), 3.9 (3 H, s), 6.8 (2 H, d, *J* 8), 6.9 (1 H, d, *J* 8.5), 7.02 (2 H, d, *J* 8), 7.08 (1 H, d, *J* 2), 7.3 (1 H, dd, *J* 2, 8.5) and 7.55 (1 H, s); ν/cm^{-1} 1585.

2,3-*Dimethyl*-3-*phenyl*-2-(4-*trinitromethylphenyl*)*butane* **17**, m.p. 77–80 °C (Found: C, 58.5; H, 5.7; N, 10.4. Calc. for $C_{19}H_{21}N_3O_6$, 58.91; H, 5.46; N, 10.85%); δ_H(CDCl$_3$) 1.33 (6 H, s), 1.38 (6 H, s), 6.9–7.2 (5 H, m), 7.15 (2 H, d, *J* 7) and 7.42 (2 H, d, *J* 7); ν/cm^{-1} 1605 and 1580.

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