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Alkylation of Alkenes by Radicals Generated through Photoinduced Single Electron Transfer.

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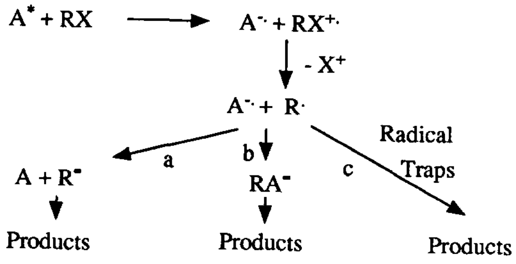
Abstract: Irradiation of 1,2,4,5-benzenetetracarbonitrile (TCB) in the presence of several donors (some 2-*t*-butyl-1,3-dioxolanes, pivalic acid, *t*-butyltrimethylstannane, *t*-butyldimethylsilyl *n*-octyl ether) leads to fragmentation of the donor radical cation to give the *t*-butyl radical. When the irradiation is carried out in the presence of electron-withdrawing substituted alkenes, the radical is trapped and the adduct radical either couples with $TCB^{-\cdot}$ (the overall process is then radical olefin coupling - aromatic substitution) or is reduced by it (resulting in TCB photosensitized alkene alkylation). The effect of the radical precursor structure and of the medium on these new reaction is discussed.

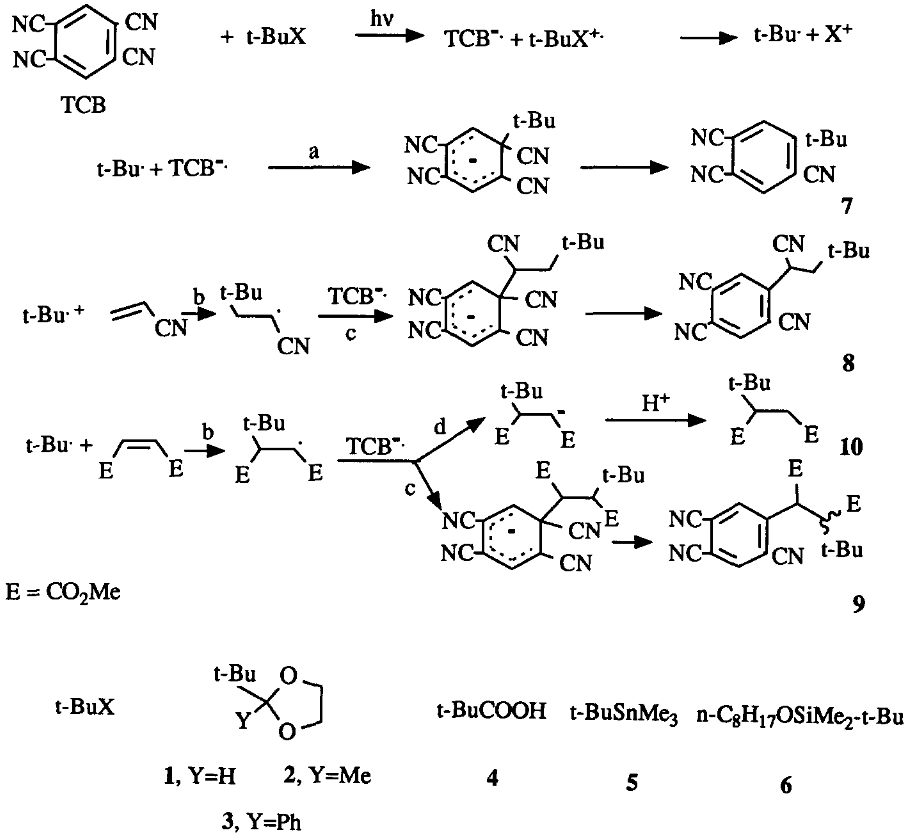
Recent evidence from several laboratories has shown that photoinduced single electron transfer (PET) followed by fragmentation of the radical cation is an efficient method for the generation of carbon-centered radicals under exceptionally mild conditions.[1-8] The fate of the thus formed radical depends primarily on its interaction with the acceptor radical anion. When this is a strongly stabilized species, as it is the case with the widely used aromatic nitriles, either electron transfer or radical coupling are tipically observed, according to whether the ground state reduction potential of the acceptor is higher or lower than that of the radical (Scheme 1, paths a and b). A further, and from the synthetic point of view, particularly appealing possibility is that the radical is trapped by a suitable substrate, such as an olefin (path c), thus offering yet a new way of forming C-C bonds via radical addition.



Scheme 1.

We recently found a first indication of the feasibility of this strategy by irradiating the good electron acceptor 1,2,4,5-benzenetetracarbonitrile (TCB), some ketals as the donors and electron-withdrawing substituted alkenes as traps, and observed that under those conditions addition of the radicals to the alkene competes with reaction with TCB$^{-\cdot}$.[9] In order to explore the generality and the selectivity of this reaction, we presently report an explorative study of the generation of alkyl (*t*-butyl) radicals via PET oxidation with TCB and of their trapping with electron poor alkenes, as well as upon the effect of the medium on the reactions we found.

The results obtained are gathered in Scheme 2 and Table 1. We considered a variety of donors which could function as precursors of the *t*-butyl radical through the oxidation path, viz the dioxolanes **1-3**, pivalic acid **4**, the stannane **5**, and the silyl ether **6**. Each of these substrates gave 5-*t*-butyl-1,2,4-benzenetricarbonitrile **7** in good yield when irradiated with TCB in MeCN. Thus, the normal course of PET induced aromatic substitution (Scheme 1, path a) was followed as previously observed in related cases.[8,10-12]



Scheme 2.

Table 1. Alkylation of acrylonitrile (AN, 0.2 M) and dimethyl maleate (DMM, 0.08 M) with *t*-butyltrimethylstannane by irradiation in the presence of TCB.

Substrate	Alkene	Relative Efficiency	Products, % Yield		
1	AN	1	**7**, 10 (3.5)[a]	**8**,42(54)	
1	DMM	1.7	**7**, 62 (48)[a]	**9**, 16 (7.5)[a]	**10**, 11.5 (9.5)[a]
2	AN	2.6	**7**, 17 (7.5)[a]	**8**, 52 (44)[a]	
2	DMM	3.1	**7**, 26 (7)[a]	**9**, 32(14)[a]	**10**, 62 (32)[a]
3	AN	4.4	**7**, 13.5 (8.5)[a]	**8**, 62 (50)[a]	
3	DMM	4.1	**7**, 30 (46)[a]	**9**, 36 (28)[a]	**10**, 64 (62)[a]
4	AN	0.3	**7**, 22 (13.5)[a]	**8**, 28 (44)[a]	
4	DMM	1.5	**7**, 54 (30)[a]	**9**, 16 (40)[a]	**10**, 44 (66)[a]
5	AN	3.6	**7**, 11 (6)[a] (5)[b]	**8**, 74 (58)[a] (60)[b]	
5	DMM	5	**7**, 36 (24)[a] (16)[b] (12)[a,b]	**9**, 56 (64)[a] (60)[b](44)[a,b]	**10**, 62 (120)[a] (132)[b](56)[a,b]
6	AN	0.35	**7**, 4 (1)[a] (0)[b,c]	**8**, 40 (34)[a] (50)[b,c]	
6	DMM	1.2	**7**, 17 (12)[a] (0)[b,c]	**8**, 58 (64)[a] (70)[b,c]	**10**, 84 (116)[a] (112)[b,c]

The experiments in the presence of additives carried out for the same time as without, except then otherwise stated. (a). with tetraethylammonium perchlorate 0.1 M. (b). with biphenyl 0.1 M. (c). time prolonged by 50%.

Table 2. Effect of some additives on the alkylation of dimethyl maleate (0.08 M).

Donor	Additive	Products (% Yield)		
3		**7** (30)	**9** (36)	**10** (64)
	$C_{12}H_{25}SH$, 0.01 M	**7** (28)	**9** (12.5)	**10** (18.5)
	CF_3CH_2OH, 0.2 M	**7** (30)	**9** (24)	**10** (62)
5		**7** (36)	**9** (56)	**10** (62)
	$C_{12}H_{25}SH$, 0.01 M	**7** (30)	**9** (7.5)	**10** (12)
	CF_3CH_2OH, 0.2 M	**7** (40)	**9** (9.5)	**10** (40)

However, the course of the reaction completely changed when the irradiation was carried out in the presence of either acrylonitrile (AN) or dimethyl maleate (DMM), and olefin containing compounds became the main products. Thus, in the first case the 2-arylpentanenitrile **8** was obtained in yields from 30 to 74%. In the latter case, two new products were formed, viz the 2-aryl-3-*t*-butylsuccinate **9** (mixture of diastereoisomers) and dimethyl 2-*t*-butylsuccinate (**10**). These reactions are rationalized by admitting that the *t*-butyl radical formed from the precursors **1**-**6** is trapped by the electron-poor alkenes (path b in Scheme 2). In turn, the adduct radical couples with the TCB radical anion (path c) or is reduced by it to yield the corresponding carbanion, which is then protonated (path d). Path c leads to the arylated derivatives **8** and **9**, and we indicate this reaction with the acronym ROCAS (Radical Olefin Coupling - Aromatic Substitution), while path d leads to the simple alkylation of the olefin, and is equivalent to known radical alkylation, e.g. via tin or mercury hydride, with the difference that the adduct radical instead of abstracting a hydrogen atom is first reduced and the protonated (in this case TCB is regenerated and functions as a non consumed sensitizer; as a result the overall yield, calculated with reference to the consumed sensitizer may, and actually does, exceed 100%).

The overall efficiency of the reaction, both in the presence and in the absence of the alkenes, depends on the competition between radical cation fragmentation and chemically unproductive back electron transfer. This is related to the presence of a good electrofugal group. Thus, in the series of the three dioxolanes, the relative rate of reaction follow the order **3** > **2** > **1**, corresponding to the stability of the leaving (2-substituted)-1,3-dioxoalnyl carbocation. Destannylation of $\mathbf{5}^{+\cdot}$ is also very effective, while cleavage of the carbon-silicon bond in $\mathbf{6}^{+\cdot}$ and deprotonation (followed by CO_2 loss) from the radical cation of pivalic acid are slower.

As for the competion between coupling with $TCB^{-\cdot}$ (path a in Scheme 2) and addition to the alkene (path b), this depends on the fine mechanism of the reaction. The trapping by the alkene is expected to be more efficient if fragmentation occurs form the free solvated radical cation, whereas it wil be less so if fragmentation occurs within the geminate radical ion pair, and is essentially concerted with bonding with the TCB radical anion. In a previous study based on the radical clock method,[13] we showed that aromatic substitution (Scheme 3, path a) does occur in cage before separation. This part of the reaction is expected to be scarcely affected by the medium characteristics and not be amenable to trapping.

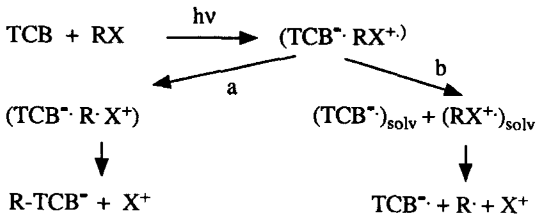
Indeed, olefins do not suppress aromatic substitution, although in most cases the olefin containing products largely predominate. It should also be noticed that the more bulky DMM is less effective in quenching aromatic substitution than AN, although the overall yield of the ROCAS product **9** and and the product of simple alkene addition **10** from DMM is larger than that of **8** from AN, in accordance with the idea that quenching of the reaction occurring in cage suffers sterical hindering, while on the other hand DMM is known to react with free radicals faster than AN, and therefore it scavenges them more effectively, so that these species are subtracted to undesired reactions such as homo-coupling or reactions with impurities. Furthermore, the data in Table 2 also support the notion that free radicals are involved in the formation of products **8**-**10** (path a in Scheme 3) and not of **7**. Thus, an alkyl mercaptane strongly quenches the formation of the succinates **9** and **10**, while it has no effect on **7**, and a protic additive (CF_3CH_2OH) does not affect the yield of either **7** or **10**, while it lowers the yield of **9**, since in the last case recombination of the adduct radical and the slowly protonated $TCB^{-\cdot}$ is involved.

In order to improve the selectivity towards olefin addition, some changes of the medium were explored. Thus, since charge separation is a key step, increasing the ionic strength is expected to have a beneficial effect. Indeed, adding 0.1 M tetraethylammonium perchlorate somewhat shifted the distribution towards olefin containing products, with little change of the overall efficiency, but the effect was modest except than in the reaction of the stannane **5** with DMM, where the yield of **10** doubled.

Another possibility is secondary electron transfer. Thus, in the case of **5** and **6** addition of a second donor at a concentration high enough to quench a substantial fraction of TCB^{1*} (biphenyl 0.1 M) was found to be effective in directing the reaction towards olefin addition. This occurred with an overall increase of the rate with **5**, since there the secondary transfer

Biphenyl$^{+\cdot}$ + **5** $\rightarrow$ Biphenyl + **5**$^{+\cdot}$

was exothermic, while the rate decreased with the silyl ether **6**, were the transfer was endothermic. Combining both additives was detrimental (see the case of **5**). The most interesting result, however, was that with the silyl ether **6**: here, although slow, the reaction in the presence of biphenyl was completely selective for addition to the alkenes (both AN and DMM). We attribute this peculiarity to the fact that in this case the MO involve in electron donation (the non bonding oxygen orbital) is relatively far from the bond cleaved in the radical cation (the $\sigma_{C\text{-}Si}$ bond) and this disfavours concerted cleaveage (path a in Scheme 3) vs the free radical cation mechanism.



Scheme 3.

In conclusion, the present research shows that the chemistry of radicals generated through the PET mechanism is not limited to aromatic substitution. Indeed, radicals can be trapped by alkenes giving rise to two new processes, viz radical olefin addition - aromatic substitution, resulting from the *coupling* between TCB$^{-\cdot}$ and the *adduct* radical) and addition to the alkene (resulting form *reduction* of the adduct radical by TCB$^{-\cdot}$). The appropriate choice of radical precursor and experimental conditions make these reactions predominating or even exclusive. Thus, this appears to be a promising method in radical chemistry.

Experimental

1,2,4,5-tetracyanobenzene (TCB) and the donors **1-6** were prepared as previously reported.[11,12] Isolation and characterization of the photoproducts **7-10** have been separately reported.[9]

Photochemical reactions were carried out on 3 mL aliquots of solutions of TCB (5×10^{-3} M) and the appropriate donor (5×10^{-2} M) in acetonitrile in quartz tubes capped with a rubber septum under the conditions detailed in Tables 1 and 2. The solutions were purged with argon and irradiated by means of a multilamp apparatus fitted with six 15 W phosphor coated lamps (centre of emission 320 nm) while rotating in a merry go round apparatus. The irradiation time was between 25 min an 5 h. The product formation was monitored by glc (methylsilicone column, 25mx0.2mmxo.3μm). Dodecane was used as an internal standard.

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