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OXYGEN TRANSFER BY DISSOCIATIVE ELECTRON TRANSFER. REACTION OF TETRANITROMETHANE WITH DIAZO COMPOUNDS AND SULFIDES

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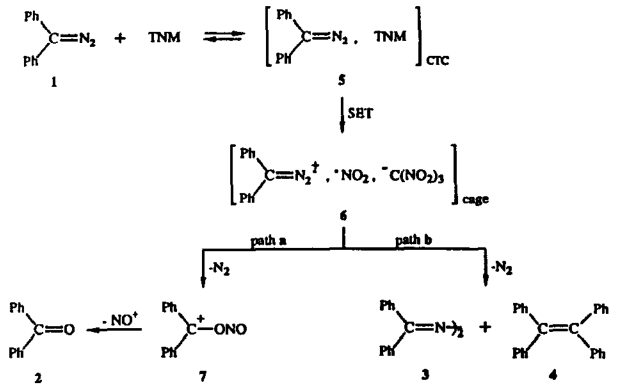
Abstract - In the absence of oxygen, diphenyldiazomethane is oxidized by tetranitromethane (TNM) to afford benzophenone and products derived from the diazoalkane radical cation, in yields strongly dependent on the reaction conditions. Sulfides were also found to undergo this oxygen transfer process with TNM. An initial dissociative electron transfer step is postulated to account for the observed results.

One electron oxidation of diazo compounds has attracted increasing interest from both the mechanistic and synthetic points of view. [1-5] The generation of radical cations of diazoalkanes and their denitrogenation into carbene radical cations have recently been demonstrated [10] and studies to clarify the chemistry of these unusual species have been reported. Such oxidations have been performed electrochemically, [1,6] by means of metal salts, [2] by triarylaminyl radical cations, [3] by tetracyanoethylene or chloranil, [4] and by photosensitized electron transfer [5]. Recently it has been reported [7] that diazoalkanes react with cyanotrinitromethane to give the corresponding ketones. Although a redox process was mentioned, no mechanistic studies were made.

In this context we wish to report presently that diphenyldiazomethane reacts with TNM in the dark or under photochemical conditions to give oxygen transfer products through an initial dissociative electron transfer process. In an analogous process, sulfides are also oxidized by TNM on irradiation to yield the corresponding sulfoxides by the same mechanism.

Scheme I.



Results and Discussion

Diphenyldiazomethane (**1**) was readily oxidized by TNM to afford benzophenone (**2**) in significant amounts, as well as benzophenone azine (**3**) and tetraphenylethylene (**4**), in yields which depended markedly on the reaction conditions. When TNM was added to a solution of diphenyldiazomethane and the resulting reaction mixture allowed to stand at room temperature in the dark, slow nitrogen gas evolution was observed until complete consumption of the starting diazo compound. The yields in a variety of solvents are shown in Table 1.

Table 1: Product Data for the Oxidation of Diphenyldiazomethane (**1**) by TNM

Entry	Solvent	Reaction Conditions[a] Concentration (M) [1]	[TNM]	Time (min)	Temp. (°C)	Conversion (%)	Product Composition (%)[b] 2	3	4	Mass Balance[c] (%)
1	THF	0.25	0.25	420	20	100	75	17	8	96
2	THF	0.25	0.03	420	20	40	80	20	-	93
3	CH_2Cl_2	0.25	0.25	420	20	100	91	9	-	94
4	CH_2Cl_2	0.25	0.04	420	20	35	85	15	-	91
5	CH_3CN	0.25	0.25	60	20	100	22	31	47	95
6	CH_3CN	0.25	0.03	60	20	100	16	11	73	92
7	$CDCl_3$	0.25	0.25	5	- 5	100	86	13	-	90

a) In the dark, except Entry 7, in which irradiation at $\lambda > 380$ was used. b) The products were identified by employing 63 MHz ^{13}C NMR and comparing with authentic samples; conversion, mass balance, and product composition were obtained from the intensity of the ^{13}C NMR signals which correspond to the aromatic carbon atoms in the spectra of the crude reaction mixtures; measurement of mixtures of **2**, **3** and **4** of known composition showed that the error limits of this procedures were within 10% of the stated values; all spectra were recorded in deutero- chloroform by using the same standard set of instrumental parameters. c) Relative to the starting diazo compound; determined gravimetrically on the crude reaction mixture; the error was established to be within 10% of the stated values.

Benzophenone (**2**) was the main product in the nonpolar solvent THF together with substantial amounts of benzophenone azine (**3**), cf. Entry 1, Table 1; also an appreciable yield of tetraphenylethylene (**4**) was detected. The latter product was avoided when catalytic amounts of TNM (Entry 2, Table 1) were employed; however, under these conditions merely 40% conversion was achieved *versus* 100% under equimolar conditions (Entries 1 and 2, Table 1).

The nonpolar solvent dichloromethane gave similar results (Entries 3 and 4, Table 1), except that now the highest yields (91%) of benzophenone and no tetraphenylethylene were observed. Again, using catalytic quantities of TNM (Entry 4, Table 1) led to only 35% conversion.

Dramatic differences in the product composition were noted when the polar solvent acetonitrile (Entries 5 and 6, Table 1) was used. The major product (73%) was now tetraphenylethylene (**4**), especially when catalytic amounts of TNM were used. Not only was the reaction in acetonitrile ca. sevenfold faster than in THF under comparable conditions (Entries 2 and 6, Table 1), but even for catalytic amounts of TNM 100% conversion of diazoalkane **1** took place. Astounding is that so little benzophenone (ca. 20% yield) was obtained in acetonitrile, which of course is of mechanistic significance.

Of particular mechanistic interest was the fact that on mixing the solutions of diazoalkane **1** and TNM (25-fold excess) considerable darkening of the reaction mixture was observed. The absorption spectrum showed a markedly increased intensity (ca. fivefold) at the 400-nm minimum and broad tailing out to 700 nm. Indeed, irradiation into this charge transfer band at $\lambda > 380$ nm by using a mercury high pressure lamp (150 W) promoted higher reactivity (over 80-fold) and complete consumption of the diazoalkane **1** within 5 min (Entry 7, Table 1). Monitoring the diazoalkane **1** absorbance at 524 nm ($\varepsilon = 98\ M^{-1}cm^{-1}$) in dichloromethane under pseudo first-order conditions (ca. 25-fold excess of TNM) at 5 °C in the dark, afforded a pseudo first order rate constant $k_{obs} = (6.73\pm0.6) \times 10^{-3} s^{-1}$ and thus $k_2 = k_{obs}[TNM]^{-1} = 2.69 \times 10^{-2} s^{-1}M^{-1}$. Consequently, these second order kinetics require that in the slow step of the reaction both the diazoalkane **1** and TNM participate.

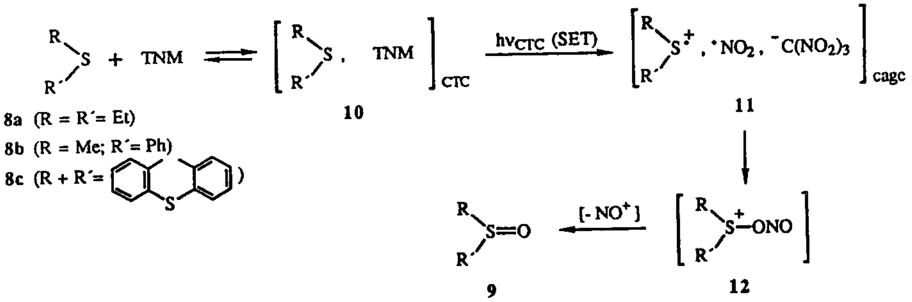
These experimental data are best accommodated in a mechanism (Scheme 1) in which a dissociative single-electron transfer (SET) from the diazoalkane to TNM takes place and leads to the solvent-caged triad of reactive species, [6a)] namely the diazoalkane radical cation, the nitrite radical, and the nitroform anion. Coupling of the diazoalkane radical cation with nitrogen dioxide leads, after denitrogenation, to the cation **7** (path a, Scheme 1) [9]. The loss of the nitrosyl cation releases benzophenone. The resulting nitrosyl cation could couple with the nitroform anion to give nitrosotrinitromethane (no efforts were made to detect it), which by oxygen transfer could oxidize the diazoalkane to afford benzophenone. This would explain the fact that more ketone is formed than the amount of TNM allows for a 1:1 stoichiometric process between TNM and diazoalkane.

In nonpolar solvents, which discourage the ionic partners to escape from the solvent cage, diphenyldiazomethane (**1**) favors path a. In a reaction medium of higher polarity, the escape from the solvent cage is enhanced and subsequent the reaction of the diphenyldiazomethane radical cation with unreacted diazo compound **1** affords the azine **3** and the olefin **4** by the well established chain reaction (path b, Scheme 1). [1-5]

The driving force for the oxygen transfer process from TNM to diazoalkanes presumably derives from the loss of molecular nitrogen of the diazoalkane radical cation to afford a radical cation in which the cation charge and unpaired electron lie on one and the same atom. It was, therefore, of interest to see whether monocentric radical cations such as those of sulfides, could be directly generated by investigating their single-electron oxidation by TNM. Indeed, when TNM was added to a solution of diethylsulfide (**8a**) in acetonitrile or dichloromethane, a yellow color immediately developed. The formation of a charge transfer complex **10a** was detected by UV spectroscopy, which showed a broad absorption band that extended from 400 to 550 nm. When the mixture was kept in the dark

for 24 h, no reaction was observed. Irradiation of the solution with filtered light (λ > 400 nm) of a mercury high pressure lamp (150 W) led to complete conversion of the substrate after ca. 60 min. The corresponding sulfoxide **9a** was the only product of the reaction (Table 2). The oxygen transfer was carried out in dichloromethane and in acetonitrile, but no solvent effect could be observed on the product distribution. Analogous observations were made for the sulfides **8b,c** (Table 2, Equation 2).

Scheme 2.



Also for sulfides a SET mechanism similar to the diazoalkane-TNM reaction operates (Scheme 2). After initial formation of the CT complex **10**, light-induced electron transfer leads to a triad **11** of reactive species, namely the sulfide radical cation, nitrogen dioxide, and the nitroform anion. Coupling of the sulfide radical cation with nitrogen dioxide to give the sulfonium ion **12** and loss of the nitrosyl cation yields the corresponding sulfoxide **9**. A related process is known[10] for the reaction of sulfides with the nitronium cation (NO_2^+), in which an oxygen transfer process takes place through the sulfonium ion **12**. Since the reaction of sulfides **8** with TNM occurs by photochemical excitation of the corresponding charge transfer complex band of **10**, a mechanism initiated by the ionic dissociation of TNM to give the nitronium cation and the nitroform anion can be rejected.[11] Moreover, an alternative process, in which the nitroform anion deprotonates the sulfoxide radical cation and the resulting radical couples with nitrogen dioxide, which would be favored when a more polar solvent induces ion pair separation, does not compete effectively under these conditions.

Table 2: Product Data for the Oxidation of Sulfides **8** by TNM

Entry	Substrate	Reaction Conditions[a] Solvent	Time (min)	Conversion [b] (%)	Yield [b] (%)
1	**8a**	CD_2Cl_2	30	100	99
2	**8a**	CD_3CN	30	100	99
3	**8b**	CD_2Cl_2	90	100	98
4	**8b**	CD_3CN	90	100	99
5	**8c**	CD_2Cl_2	45	100	98
6	**8c**	CD_3CN	45	100	99

a) Irradiation was performed at $\lambda > 400$ nm with a mercury high pressure lamp (150 W) at -5 °C; equimolar amounts of TNM were used and the solutions were 0.1 M in the sulfide. b) The reactions were monitored by ^1H NMR (250 MHz); product yields were obtained by integration of the ^1H NMR signals of the reaction mixture against an internal standard; the error was established to be within 5% of the stated values.

In the present investigation a novel oxygen transfer process from TNM to diazoalkanes and sulfides was discovered. These reactions proceed through initial formation of a charge transfer complex, followed by electron transfer, and reveal new reaction pathways, e.g. oxygen transfer. The interesting chemistry of the versatile diazoalkane radical cation species remains largely unexplored. Moreover, the unprecedented SET reactivity of TNM derives from the ease of formation of the corresponding radical cation partners. It should be of interest to examine the SET-type chemistry of TNM with other electron donors.

EXPERIMENTAL

Diphenyldiazomethane was prepared by standard procedures. The sulfides were commercially available and were distilled before use. Tetranitromethane (Aldrich) was used as received. All solvents were dried according to standard procedures, after distillation degassed by at least five freeze-pump-thaw cycles, and used immediately. The reactions were carried out under an inert argon gas atmosphere. The crude reaction mixtures were analyzed by ^{13}C NMR spectroscopy (Bruker, 63 MHz) and the products identified by comparison with authentic samples of the known compounds. The product composition was determined from the intensity of the ^{13}C NMR signals, by considering in every case those resonances which corresponded to carbon atoms with comparable relaxation times. The error of this procedure was estimated by measurement of samples of known composition and was found to be within ca. 10% of the stated values.

Reaction of Diphenyldiazomethane (1) with TNM (General Procedure).

To a 0.25 M solution of diphenyldiazomethane (1) in dichloromethane an equimolar amount of TNM was added under an argon gas atmosphere. The reaction mixture was allowed to react in the dark at room temperature for

7-8 h until complete decoloration and cessation of nitrogen gas evolution. The solvent was removed under vacuum, the resulting solid residue dissolved in deuterochloroform and the ^{19}C NMR spectrum of the resulting solution measured. When acetonitrile was employed as solvent, faster nitrogen evolution was observed and the reaction was complete within 60 min.

*Photolysis of the Charge Transfer Complex between Diphenyldiazomethane (**1**) and TNM.*

To a 0 25 M solution of diphenyldiazomethane (**1**) in deuterochloroform an equimolar amount of TNM was added and the resulting solution placed in an NMR tube under an argon gas atmosphere. The sample was cooled down to -50 °C and irradiated with light at $\lambda > 380$ nm (filtered mercury high pressure lamp, 150 W). After 5 min the reaction was complete and the ^{13}C NMR spectrum was measured.

*Reaction of Diethylsulfide (**8a**) with TNM (General Procedure).*

To a 0.1 M solution of the sulfide **8a** in the corresponding deuterated solvent (cf. Table 2) an equimolar amount of TNM was added and the resulting solution placed in an NMR tube, kept under an argon gas atmosphere. The reaction mixture was cooled down to -5 °C and irradiated for 30 min at $\lambda > 400$ nm with a mercury high pressure lamp (150 W). The reaction was monitored and analyzed by ^{1}H NMR spectroscopy; chloroform was used as internal standard for sulfide **8a** and *tert*-butanol for **8b,c**.

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