

¹⁴C-TNT SYNTHESIS REVISITED

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Mineralization experiments requiring the synthesis of substantial amounts of [ring-¹⁴C]-trinitrotoluene, led us to reinvestigate the published procedures for labeled TNT. Here we describe an efficient, economical and reproducible procedure that results in crystalline ¹⁴C-TNT in 83 % yield with chemical and radiochemical purity of > 99 %. Determination of the specific activity (1.12 GBq/mmol) by mass spectrometry disclosed that the radioactive TNT molecules exhibit an uneven distribution of four to six aromatic ¹⁴C-atoms.

Keywords: trinitrotoluene, TNT, ¹⁴C-synthesis, explosive, specific activity

INTRODUCTION

Extensive production and use of 2,4,6-trinitrotoluene (TNT), particularly during World War II, caused severe contamination of former TNT-manufacturing and -handling sites. TNT and its biological and chemical transformation products exhibit an acute toxicity as well as mutagenic and cancerogenic potencies [1]. Because of their chemical persistence and the low water solubility, these substances contaminate ground- and surface-water and hence still confront us with a problem that has yet to be solved [2].

Therefore, biological [3,4,5] and chemical [6,7,8] procedures that convert the pollutants into ecologically and toxicologically safe compounds are under development. The ultimate goal of such detoxification is the complete degradation of TNT to carbon dioxide (CO₂), water and inorganic nitrogen compounds. Such investigations are dependent on radiotracers, which unambiguously prove the decomposition of the contaminants. The necessity for these experiments prompted us to synthesize a substantial amount of ring-labeled ¹⁴C-TNT of about 1.11 GBq/mmol. Because of the comparatively large amount of labeled material needed, we reinvestigated the literature procedures for isotopically labeled TNT and compared toluene and *p*-nitrotoluene as starting material for ¹⁴C-TNT.

RESULTS AND DISCUSSION

Kinetic, thermodynamic and equilibrium data

Kinetic investigations revealed that the nitration of *p*-nitrotoluene (*p*-MNT) to dinitrotoluene (DNT) [9] and of 2,4-dinitrotoluene to TNT [10] give optimal results, when 90% and 92% sulfuric acid is used as solvent, respectively. The nitration of DNT to TNT is the rate limiting step of the synthesis. Despite the exothermic character of the reactions, with enthalpies between 60 and 140 kcal/mol, the necessary activation energy, particularly for the final nitration step, requires additional heating for the activation and a thorough control of the reaction temperature. This is particularly important because TNT itself shows measurable decomposition at temperatures higher than 110 °C due to oxidation and decarboxylation [12].

The three consecutive nitration steps are convergent so that *o*- and *p*-mononitrotoluene (MNT) both lead to the desired 2,4,6-TNT, while only about 5 % of *m*-orientation occurs in the first nitration step that gives rise to low contamination of 2,4,6-TNT by three other possible isomers (see Fig. 1) [11].

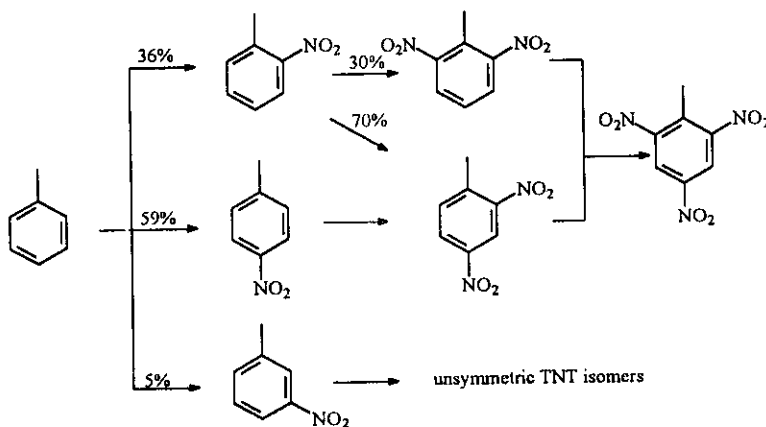


Fig. 1 Nitration sequence from toluene to TNT isomers.

Literature procedures described for the synthesis of isotopically labeled TNT

Over the past 25 years numerous syntheses for isotopically labeled TNT, mainly with ^{14}C -labeling at aromatic ring carbon, have been published (see Table 1). The earliest approach is that of Murray [13] which is an adaptation of the classical three-step TNT synthesis in which, however, isolation of intermediates (MNT and DNT) was omitted. Nitration to MNT was achieved at 0 °C in a mixture of conc. H_2SO_4 and conc. HNO_3 . The dinitration step was carried out at 50 °C using the same nitration mixture, while further nitration of DNT to TNT finally afforded fuming H_2SO_4 (oleum) and fuming HNO_3 at 120 °C.

Table 1: Literature procedures for the synthesis of isotopically labeled TNT.

year of publication	labeling position	starting material	scale of experiment (mmol)	max. reaction temperature (°C)	reagent mixture (H ₂ SO ₄ :HNO ₃ :H ₂ O)	yield (%)
1958 [13]	methyl- ¹⁴ C	toluene	3.5	120	78:17.5:4.5	32
			40			76
1984 [14]	2,4,6- ¹⁵ NO ₂	toluene	10.9	95	90:10:0	26
	2,4- ¹⁵ NO ₂	<i>p</i> -MNT	7.2			42
1994 [15]	ring- ¹⁴ C	toluene	0.003	103	78:22:0	59
1995 [16]	ring- ¹⁴ C	toluene	21.8	95	90:10:0	61
	methyl- ¹⁴ C					47
1995 [17]	ring- ¹⁴ C	toluene	1	120	50:49:1	60
1996 [18]	ring- ¹⁴ C	<i>p</i> -MNT	3.7	95	95:5:0	67

Dorey et.al. [14] developed a synthesis of ¹⁵N-labeled DNT and TNT using H¹⁵NO₃ as labeling reagent. In order to gain high consumption of H¹⁵NO₃, nitration was carried out in three single nitration steps with precise heating and cooling conditions for each step. Despite the relatively low yields, ¹⁵N was incorporated with high enrichment (99 %). The ¹⁴C-TNT synthesis of Michels et.al. [15] is the smallest scale procedure (μl amounts of reagents) described in the literature, and is based on the Houben-Weyl method [19]. The procedure of Ampleman [16] is a direct adaptation of the Dorey [14] method, even though the synthesis was performed with ¹⁴C-labeling rather than to achieve an incorporation of ¹⁵N. Bennett [17] described a one step nitration from toluene directly to TNT using a 1:1 mixture of conc. H₂SO₄ and HNO₃ which is remarkable, as, usually, H₂SO₄ is not only used as part of the nitration mixture but also as a solvent. The reaction was achieved by slowly increasing the temperature from 0 °C to 120 °C over 5 hours. Finally, the synthesis of Klapproth et.al. [18] started from *p*-nitrotoluene in order to begin with a solid starting material rather than with a liquid. In this case *p*-MNT was nitrated in one step using fuming HNO₃ in oleum of 30 % SO₃.

To sum up, despite the various procedures for the synthesis of isotopically labeled TNT, none of the described methods is satisfactory with respect to the simplicity of procedures and to the yields achieved, particularly when compared to the 85 % literature yield of unlabeled material [19]. These experiences prompted us to reevaluate the approaches to ¹⁴C-labeled TNT by varying the

- number of separate nitration steps (between 1 and 3)
- reaction temperature (90-120 °C for the final step)
- nitration reagent (various mixtures of concentrations of H₂SO₄ and HNO₃)
- starting material (toluene and *p*-nitrotoluene) and the
- workup procedure (extraction or precipitation, both followed by recrystallization).

Optimization of TNT synthesis from *p*-nitrotoluene

Starting with the procedure described by Klapproth et al. [18], *p*-MNT (between 0.5 and 7.3 mmol) was dissolved in 5 ml of oleum (30 % SO₃) followed by slow addition of the nitration mixture that consisted of another 5 ml of oleum and 1 ml of fuming HNO₃. A fresh preparation of the reaction mixture turned out to be essential for good results.

After complete addition of reagent, the resulting yellow mixture was stirred for a further 30 min at 0 °C and then heated with stirring overnight at about 100 °C. Workup was generally performed by extraction of the TNT and recrystallization from ethanol.

Table 2: Result of optimizing the conversion of *p*-MNT to TNT.

<i>experiment</i>	<i>scale (mmol)</i>	<i>H₂SO₄</i>	<i>HNO₃ : p-NT</i>	<i>temp. (°C)</i>	<i>yield (%)</i>
NT-07	7.3	oleum (30 %)	3.3 : 1	106	74
NT-08	7.3	93 %	3.3 : 1	90	81
NT-10	2.0	93 %	3.6 : 1	100	86
NT-12	7.3	93 %	3.3 : 1	100	85
NT-13	2.0	98 %	3.6 : 1	100	86
NT-14	7.3	98 %	3.3 : 1	100	89

Gas chromatographic control of the reaction mixture after one hour revealed that most of the MNT had already been transformed to DNT (99.3 %) and that a small amount (0.6 %) of TNT was present at that time. Adapting results from kinetic experiments (see above) 93 % H₂SO₄ was used instead of oleum which gave another increase of total TNT yield to more than 85 % at 100 °C (see Table 2). In order to cut down the reaction time the time dependence of TNT yield was also investigated by gas chromatographic control. From this experiment it became evident that conversion of DNT to TNT is complete after 4 hours of reflux.

Overall, synthesis of TNT from *p*-nitrotoluene can reproducibly be achieved in high yields of 85-90 % for the two reaction steps without workup of the intermediate DNT. Major improvement of the yield could be gained by using concentrated H₂SO₄ instead of oleum. The synthesis can be carried out with a comparatively simple experimental setup, because a non volatile solid starting material is employed. Workup procedure is simple and results in the desired crystalline product of 100 % chemical purity.

Optimization of TNT synthesis from toluene

The initial nitration of toluene to MNTs is the fastest and most exothermic reaction in the three-step sequence from toluene to TNT and therefore affords the most thorough reaction control. Dissipation of

the heat of reaction was supported by dissolving the toluene in half of the total amount of sulfuric acid necessary for the complete nitration. In addition drop rates of one drop of mixed acid in 5 sec under intensive ice cooling ensures a reaction temperature of less than 10 °C for the mono- and dinitration. For instance, if drop rates of 1/sec were used, the reaction temperature increased up to 40 °C in this reaction step.

For the final nitration of DNT to TNT, the temperature should not exceed 100 °C, in order to avoid oxidation of the aromatic methyl group. In this reaction step, the presence of small amounts of water is shown to be much favored over an oleum based mixed acid, as again this nitration step is exothermic, which easily results in temperatures of more than 110 °C. Reactions in which the mixed acid was prepared from oleum therefore showed considerably lower yield (see Table 3). If on the other hand sulfuric acids with a concentration of 98 % and 93 % are employed, water is evaporated and condensed, thereby allowing the reaction temperature to stay between 90-95 °C (see Table 3). These temperature conditions gave the best results in terms of yield and purity of the product.

Table 3: Result of optimizing the one step, consecutive nitration of toluene to TNT.

experiment	scale	H ₂ SO ₄	HNO ₃ : toluene	Temp. (°C)	workup	yield (%)
NT-705	9.4	oleum (30 %)	7.7 : 1	n.d.	extraction	61
NT-706	9.4	oleum (30 %)	4.6 : 1	120	extraction	41
NT-709	9.4	93 %	4.6 : 1	90	extraction	84
NT-711	3.4	93 %	4.4 : 1	90	extraction	70
NT-801	6.8	98 %	4.4 : 1	95	extraction	68
NT-803	7.2	oleum (98%)	4.0 : 1	118	extraction	53
NT-806	7.2	98 %	4.0 : 1	90	ice	80
NT-807	7.2	95 %	5.0 : 1	93	ice	79
NT-809	7.3	95 %	5.0 : 1	92	ice	74
NT-810	7.3	98 %	5.0 : 1	95	ice	79
NT-812	7.3	93 %	5.0 : 1	90	ice	78
NT-813	7.3	98 %	5.0 : 1	n.d.	ice	80

nd = no data

Gas chromatographic control of the reaction revealed that toluene is instantaneously converted to MNT during the addition of mixed acid, so that this product is only detectable within the first few minutes of the reaction time. Analysis of the MNT-ratio showed that mainly *ortho*- (53 %) and *para*-MNT (45 %) are formed while the formation of *meta*-product (1-2 %) can be neglected. In the second nitration step the 2,4-DNT dominated (85 %) over small amounts of 2,6-DNT (15 %) which is in agreement with literature data [11]. DNT-isomers that could derive from *m*-MNT (2,3-DNT, 2,5-DNT, 3,4-DNT) were not detected in the reaction mixture.

The third nitration step is the slowest and needs a temperature increase to almost 100 °C. After 2 h of reaction at 96 °C the nitration is complete, yielding TNT with only minor amounts of undesired isomers (1.0 % of 2,4,5-TNT and 0.9 % of 2,3,4-TNT). It is evident from the variation described in Table 3 that this procedure allows satisfactory yields of up to 80 % and that small variations of the acid concentration, the toluene to HNO₃ ratio, and the temperature, respectively, do not have large effects on the yield of TNT. However, workup procedure favorably should involve precipitation of the reaction mixture on ice after complete nitration rather than extraction of the organic products, because this results in a higher yield and better reproducibility. Therefore, the reaction usually was terminated by transferring to the 4-5 fold volume of ice. The crude TNT was recrystallized from ethanol by carefully employing solubility data from the literature. Solubility of TNT in 100 g of 95 % ethanol is 19.5 g at 75 °C, 1.23 g at 20 °C, and 0.65 g at 0 °C, respectively [12].

In summary, synthesis of TNT from toluene can reproducibly be achieved in high yields of up to 80 % for the complete reaction without workup of the intermediates. Again, a major improvement of the TNT yield could be achieved by using concentrated H₂SO₄ instead of oleum, thereby maintaining the reaction temperature between 90-95 °C. The reaction time is unexpectedly lower than for the corresponding nitration of *p*-MNT which can perhaps be attributed to the high amount of *o*-MNT that results from the initial nitration of toluene. The procedure, however, affords liquid toluene as the starting material rather than the solid, non volatile *p*-MNT, which requires more difficult handling of radioactive material.

Synthesis and characterization of ¹⁴C-TNT

The final synthesis of ¹⁴C-TNT was carried out using 6.29 GBq [U-ring-¹⁴C]-toluene of 2 GBq/mmol specific activity. To reach a desired specific activity of 0.9 - 1.1 GBq/mmol, radioactive toluene was diluted with equimolar amounts of unlabeled starting material. Following the optimized reaction protocol as described in the experimental section, ¹⁴C-TNT was obtained as white crystals in 83 % yield after recrystallization from ethanol. Chemical and radiochemical purity were determined to be > 99 % by GC and radio-GC methods, and additionally by a combination of HPLC and liquid scintillation counting.

For the detection of the specific activity two independent methods were employed. First, exact amounts of 4.0 mg and 5.8 mg, respectively, were dissolved in methanol (250 ml and 500 ml, respectively) and volumes of 20 to 200 µl of these solutions were directly counted in a β-counter (experiment 1a-d). In a complementary experiment a ten-fold dilution of the original methanol solution was measured using volumes of 50-750 µl (experiment 2a-c). Table 4 displays the results of

these experiments, which show an average specific activity of 0.95 and 1.03 GBq/mmol with a total variation of about 15 %.

Table 4: Results from determination of the specific activity of ¹⁴C-TNT by dilution experiments.

experiment	mass (mg)	volume (L)	R ²	specific activity (GBq/mmol)
1a	4.0	2.5	0.9934	0.93
1b	4.0	2.5	0.9912	0.90
1c	4.0	2.5	0.9979	0.95
1d	4.0	0.25	0.9996	1.02
2a	5.8	5.0	0.9954	0.97
2b	5.8	0.5	0.9981	1.05
2c	5.8	0.5	0.9967	1.05

Besides an error range of up to 5 % of the β-counter, the major reason for the variation in the determined specific activity presumably results from absorption of TNT to glass and plastics during the dilution processes. Alternatively, the specific activity was determined from a GC/MS experiment. TNT is known to show an *ortho*-effect in mass-spectrometers which results in an M-OH fragment as the base peak. Therefore, in the spectrum of unlabeled TNT, *m/z* = 210 is found to be the main fragment rather than the MW of 227. In addition, at *m/z* = 211 and at *m/z* = 212 peaks of 9.2 % and 1.3 % of the base peak are detected mainly because of the ¹³C-content. In contrast, due to the presence of 7 carbon atoms, a maximum of 7.7 % of the base peak should be found at *m/z* = 211. The difference to the observed peak height is due to additional fragmentation of an oxygen atom from the TNT [20].

The mass spectrum of the synthesized ¹⁴C-TNT displays additional peaks at *m/z* up to 222 which account for the presence of up to 6 radioisotopes of carbon in the aromatic ring (Fig. 2).

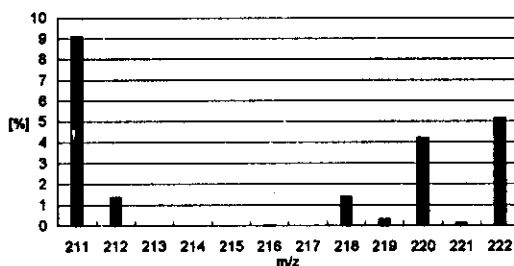


Fig 2: Peak heights (relative to base peak at *m/z* = 210, 100 %, not shown) of masses higher than *m/z* = 210 in the mass spectrum of the synthesized [ring-¹⁴C]-TNT.

It is evident from Fig. 2 that the highest peak with *m/z* = 222 corresponds to a completely labeled benzene ring with six aromatic ¹⁴C-atoms, while *m/z* = 220 and 218 are attributed to a five-fold and

four-fold labeling, respectively. This rather unexpected finding discloses that the [U-ring- ^{14}C]-toluene did not consist of uniformly, e.g. monolabeled starting material with randomly distributed radioisotopes in the ring, but rather displayed an uneven mixture of toluene of four to six ^{14}C -atoms. In addition a minor amount of triple labeled material is also found. No double- or monolabeled TNT is present as the detected 1.35 % of $m/z = 212$ is well in agreement with the identical mass peak in unlabeled TNT. Peaks of uneven m/z values ($m/z = 219$ and 221) correspond to isotopes of uneven mass, such as ^{13}C . From the frequency of the peaks at $m/z = 222$, 220 , and 218 , respectively, it can be deduced that about 48 % of the radioactive TNT molecules are indeed uniformly labeled with each ring atom being substituted by ^{14}C . On the other hand, in case of the five-fold (39 %) and four-fold (13 %) labeled TNT the term uniformly labeled strictly speaking is wrong.

The results from the mass spectrum have been used to determine the specific activity of the ^{14}C -TNT. Several methods for this procedure, all being based on the same principle, are described in the literature [21,22]. The crucial step is the comparison of the abundance of the unlabeled fragment at $m/z = M$ with labeled ones at $m/z = M + 2n$ (n = number of labeled atoms in the fragment). The abundance of each labeled peak is multiplied with the number of incorporated labeled atoms. The overall percentages are summed up and divided by the overall occurrence of the fragment (see equation 1). The specific activity can then be calculated by multiplication of this ratio with the maximum specific activity of a singly ^{14}C -labeled molecule (2.31 GBq/mmol), according to equation 1.

$$\frac{A}{A_{\max}} = \frac{\sum n_{(F)} * H_{(F)}}{H_{\max}} \quad (\text{equation 1})$$

(A = specific activity; A_{\max} = maximum specific activity; $H_{(F)}$ = spectral abundance of fragment F ; n = number of labeled isotopes in fragment F ; H_{total} = overall abundance of the fragment)

Kanamaru et. al. have refined this calculation by taking into account unlabeled fragments with $m/z = M + 2n$ [22]. Such peaks must be taken from the spectrum of the "cold" compound. On the basis of this procedure we further improved the calculation method by additionally including peaks of odd mass numbers. These peaks originate mainly from the occurrence of stable isotopes like ^{13}C . This would be of no significance for a single label, but has a growing influence as the number of labeled atoms per molecule increases. About one percent of the unlabeled atoms occur as ^{13}C , which clearly is not the case for a ^{14}C -labeled atom. Therefore the fraction of molecules containing a ^{13}C is smaller in a multiple ^{14}C -labeled compound than in an unlabeled fragment. Hence the specific activity is overrated by calculations neglecting odd mass numbers.

Consequently, we have added the $m/z = M + 1$ peak to the fraction of the unlabeled compound, while the abundance of mass numbers $m/z = M + 2n + 1$ was added to the corresponding labeled species with $m/z = M + 2n$.

Table 5: Calculation of specific activity from mass spectral data of ¹⁴C-labeled TNT.

<i>m/z</i>	<i>H [%]</i>	<i>x</i>	<i>calculation [H * x] according to</i>		
			<i>Goldstein [21]</i>	<i>Kanamaru [22]</i>	<i>this work</i>
210	100				
211	9.12				
212	1.35				
216	0.01	3	0.03	0.03	0.03
217	0.00	3			
218	1.41	4	5.66	5.66	5.66
219	0.29	4			1.15
220	4.20	5	20.99	20.91	20.99
221	0.11	5			0.56
222	5.13	6	30.77	30.49	30.77
sum of H radioactive			57.45	57.09	59.16
sum of H total			112.10	112.10	121.62
specif. act. (GBq/mmol)			1.183	1.176	1.124

With this procedure we calculate a specific activity of 1.12 GBq/mmol in contrast to 1.18 GBq/mmol calculated according to Goldstein and Rainey [21] and Kanamaru [22]. The difference between the 1.12 GBq/mmol calculated from the mass spectrum and the 0.95 and 1.03 GBq/mmol, respectively, obtained from liquid scintillation counting is well in line with deviations found by other authors [21] between dilution experiments and mass spectrometry results.

In summary, the described procedure for the synthesis of ¹⁴C-TNT displays a major improvement in terms of the TNT-yield and was shown to be a reliable and reproducible process which most economically can be done starting from labeled toluene. The derived product is of excellent purity and of high specific activity and can now be employed in the investigation of TNT degradation and mineralization by biological and/or chemical methods. Experiments along these lines are presently in progress in our laboratory.

EXPERIMENTAL

General procedure for the synthesis of TNT from p-nitrotoluene

The nitrating agent, a mixed acid, was produced by stirring nitric acid under ice cooling and carefully adding the three-fold volume of sulfuric acid. Then, 4-nitrotoluene was dissolved in sulfuric acid and the freshly prepared mixed acid was added dropwise under stirring and cooling. After stirring at room temperature for 30 minutes the reaction mixture was heated for 5 hours. Recovery of the product was achieved through extraction with methylene chloride (3 x 50 ml), washing of the combined organic

phases with water and drying over MgSO_4 . After evaporation of the solvent the crude product was purified by crystallization from ethanol.

General procedure for the synthesis of TNT from toluene

Toluene was dissolved in sulfuric acid and freshly prepared mixed acid was added dropwise under stirring and cooling. After stirring at room temperature for 30 minutes the reaction mixture was heated for 3 hours. Workup was carried out either by extraction with methylene chloride as described above or by pouring the reaction mixture onto crushed ice, collecting the product by filtration, followed by washing with water. The crude material was purified by crystallization from ethanol.

Synthesis of ^{14}C -TNT

The reaction apparatus consisted of a reaction tube (100 ml) and a break seal ampoule, both of which were attached to a vacuum manifold. Toluene (0.29 g, 3.15 mmol) was dissolved in concentrated sulfuric acid (98 %, 4 ml) and frozen to $-196\text{ }^\circ\text{C}$ in the reaction tube. [U-Ring- ^{14}C]-Toluene (6.29 GBq, 2 GBq/mmol) was added to the mixture by vacuum distillation (0.2 mbar, $20\text{ }^\circ\text{C}$) from the break seal ampoule after the seal was broken with a "magnetic hammer". During thawing of the reaction mixture, mixed acid is added dropwise. The mixed acid had been prepared by slow addition of concentrated sulfuric acid (4 ml) to fuming nitric acid (1.5 ml) at $0\text{ }^\circ\text{C}$. The reaction mixture was then stirred at room temperature for 30 min, further heated at $90\text{ }^\circ\text{C}$ for 3 hours and poured onto crushed ice (50 g) after cooling to room temperature. The crude product was collected, washed with a few ml of cold water and recrystallized from ethanol (95 %, 15 ml) to give 0.97 g (67.5 %) colorless needles of [U-Ring- ^{14}C]-TNT. Careful concentration of the filtrate resulted in another 0.23 g (16 %) of product to yield an overall amount of 1.2 g (83 %) of ^{14}C -TNT. GC and HPLC analysis proved the chemical and radiochemical purity to be greater than 99.9 %.

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REFERENCES

- [1] J. Yinon, *Toxicity and Metabolism of Explosives*, CRC Press, Boca Raton, 1990.

- [2] D. Martinetz, G. Rippen in *Handbuch Umweltchemikalien* (Ed.: G. Rippen), 3rd ed, ecomed Verlag, Landsberg/Lech, 1990, vol. 2, chapter 2.6.
- [3] K. Scheibner, M. Hofrichter, A. Herre, J. Michels, W. Fritsche, *Appl. Environ. Microbiol.*, 1997, 47, 452-457.
- [4] J. Breitung, D. Bruns-Nagel, K. Steinbach, L. Kaminski, D. Gemsa, E. von Löw, *Appl. Environ. Microbiol.*, 1996, 44, 795-800.
- [5] H.-J. Knackmuss, G. Daun, H. Lenke, M. Reuss, *Environ. Sci. Technol.*, 1998, 32, 1956-1963.
- [6] Z. Wang, C. Kotal, *Chemosphere*, 1995, 30, 1125-1136.
- [7] R. Dillert, U. Fornefett, D. Siebers, *J. Photochem. Photobiol. A: Chemistry*, 1996, 94, 231-236.
- [8] M. Nahen, R. Bahnemann, R. Dillert, G. Fels, *J. Photochem. Photobiol. A: Chemistry*, 1997, 110, 191-199.
- [9] M. I. Vinnik, Zh. E. Grabovskaya, L.N. Arzamaskova, *Russ. J. Phys. Chem.*, 1967, 41, 580-583.
- [10] G. M. Bennett, J. C. D. Brand, T. G. Saunders, G. Williams, *J. Chem. Soc.*, 1947, 474-492.
- [11] F. A. Carey, R. J. Sundberg, *Organische Chemie*, VCH, Weinheim, 1995.
- [12] T. Urbanski, *Chemistry and Technology of Explosives*, Pergamon Press, Oxford, 1964, vol. 1.
- [13] A. Murray III, D. L. Williams, *Organic Synthesis with Isotopes*, Interscience Publ. Inc. , New York, 1958, p. 893.
- [14] R. C. Dorey, W. R. Carper, *J. Chem. Eng. Data*, 1984, 29, 93-97.
- [15] J. Michels, G. Gottschalk, *Appl. Environ. Microbiol.*, 1994, 60, 187-194.
- [16] G. Ampleman, S. Thiboutot, Lavigne, A. Marois, J. Hawari, A.M. Jones, D.Rho, *J. Labelled Cpd. Radiopharm.*, 1995, 36, 559-577.
- [17] J. W. Bennett, P. Hollrah, A. Waterhouse, K. Horvath, *Int. Biodet. Biodeg.*, 1995, 421-430.
- [18] G. Fels, A. Klapproth, S. Linnemann, D. Bahnemann, R. Dillert, *J. Labelled Cpd. Radiopharm.*, 1998, 41, 337-343.
- [19] D. Pawellek, W. Seidenfaden, *Aromatische Nitroverbindungen in Houben-Weyl: Methoden der Organischen Chemie*, 4th ed, VCH, Weinheim, 1972, p. 524.
- [20] S. Bulusu, Th. Axenrod, *Org. Mass Spectrom.*, 1979, 14, 585-592.
- [21] G. Goldstein, W. T. Rainey, *J. Labelled Cpd. Radiopharm.*, 1973, 9, 805-815.
- [22] H. Kanamaru, R. Takai, M. Horiba, I. Nakatsuka, A. Yoshitake, *Radioisotopes*, 1985, 34, 67-71.