Nineteen grams of the crude IV was added with stirring over a period of 1 hr to 17.1 grams (0.135 mole) of oxalyl chloride dissolved in 100 ml of dry pyridine. The reaction mixture was stirred at room temperature for 2 hr and then refluxed for an additional hour. After cooling in an ice bath, the reaction mixture was poured into water and allowed to stand overnight. The precipitate was filtered, dried, and recrystallized from ethyl acetate. The semipurified material was then taken up in methylene chloride and chromatographed through alumina. Recrystallization of this material from ethanol gave 9.0 grams of *N,N'*-(2-methylphenacyl) oxamide (V), mp 153–157°C in 19% overall yield from III. Repeated chromatography of V through alumina in methylene chloride followed by recrystallizations from ethanol gave a more pure product, mp 162–162.5°C.

5,5'-Diphenyl-2,2'-bi(4-methyloxazole)(If). One and three-tenths grams (0.0037 mole) of *N,N'*-(2-methylphenacyl) oxamide (V), mp 156–158°C, was heated at 80°C with stirring in 60 ml of phosphoryl chloride for 48 hr. Upon cooling, the reaction mixture was poured into water, and the resulting precipitate filtered. Recrystallization of the crude precipitate from ethyl acetate, followed by chromatography through alumina in benzene and another recrystallization from ethyl acetate, gave 0.72 gram (62%) of If as pale green crystals, mp 218–219.5°C. Shorter reaction times gave substantially lower yields. Repeated recrystallization from ethyl acetate gave an analytical sample, mp 219.5–220°C.

Acknowledgment

Special thanks are due Guido H. Daub of the University of New Mexico for assistance with the determination of the relative pulse heights and to Dale Robertson and Thomas Waugh for many stimulating discussions.

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Received for review June 16, 1972. Accepted July 9, 1973.

Mass Spectra of Isomers of Trinitrotoluene

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The mass spectra of the six isomers of trinitrotoluene are presented. The fragmentation pathways leading to the major fragment ions are outlined.

Detection of explosives by sensing associated vapors has been under investigation in this and other laboratories for some time (*1, 2, 5, 9*). During a study to define the composition of vapor emitted by production grade TNT, a requirement developed for accurate mass spectra of the individual isomers of trinitrotoluene. Since these data were not available in the literature, it was necessary to make these determinations.

Table I is a compilation of the mass spectra of the six isomers of trinitrotoluene at 75 eV. Mass spectra were also taken (*8*) at ionizing energies intermediate between this value and the ionization potential of the molecules, but no anomalous behavior was observed; therefore, these spectra are not presented here. Mass spectra were similarly obtained (*8*) for the isomers of DNT and were consistent with earlier published results (*7*).

Discussion

The major route of decomposition, for all isomers except 3, 4, 5, originates with a loss of the hydroxyl radical (OH) from the molecular ions. This fragmentation is important in cases where a methyl group is located ortho to an aromatic nitro substituent (*4, 8*). This path leads to a rearranged species of mass 210 which subsequently loses NO and NO_2, giving ions of mass 180 and 134, respectively. Prevalent lower mass ions generally are formed from further decomposition of these species, although a portion of the mass 30 ion may originate from primary fragmentation of the molecular ion.

In contrast, the mass spectrum of the 3, 4, 5 isomer is dominated by a large mass 30 ion (NO^+) accounting for more than 25% of the total ion current. This ion is formed at least in part from the molecular ion as confirmed by the presence of a metastable at $m/e = 4.0$. The remaining ions are generally the result of successive loss of NO_2 molecules followed by normal hydrocarbon fragmentation. The total absence of a mass 210 ion for this compound is to be expected, since it is the only isomer without an ortho methyl group.

Experimental

The mass spectra reported in Table I were obtained on a Perkin-Elmer 270B mass spectrometer operated at 75 eV with the ion source temperature maintained at 150°C. The samples were introduced via a quartz capillary from the standard solids probe inlet system. The probe was not intentionally heated, although a thermocouple within the solid probe indicated a temperature of 70°C. The purity of the individual isomers was established (*6*) by melt-

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Table I. Mass Spectra of Isomers of Trinitrotoluene at 75 eV (Given as % of Base Peak)

M/e	2, 3, 4	2, 3, 5	2, 3, 6	2, 4, 5	2, 4, 6	3, 4, 5
30	85	72	85	88	41	100
38		7	15		4	
39	34	27	47	24	25	12
46	16	7	8	5	5	12
50	13	17	26	16	12	4
51	40	48	71	38	20	16
52	15	15	16	14	5	7
53	10	6	12	14	4	4
61		6	10		6	
62	16	21	35	17	21	7
63	52	44	78	38	38	21
64	8	7	18	6	8	2
65		5	9	6	8	4
69					6	
74		6	11		11	2
75		6	19	5	9	
76	11	14	28	14	20	2
77	20	13	23	10	10	12
78		7	15	5	6	2
79			6			
80			12			
86		6	9	5	7	2
87		8	15	7	9	3
88		5	5		10	
89	18	12	15		48	13
90			17		6	
91			6			
92			7		6	
93			9			
103					4	
104			9		4	
105			15		6	
106			13		5	
107	7	5	9			5
116					3	
118			6	13		
119			5			
120			6		4	
134	100	26	44		16	
135	10		6		4	3
149			15		12	
164					6	
166					4	
179					8	
180	41	73	32		15	
181		6				
182			4			
184				13		
193			6		13	
209					5	
210	48	100	100	100	100	
211	6	9	14	11	10	2
227	10	13	14	20	3	10

Table II. Melting-Point Data for Isomers of Trinitrotoluene

Trinitro- toluene isomer	Value obtained (*6*)	Lit value (*3*)
2, 3, 4	111.5 (*6*)	112
2, 4, 5	104.0 (*6*)	104
2, 3, 6	111.0 (*6*)	111
2, 3, 5	97.0 (*6*)	97
3, 4, 5	137.0 (*6*)	137.5
2, 4, 6	80–81°C	80.5

ing-point determinations (Table II). We also confirmed the purity by gas chromatography prior to obtaining the mass spectra. The preparation and characterization of the isomers have been described by other investigators (*6*).

Acknowledgment

Samples were provided by Charles Ribaudo and Frank Pristera, Picatinny Arsenal, Dover, N.J.

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Received for review November 6, 1972. Accepted April 26, 1973. Support was provided by the Mine Detection Division, USAMERDC, Ft. Belvoir, Va.