

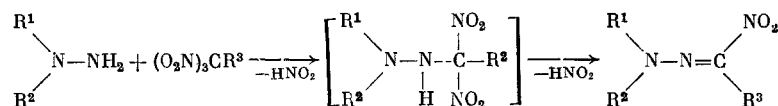
SYNTHESIS AND PROPERTIES OF α -C-NITROHYDRAZONES

2. REACTION OF HYDRAZINES WITH TRINITROMETHYL COMPOUNDS

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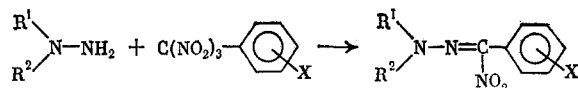
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The previous paper [1] described the use of tetranitromethane (TNM) for "gem-dinitromethylation," and the scope of this reaction was considerably extended; the reaction was found to proceed smoothly with a series of 1,1-disubstituted hydrazines. In the present work, this reaction has been extended to include compounds with trinitromethyl groups. By analogy with the gem-dimethylation reaction, the formation of α -C-nitrohydrazones can be assumed to take place according to the following scheme:



However, the reaction of nucleophilic reagents with trinitromethyl compounds is influenced by the structure of the latter, and loss of HNO_2 to give salts of the dinitro compound or decomposition of the trinitromethyl adducts may also occur.

A number of trinitromethyl compounds were prepared in order to study their reaction with 1,1-disubstituted hydrazines. Aryltrinitromethanes, 1,1,1-trinitroalkanes, and some trinitromethyl adducts were prepared by the Michael and Mannich reactions, and the reactions between these compounds and 1,1-dimethylhydrazine (UDMH) and aminopiperidine were investigated. Treatment of phenyltrinitromethane with UDMH, N-aminopiperidine, and N-methyl-N- β -cyanoethylhydrazine afforded 1-nitro-1-phenyl-2,3-diaza-3-methyl-1-butene (I), 1-nitro-1-phenyl-2,3-diaza-3,3-(pentamethylene)prop-1-ene (II), and 1-nitro-1-phenyl-5-cyano-2,3-diaza-1-pentene (III) respectively in good yields (Table 1). The presence of a strong electron-withdrawing substituent such as a nitro group in the para or meta position, as in the case of compounds (IV) and (V), reduces the yield only slightly. High yields were obtained when the reaction was carried out at $\sim 20^\circ\text{C}$



with the following solvents: ether, MeOH, THF, and dioxane. The formation of the α -C-nitrohydrazone was not inhibited by the presence of an α -hydrogen atom. Compounds such as 1,1,1-trinitroethane and 1,1,1-trinitro-3-cyanobutane, which readily eliminate HNO_2 [3], gave $\sim 85\%$ yields of the α -C-nitrohydrazones (VI)-(VIII). A number of trinitromethyl adducts, obtained by the Mannich reaction, also undergo this reaction; N,N'-bis(trinitroethyl)urea, N-trinitroethylacetamide, and N-methyl-N-(trinitroethyl)nitramine reacted with UDMH and with N-aminopiperidine to give compounds (IX)-(XIV) in yields of over 80%.

This reaction thus seems to be generally applicable and can be used to prepare a variety of structurally different trinitro compounds in high yields. The reaction gives only one of several possible products, indicating that it follows a thermodynamically favorable pathway. The driving force in the process appears to be the formation of the conjugated system of the α -C-nitrohydrazone.

The α -C-nitrohydrazones are convenient starting compounds for the synthesis of amidrazones [4], and they are also reported to exhibit physiological activity [5], but the method of synthesis formerly used involving the nitration of arylhydrazones generally gave low yields [6]. An exception to this is the nitration of arylhydrazones with alkyl nitrates in liquid NH_3 in the presence of KNH_2 [7] to give aromatic α -C-nitrohydrazones. However, all these methods were used only for aromatic compounds and gave α -C-nitrohydrazones of general formula $\text{RC}(\text{NO}_2)=\text{N}-\text{NHA}r$. The method we have developed is the first general method for the synthesis of α -C-nitrohydrazones starting from unsymmetrical dialkylhydrazines and trinitromethyl compounds.

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TABLE 1

Compound	Formula	Yield, %	mp, °C	IR spectrum (KBr) ν , cm^{-1}	UV spec- trum (CH_3OH), λ , nm	PMR spectrum δ , ppm (in CDCl_3)	Found Calculated, %		
							C	H	N
(I)		92	124,5-125	1295, 1512, 1618	346	2,93 s (6H) 7,39 s (5H)	55,99 55,98	5,70 5,70	21,83 21,77
(II)		95	94-95	1300, 1512, 1620, 1600 (Ar)	348	1,90 m (6H) 3,44 m (4H) 7,39 s (5H)	61,43 61,80	6,52 6,43	17,84 18,03
(III)		88	105-106	1290, 1510, 1625, 2140 (C=N)	336	2,71 m (5H) 3,72 s (2H) 7,38 s (5H)	57,06 56,89	5,23 5,17	24,17 24,14
(IV)		83	148	1506, 1542, 1610	342	3,00 s (6H) 7,94 q (4H)	42,39 42,48	4,46 4,42	24,92 24,78
(V)		78	129-131	1506, 1532, 1610	336	3,00 s (6H) 8,05 m (4H)	42,53 42,48	4,40 4,42	24,34 24,78
(VI)		86	81-82	1286, 1510, 1620	355	3,17 s (6H) 2,51 s (3H)	36,50 36,61	6,88 6,87	32,17 32,24
(VII)		83	77,5	1290, 1512, 1610, 2240 (C=N)	347	3,34 s (6H) 3,02 m (4H)	42,14 42,35	5,90 5,88	33,38 33,57
(VIII)		88	89-90	1240, 1522, 1624, 2260 (C=N)	226, 347	1,61 m (4H) 1,94 m (4H) 2,66 m (2H) 3,4 t (4H)	51,30 51,43	6,72 6,66	26,47 26,66
(IX)		90	96-97	1305, 1510, 1575, 1605, 1635, 3320, 3380	340	3,37 (12H) 1,67 m (4H)	34,20 33,96	5,87 5,70	34,92 35,20
(X)		80	90-92	1300, 1510, 1610, 1680, 3380	209, 346	3,18 s (6H) 2,9 m (1H) 4,51 d (2H) 1,91 s (3H)	38,52 38,30	6,53 6,38	30,05 29,78
(XI)		82	91-93	1290, 1515, 1602, 1650, 3250	223, 348	1,65 m (10H) 1,90 s (3H) 2,83 m (1H) 4,55 d (2H)	47,72 47,37	7,24 7,01	24,46 24,56
(XII)		68	108,5	1300, 1515, 1612	340	3,42 s (9H) 4,78 s (2H)	29,35 29,24	5,78 5,36	33,76 34,14
(XIII)		70	98,5	1300, 1515, 1525, 1622, 2200 (C=N)	333	3,98 s (6H) 3,2-3,8 m (6H)	33,98 34,42	5,25 4,91	34,16 34,43
(XIV)		73	71-72	1305, 1507, 1515, 1595	218, 240, 353	1,72 m (6H) 3,51 m (4H) 5,21 m (2H) 1,84 s (3H)	39,40 39,18	6,28 6,12	28,59 28,57
(XV)		81	102-104	1100, 1290, 1470, 1510, 3120, 3290, 3350	369	2,69 s (3H) 4,34 s (4H) 7,35 s (5H)	42,04 42,10	5,18 5,26	24,89 24,56

All the C-nitrohydrazones obtained are yellow crystalline substances, soluble in organic solvents and stable in air without visible change. The IR spectra of these compounds show bands characteristic of symmetrical vibrations of the conjugated nitro group in the region $1280-1300\text{ cm}^{-1}$ and of unsymmetrical vibrations in the region $1500-1520\text{ cm}^{-1}$, and also absorption bands from the C—N bond in the region $1600-1620\text{ cm}^{-1}$. The UV spectrum of the C-nitrohydrazones have sharp peaks in the region $330-360\text{ nm}$.

The reaction is inhibited by the presence of strongly electron-withdrawing substituents on the N atom, which sharply lower the basicity of the hydrazine. Thus, after heating 1-methyl-1-nitrosohydrazine or 4-amino-1,2,4-triazole with a number of different trinitromethyl compounds for a prolonged period, the starting compounds were isolated.

In the absence of 1,1-disubstituted hydrazines, the monomethyl hydrazine reacts with trinitromethyl compounds to give the corresponding salts of the dinitromethyl compound. The majority of these salts are unstable and they were characterized by UV spectra. The absorption maximum of these salts lie in the region 360-380 nm, which is characteristic for the anions of dinitromethyl compounds. The product of the reaction of methyl hydrazine and phenyl trinitromethane is very stable and was characterized completely. Under the same conditions, the free hydrazine and 1,1,1-trinitroethane forms the salt of dinitroethane.

Compounds containing secondary geminal dinitro groups did not appear to react with 1,1-disubstituted hydrazines and a mixture of 2,2-nitropropane and UDMH after standing for several months gave only the starting 2,2-nitropropane.

EXPERIMENTAL

General Methods of Preparation of α -C-Nitrohydrazones. To a stirred solution of 0.01 mole of the trinitromethyl compound in 50 ml of absolute ether, MeOH, dioxane, THF, or MeCN at $\sim 20^\circ\text{C}$ was added dropwise over a period of 15-20 min 0.012-0.015 mole of the 1,1-disubstituted hydrazine in 50 ml of solvent. Stirring was continued for a further 30-40 min, the solvent evaporated, and the C-nitrohydrazone which separated recrystallized from ether.

CONCLUSIONS

A new convenient method for the synthesis of α -C-nitrohydrazones starting from unsymmetrical dialkylhydrazines and trinitromethyl compounds is suggested.

LITERATURE CITED

1. I. Sh. Shvartz, M. M. Kravushkin, V. V. Sevost'yanova, and V. N. Yarovenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 813 (1979).
2. K. V. Altykhov and V. V. Perekalin, *Usp. Khim.*, **45**, 2050 (1976).
3. A. D. Nikolaeva, L. B. Zamirova, and N. M. Lyalin, *Zh. Org. Khim.*, **10**, 2304 (1974).
4. D. Nelson, R. Roger, J. Heatle, and L. R. Newlands, *Chem. Rev.*, **70**, 151 (1970).
5. L. S. Pupko, A. I. Dyachenko, and P. S. Pel'kis, *Inventor's Certificate No. 237882*, 1969; *Ref. Zh. Khim.*, 9N301 (1970).
6. E. Bamberger and E. Pensel, *Ber.*, **36**, 57 (1903).
7. N. Feuer and L. Spinicelli, *J. Org. Chem.*, **41**, 2981 (1976).