HETEROCYCLIC ANALOGS OF PLEIADIENE. XVII.* NITRATION OF PERIMIDINES WITH NITROUS ACID AND NITROGEN DIOXIDE

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The corresponding nitroperimidines are formed instead of the expected nitroso compounds in the reaction of nitrous acid with perimidine and aceperimidine derivatives. Nitrogen oxides formed during the decomposition of nitrous acid are apparently the nitrating agent. In fact, nitrogen dioxide very readily nitrates perimidines and aceperimidines.

We have investigated the possibility of nitrosation of perimidines with nitrous acid. The formation of a deep-red color is observed when crystalline sodium nitrate or an aqueous solution of sodium nitrite is added to an acetic acid solution of perimidines and aceperimidines even in the cold, and this could attest to the formation of a C-nitroso compound. However, all of the red or orange substances that we isolated unexpectedly corresponded to nitro compounds rather than to nitroso compounds according to the results of elementary analysis. Their IR and UV spectra, like their melting points, were completely identical to the nitroperimidines that we previously obtained [1].

We made a detailed study of the action of nitrous acid on aceperimidine Ia: we varied the temperature, amounts of solvent and sodium nitrite, reaction time, investigated the possibility of replacement of acetic acid by hydrochloric acid, etc. The results (Table 1) make it possible to draw the following conclusions: 1) the reaction proceeds at room temperature and is complete after 30 min; 2) extremely dilute solutions must be used to obtain the maximum yields of nitro compounds (experiments Nos. 3 and 7); 3) increasing the amount of sodium nitrite above 1 mole does not cause an increase in the yield of the mononitro derivative but rather reduces it (experiments Nos. 1 and 3).

In addition to 4(9)-nitroaceperimidine, 4,9-dinitroaceperimidine (IIIa), which is formed in 55% yield in the reaction of 1 mole of nitrous acid with 4(9)-nitroaceperimidine, was

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*See [1] for communication XVI.

TABLE 1. Reaction of Aceperimidine with Nitrous Acid

No.	Reaction conditions					Yield, %	
	$NaNO_2$, mole	CH_3COOH, ml	H_2O, ml	Temp., °C	Time, min	II	III
1	1,5	20	5	20	60	30	—
2	1,5	20	5	40—50	60	38	—
3	1	85	5	20	30	47	—
4	1	85	5	40—50	30	32	—
5	1	85	5	20	90	50	12
6	1	85	2	20	90	40	16
7	1	20	2	20	30	31	—

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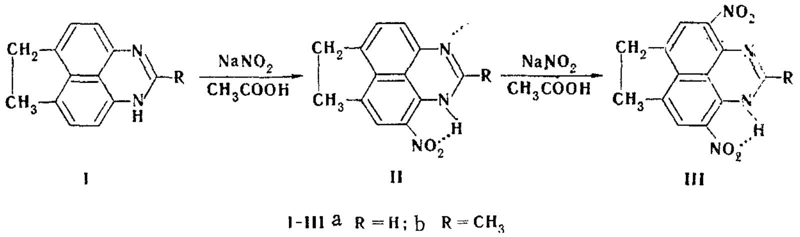
TABLE 2. Results of Nitration

Starting compound	Nitrating agent	Reaction product	Yield, %
Aceperimidine	HNO_2	4(9)-Nitroaceperimidine	50
		4,9-Dinitroaceperimidine	12
2-Methylaceperimidine	HNO_2	4(9)-Nitro-2-methylaceperimidine	25
1-Methylaceperimidine	HNO_2	4-Nitro-1-methylaceperimidine	28
4(9)-Nitroaceperimidine	HNO_2	4,9-Dinitroaceperimidine	55
Perimidine	HNO_2	4(9)-Nitroperimidine	26
		6(7)-Nitroperimidine	33
2-Methylperimidine	HNO_2	4(9)-Nitro-2-methylperimidine	23
		6(7)-Nitro-2-methylperimidine	40
4(9)-Nitroperimidine	HNO_2	6,9-dinitroperimidine	27
6(7)-Nitroperimidine	HNO_2	6,9-dinitroperimidine	29
Aceperimidine*	Liquid NO_2	4(9)-Nitroaceperimidine	70
		4,9-Dinitroaceperimidine	19
2-Methylperimidine	Liquid NO_2	4(9)-Nitro-2-methylperimidine	33
		6(7)-Nitro-2-methylperimidine	54
Perimidine	Liquid NO_2	4(9)-Nitroperimidine	23
		6(7)-Nitroperimidine	10

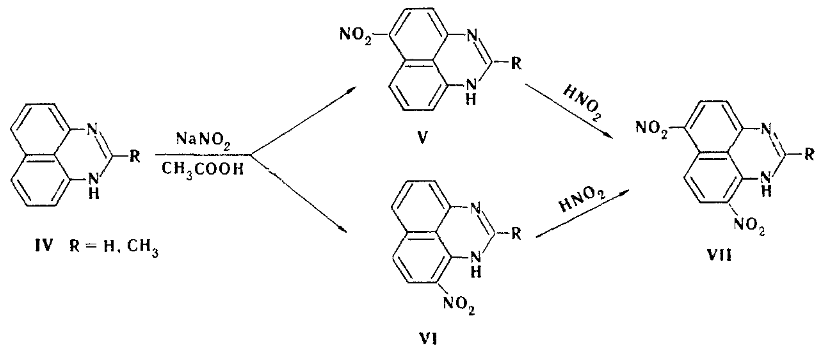
*The experiment was carried out with 2 moles of NO_2.

also isolated in several experiments even when 1 mole of sodium nitrite was used:



The formation of 4(9)-nitroaceperimidine is also observed in the reaction of sodium nitrite with an aqueous solution of aceperimidine hydrochloride.

Perimidine and 2-methylperimidine are nitrated by nitrous acid to give a mixture of 4(9)- and 6(7)-nitro derivatives. Both isomers are converted to the same dinitro derivative — 6,9-dinitroperimidine (VII)* — in 30% yield by the action of a second mole of nitrous acid:



Instances of nitration by means of nitrous acid have been described in the literature [2]. All of these cases pertain to phenols and aromatic amines that do not contain electron-acceptor groups. It is supposed that nitration of phenols and amines under these conditions proceeds through an intermediate step involving the formation of a C-nitroso compound, which is subsequently oxidized to a nitro compound under the influence of air oxygen or, which

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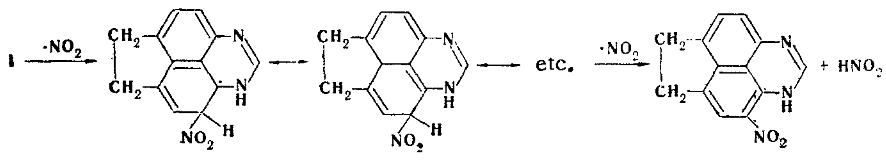
*We did not attempt to isolate the other dinitro compounds, the formation of which was observed in the nitration of perimidine with 2 moles of nitric acid [1].

seems more likely, nitrous gases [2]. We feel that this sort of nitration mechanism is unlikely in our case. First of all, we were unable to chromatographically and preparatively detect even traces of a C-nitroso compound (this was also noted during the analogous nitration of phenols [2]). If it is assumed that the oxidation of C-nitrosoperimidine proceeds very rapidly, for whatever reasons, it is impossible to assume that the same thing would also be observed during the second nitration of perimidine with nitrous acid: the nitro group already in the ring would retard oxidation. There is also no basis for the assumption of participation of N-nitrosoperimidines in the reaction, inasmuch as nitrous acid also nitrates 1-methylaceperimidine (Table 2).

We assumed that the nitrating agent in the reaction of nitrous acid with perimidine is the nitrogen dioxide formed during the decomposition of nitrous acid [3]:

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O \qquad 2NO + O_2 \longrightarrow 2NO_2$$

The validity of this assumption was confirmed by the successful nitration of aceperimidine, perimidine, and 2-methylperimidine with nitrogen dioxide in acetic acid. The reaction proceeds very rapidly at room temperature to give high yields of products (except in the case of perimidine). All of this in conjunction with the literature data regarding the mechanism of nitration by means of nitrogen dioxide makes it possible to assume radical character for it [4].



VIII

The ease of nitration of perimidines with nitrogen dioxide is apparently due to the stability of intermediate resonance-stabilized radical VIII.

It should be noted that in the reaction of both nitrogen dioxide and nitrous acid the ratio of o- and p-nitro derivatives formed in the case of 2-methylperimidine favors the latter, whereas just the opposite is observed in the case of perimidine. A similar principle is observed in the nitration of these compounds with nitric acid [1].

EXPERIMENTAL METHOD

4(9)-Nitroaceperimidine (II). A) A 0.16-g (2.5 mmole) sample of sodium nitrite was added in small portions with stirring to a solution of 0.49 g (2.5 mmole) of aceperimidine (I) in 85 ml of glacial acetic acid, and the resulting bright-red solution was stirred at room temperature for 1 h, after which it was neutralized with ammonia. The resulting precipitate was dried and extracted with chloroform in a Soxhlet extractor until the color of the chloroform solution vanished. The chloroform extract was passed through a column filled with aluminum oxide to give initially 0.3 g (50%) of II and then 0.09 g (12%) of III. The UV and IR spectra of recrystallized II and III were completely identical to the spectra of authentic samples obtained in [1].

B) Aceperimidine hydrochloride [1.03 g (4.4 mmole)] was dissolved in 150 ml of water, the solution was cooled to 0°, and a saturated solution of 0.31 g (4.4 mmole) of $NaNO_2$ in water was added slowly dropwise at this temperature in the course of 1 h. The mixture was then stirred for another hour at the same temperature. The resulting dark-red precipitate was removed by filtration, dried, and extracted with chloroform in a Soxhlet extractor. The extract was passed through a thin layer of aluminum oxide to give 0.27 g (26%) of II.

C) A 0.16-ml (5 mmole) sample of liquid nitrogen dioxide* obtained by the action of

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*The liquid nitrogen dioxide for the remaining experiments was obtained by heating $Pb(NO_3)_2$ with sand [5].

concentrated HNO_3 on copper turnings was added to a solution of 0.49 g (2.5 mmole) of I in 85 ml of glacial acetic acid, and a bright-green precipitate formed instantaneously. The mixture was then stirred for 30 min, after which it was neutralized with ammonia. The raspberry-red precipitate was removed by filtration, dried, and extracted with chloroform in a Soxhlet extractor. The extract was then passed through a column filled with aluminum oxide with elution by chloroform to give, successively, 0.41 g (70%) of II and 0.13 g (19%) of III.

4,9-Dinitroaceperimidine (III). A 0.17-g (2.5 mmole) sample of $NaNO_2$ was added with stirring to a suspension of 0.6 g (2.5 mmole) of II in 150 ml of glacial CH_3COOH, and the mixture was stirred at 40-50° for 30 min. It was then cooled and neutralized with ammonia, and the resulting orange-red precipitate was removed by filtration, dried, and dissolved in chloroform. The chloroform solution was passed through a thin layer of aluminum oxide to give 0.35 g (55%) of III.

A similar method was used to nitrate and isolate the other nitro compounds.

LITERATURE CITED

1. A. F. Pozharskii and V. N. Koroleva, Khim. Geterotsikl. Soedin., 550 (1975).
2. E. Yu. Orlova, Chemistry and Technology of Explosives [in Russian], Khimiya (1973), p. 88.
3. H. Remy, Treatise on Inorganic Chemistry, Vol. 1, Elsevier (1956).
4. A. I. Titov, Tetrahedron, 19, 577 (1963).
5. Yu. V. Karyakin, Pure Chemical Reagents [in Russian], ONTI, Leningrad (1936), p. 11.