2.5. *Résumé des modes de décomposition.* Les diverses fragmentations de I sont résumées dans le schéma 4. Les transitions qui sont confirmées par des pics métastables y sont indiquées en traits pleins. Les positions mesurées des pics métastables sont données dans le tab. 7. Dans ce tableau ne figurent que les pics métastables pour lesquels des transitions correspondantes ont été trouvées dans les spectres de *tous* les dérivés deutériés.

Tableau 7. *Pics métastables dans le spectre du cyclopentènediol-3,5*-trans *(70 eV)*

m_1	100	99	82	72	58	54	41
↓							
m_2	71	81	81	57	43	39	39
m^* mesuré	50,48	66,25	80,00	45,16	31,92	28,17	37,13
m^* calculé	50,41	66,27	80,01	45,13	31,88	28,17	37,10

Nous remercions le Prof. *Th. Posternak* et ses collaborateurs, MM. les Drs *F. Cocu* et *G. Wolczunowicz*, qui ont mis à notre disposition les diols non deutériés ainsi que du matériel de laboratoire. Les spectres en haute résolution ont été enregistrés par Mme *F. Kloeti* et M. *W. Kloeti* que nous remercions également. Ce travail a été financé en partie par le *Fonds National Suisse de la Recherche Scientifique* auquel nous exprimons notre gratitude (subside No 2.478.71).

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35. The Nitrosation of Primary Aliphatic Diazocarbonyl Compounds: Formation of α-Carbonyl nitrile oxides

Preliminary communication[1])

by **Hans Dahn, B. Favre**[2]) and **J.-P. Leresche**[2])
Institut de Chimie Organique, Université de Lausanne

(11. XII. 72)

Summary. Aqueous nitrosation of primary α-carbonyl diazo compounds (ethyl diazoacetate, diazoacetone, diazoacetophenones) yields α-carbonyl nitrile oxides, R—CO—CNO; their formation is demonstrated by 1,3-dipolar addition reactions.

The reaction of various nitrosating agents (N_2O_3, N_2O_4, mostly under non aqueous conditions) with ethyl diazoacetate has led to the formation of several products: ethyl dinitroacetate [1], ethyl furoxandicarboxylate (possibly formed by dimerisation

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[1]) A detailed paper will be published in Helv.

[2]) From the doctoral theses of *B. Favre*, Lausanne 1971, and *J. P. Leresche*, Lausanne 1965.

of the corresponding nitrile oxide) [1] [2] [3], and the nitrous ester of ethyl glycolate, ONO–CH_2–COOEt [2]. Analogous products have been obtained from diazoketones [3] [4] [5]; with N_2O_4 perfluorated diazoalkanes gave furoxans, nitrates and nitrolic acids [6]; with NOCl, hydroximoyl chlorides were formed from diazoketones [4] and perfluorated diazoalkanes [6]. The mechanism of formation of most of these products has not yet been explained.

We found that under aqueous nitrosating conditions, primary α-diazocarbonyl compounds (R–CO–CHN_2) like ethyl diazoacetate (**1a**), diazoacetone (**1b**), and diazoacetophenones (**1c**) form the corresponding nitrile oxides R–CO–CNO (**2**) in good yield. Aliphatic nitrile oxides cannot be isolated, but they give 1,3-dipolar additions [7] [8] with dipolarophiles present in the reaction mixture. Not only typical dipolarophiles like acrylonitrile, but also simple olefins like cyclohexene [9] can be used, leading to the formation of isoxazolines (**3**). In the absence of a sufficiently reactive dipolarophile, the nitrile oxides dimerise to furoxans **4** [8]; in the presence of chloride ions they add HCl to form hydroximoyl chlorides R–CO–C(NOH)Cl (**5**) [8][3].

We found that the best results were obtained when an aqueous solution of nitrous acid (from $NaNO_2$ plus $HClO_4$; pH = 1–2) was stirred at 0° with an ethereal solution of an equivalent amount of the dipolarophile, followed by slow addition of an ethereal solution of half an equivalent of the diazoketone or ethyl diazoacetate. The presence of nucleophiles like chloride ions should be avoided. The products formed are listed in the table.

Preparation of isoxazolines (**3**) *and furoxans* (**4**) *by 1,2-dipolar addition, resp. dimerisation, of nitrile oxides* formed by aqueous nitrosation of diazo compounds (R^1CO—CHN_2)

R^1	R^2	R^3	**3** yield in %	**4** yield [a]) in %
EtO	H	CN	80	
	H	—COOEt	84	
	—COOEt	—COOEt	50	
	—Ph	—COOEt	27	
	—CH_2—CH_2—CH_2—CH_2—		10	
	–	–	–	92
Me	H	CN	73	
	–	–	–	68
Ph	H	COOMe	75	
	–	–	–	75
p-Me—C_6H_4	–	–	–	86
p-Cl—C_6H_4	–	–	–	47
p-MeO—C_6H_4	–	–	–	66
p-NO_2—C_6H_4	–	–	–	54

[a]) In absence of added dipolarophile.

Our method of preparing carbonyl nitrile oxides avoids the high pH necessary in the reaction of **5** with bases [10]. On the other hand, the acidic medium used favours catalytic hydrolysis of the diazo compounds; by choosing a two-phase system

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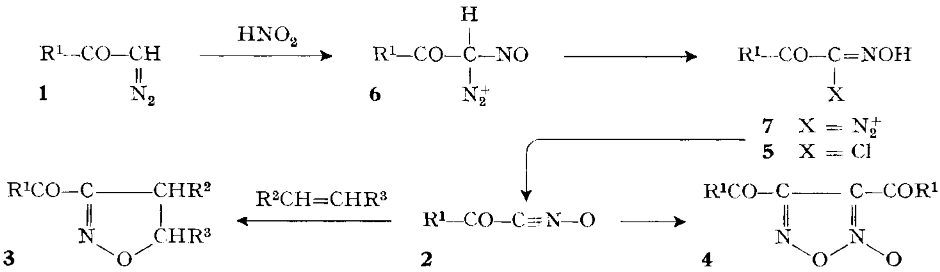
[3]) We assume that this reaction explains the well known preparation of ethoxycarbonyl-formhydroximoyl chloride EtOOC—C(NOH)Cl by diazotization of ethyl glycinate, HCl.

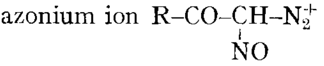


a) R^1 = EtO b) R^1 = Me c) R^1 = Ar

and an excess of HNO_2, we have diminished this side reaction. The use of other nitrosating agents (alkyl nitrites, nitrosyl perchlorate in CCl_4[4]) gave no improvement.

As ethyl diazoacetate **1a** is prepared by diazotisation of ethyl glycinate, HCl, one can in principle form **2a** by action of twice the amount of nitrous acid on the glycinate; however the chloride ions present in the starting material lower the yield of **2a** as a result of a side reaction (leading to **5a**).

Starting from dicarboxylic acids, bis-nitrile oxides $ONC-(CH_2)_n-CNO$ (n = 2 or 4) were easily prepared *via* the bis-diazoketones. With acrylonitrile, they formed bis-isoxazolines in nearly quantitative yield. In the absence of added dipolarophiles, furoxan formation proceeded by polymerisation, not by cyclisation.

We explain the formation of nitrile oxides by nitrosation of primary diazocarbonyl compounds in the following manner: electrophiles normally attack aliphatic diazo compounds at the diazo carbon atom [11] forming diazonium ions, which undergo either C-deprotonation [12] or displacement of N_2 by a nucleophile. In the case of nitrosation, a C-nitroso-diazonium ion  $R\text{–}CO\text{–}\underset{NO}{CH}\text{–}N_2^+$ (**6**) would be formed from **1**; being doubly activated, it easily loses a proton. If the proton migrates to the nitroso oxygen, we have an example of the classical tautomerism of an α-nitroso ketone to an α-ketoxime. The resulting diazonium oxime (**7**) is comparable to the chloroxime (hydroximoyl chloride **5**), which by action of a base yields the nitrile oxide **2** [10], *cf.* [7] [8]. The diazonium group of **7** is eliminated so much more readily than the chloride ion of **5**, that even water is sufficiently basic for this to occur[5]).

A mechanistic prerequisite of the proposed reaction path **1** → **2** is that C-deprotonation of the diazonium ion **6** is more rapid than its loss of N_2. By analogy with reversible protonation, this can be expected for primary diazo compounds ($-CHN_2$) deactivated by electron withdrawing groups like ROOC–, R–CO– [12], F_3C– [13] or $ArSO_2$– [14]. In diazoalkanes, however, protonation is slower than loss of N_2; in agreement with this, we never observed the formation of nitrile oxides, nor of products formed from them, starting with diazoethane, diazopropane, diazoisobutane, or phenyldiazomethane[6]).

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[4]) **1a** and $NOClO_4$ yielded mostly $EtOOC\text{—}CH_2OClO_3$, which can explode spontaneously very violently. After recovery from injury, *B. F.* was able to control the reaction by working on a diminished scale.

[5]) In principle, the loss of N_2 could occur directly from the deprotonated diazonium ion $R\text{—}CO\text{—}C(N_2^+)\text{—}NO$.

[6]) At 70°, however, *Bakke* [15] observed the formation of an hydroximoyl chloride from *n*-octylamine and NOCl.

Experimental. – *Ethyl 5-cyano-isoxazoline-3-carboxylate.* To a solution of 2.76 g $NaNO_2$ (0.040 mol) in 5 ml water, 2.12 g acrylonitrile (0.040 mol) in 15 ml ether were added; the mixture was stirred at 0° and 5.72 g 70% $HClO_4$ (0.04 mol) were added dropwise. Maintaining the temperature at 0°, 2.28 g ethyl diazoacetate (0.020 mol) in 15 ml ether were added during 6 h; stirring was continued for a 2 further h. The ethereal phase was separated, washed with $NaHCO_3$ solution and water, dried over $MgSO_4$ and distilled, to give 2.68 g (80% of theoretical) of b.p. 103°/1 Torr⁷). – NMR. spectrum ($CHCl_3$): $\delta = 3.63$ (2H, doublet, $J = 9.3$ Hz): 2H at C(4); $\delta = 5.45$ (1H, *t*, $J = 9.3$ Hz): 1H at C(5); ethyl group signals at $\delta = 1.42$ (3H, *t*, $J = 7.4$ Hz); $\delta = 4.40$ (2H, *q*, $J = 7.4$ Hz).

$C_7H_8N_2O_3$ (168,2) Calc. C 50.00 H 4.80 N 16.66% Found C 50.19 H 4.76 N 16.56%

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[7] If ethyl furoxan-3,4-dicarboxylate is present (control by TLC.), this has first to be eliminated by chromatography on a SiO_2 column (eluant: CH_2Cl_2).

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36. Stereoselektive Bildung der C-C-Bindung in der Kopplungsreaktion zwischen sek. Alkylmagnesiumbromiden und ungesättigten Halogeniden: Asymmetrische Induktion durch einen optisch aktiven Diphosphin-Nickel-Komplex

von **Giambattista Consiglio** und **Carlo Botteghi**
Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule Zürich

(12. XII. 72)

Summary. The catalyzed cross-coupling reaction of secondary racemic *Grignard* reagents with unsaturated halides takes place stereospecifically in the presence of the nickel chiral complex **4**; although some isomerisation is occurring this reaction can be useful to prepare optically active hydrocarbons.