4. Conclusion. – L'objet de cette communication n'est autre que de présenter brièvement quelques nouveaux systèmes oscillants découverts dans notre laboratoire et dont l'étude est en cours. Les quelques informations apportées plus haut suffisent sans doute néanmoins à mettre en évidence l'ampleur des perspectives qui s'offrent à ce nouveau domaine d'investigation que constituent les réactions chimiques oscillantes. Tout laisse à penser en effet que d'autres comportements inattendus, tels que celui de l'acétone seront observés dans un proche avenir.

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15. The Reaction of Nitrosoalkane Dimers with Acid Halides[1])

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(12. IV. 74)

Summary. Nitrosoalkane dimers react with acid halides to yield α-halogeno-azoxy compounds with the substituent α to the oxygen-bearing nitrogen. In the presence of silver carbonate, the corresponding α-acyloxy-azoxy compounds are formed.

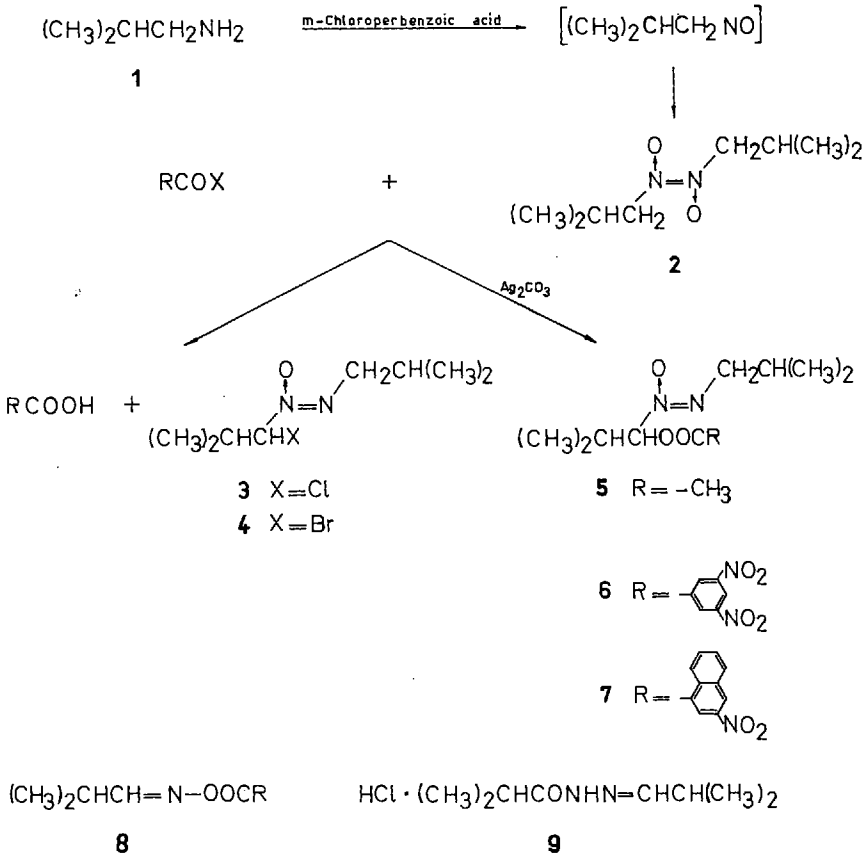
The reaction of N-isobutyl-N-nitroso-hydroxylamine salts with 3,5-dinitrobenzoyl chloride yields, among other products, 1-(3,5-dinitrobenzoyloxy)-1,1'-NNO-azoxyisobutane (**6**) [1]. The known decomposition of nitrosohydroxylamines to nitrosoalkane dimers [2] suggests that compound **6** may have originated from an acylation of nitrosoisobutane dimer. In fact, the latter reaction does yield compound **6**; a characterization of the products from such acylation of nitrosoalkane dimers is the subject of this paper.

Reactions. – *trans*-1-Nitrosoisobutane dimer (**2**) [3–5], the structure of which has been proven by X-ray [6] diffraction techniques, was obtained by the oxidation of isobutylamine with *m*-chloroperbenzoic acid as described by *Baldwin et al.* [7]. The nitroso dimer **2** reacted under very mild conditions, +20° over a period of 2 to 16 hours, with acid halides to give α-halogeno-azoxy compounds **3** and **4** in 65% and 41% yields (*Scheme 1*). Methylene chloride, tetrahydrofuran and acetonitrile were useful solvents for this reaction, whereas no reaction occurred in toluene. Our reaction conditions were different from those of *Collin et al.* [4], who treated nitrosoisobutane dimer **2** and related compounds with acetyl chloride in diethyl ether saturated with dry hydrogen chloride, and isolated the acylhydrazone hydrochloride **9** (presumably formed *via* **5**) from **2**.

[1]) Presented at the conference of the Swiss Chemical Society, Lugano, Switzerland, October 19–20, 1973.

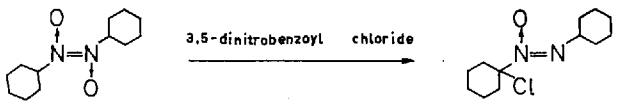
When our reaction was carried out in the presence of an excess of freshly prepared dry silver carbonate, the main products were the α-acyloxy-azoxy compounds **5–7**; the halogen ion had obvioulsy been trapped by the silver ion. For products **5**, **6** and **7**, further purified by preparative thick-layer chromatography, the yields varied from 15–50%, depending on the group R of the acid halide. To optimize the yields, higher temperatures (30–50°) and longer reaction times (16–50 h) were usually used,

Scheme 1



which led to the formation of some by-products, of which one is probably the oxime ester **8**: it is known that C-nitroso compounds rearrange to oximes under acidic or basic conditions.

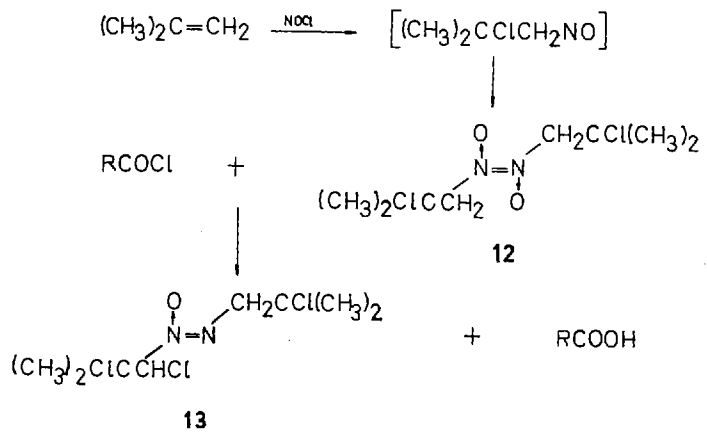
Scheme 2

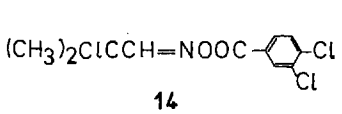


The nitroso dimer **2** did not yield compounds **5** or **6** by reaction with either acetic or 3,5-dinitrobenzoic anhydride.

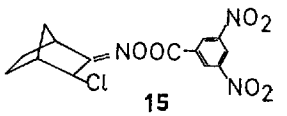
Nitrosocyclohexane dimer **10**, a secondary nitroso dimer, was much less reactive than the primary analog **2**. The α-chloro-azoxy compound **11** (*Scheme 2*) was only isolated in 25% yield after 5 days reaction time. In the presence of silver carbonate no α-acyloxy-azoxy compound similar to **5–7** (*Scheme 1*) could be detected; 50% of starting material was recovered.

Scheme 3





14



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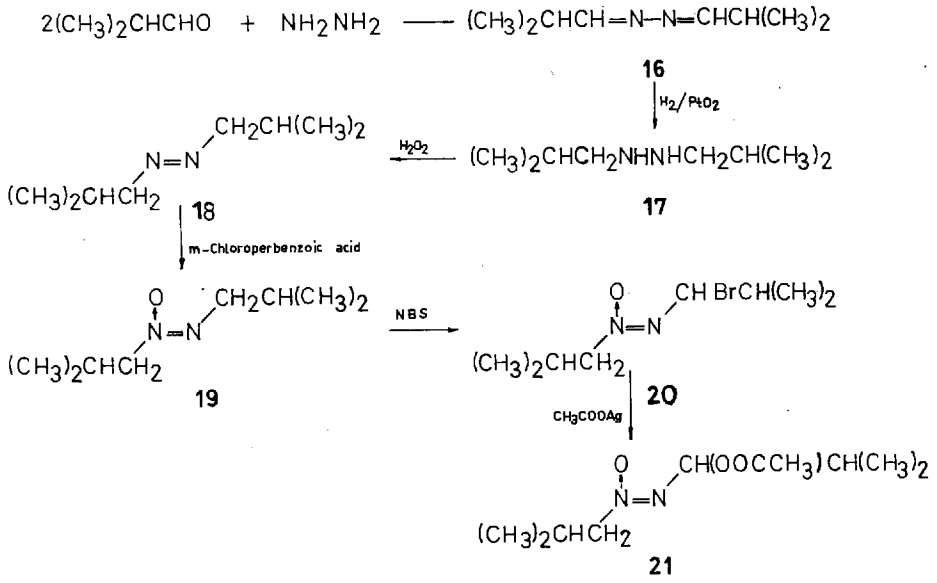
2-Chloro-2-methyl-1-nitroso-propane dimer **12** was made by adding nitrosyl chloride to isobutene in the usual manner [8]. Compound **12** reacted with acid chlorides to give the trichloroazoxy compound **13** in 65–74% yield. Using 3,4-dichlorobenzoyl chloride, the oxime ester **14** was isolated as a side product in 8% yield. In the presence of silver carbonate the α-acyloxy-azoxy compound comparable to **5–7** (*Scheme 1*) was not formed. Compound **13** can be distilled but must be stored at –10 to –20°, otherwise it decomposes at room temperature with evolution of hydrogen chloride, – already observed, but at a much slower rate, with compound **3** (*Scheme 1*). In the case of the nitroso compound obtained from norbornene by adding nitrosyl chloride, the only product isolated from the reaction with 3,5-dinitrobenzoyl chloride was the oxime ester **15**.

Matsumoto et al. [9] have described recently the successful α-bromination of azoxymethane with N-bromosuccinimide (NBS) and the subsequent reaction with silver acetate. In the same manner we synthesized the unstable compound **20** (*Scheme 4*), which was converted without difficulty by silver acetate to the stable α-acyloxy-azoxy compound **21**. With compounds **4** and **20**, and **5** and **21**, we had

Scheme 4



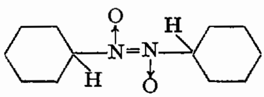
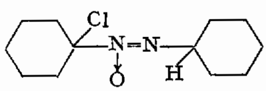
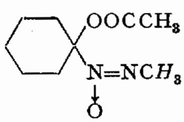
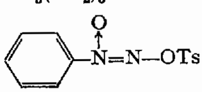
two pairs of α-substituted azoxy isomers in hand, which allowed their unambiguous structure determination by comparison of their physical data.

Structure proof. – The IR. spectra of compounds **3–7**, **11**, **13**, and **19–21** show the strong characteristic azoxy band [10] at 1500 ± 10 cm^{-1}. The UV. maximum was observed in the range 217–222 nm (log ε 3.75–3.84), which is indicative of *trans*-azoxy compounds [11]; *cis* geometry would require 228–232 nm [11]. – The NMR. spectra of compounds **3–7**, **20** and **21** show the methyl groups of the two isopropyl groups split into either 4 or 3 doublets at $\delta = 0.95$–1.15 ppm; this is not the case for the unsubstituted azoxyisobutane **19**. The magnetic non-equivalence must have its origin in the new asymmetric center. The hydrogen atom bonded to the C-atom bearing the α-substituent is shifted downfield ($\delta = 5.45$–6.20 ppm).

The position of the substituent is still to be ascertained, *i.e.* as α to the oxygen-bearing nitrogen or α to the oxygen-free nitrogen of the azoxy function. From the Table it can be concluded, that the protons of the methylene group attached to the oxygen-bearing nitrogen in the azoxy compounds are found at lower field than the protons of the methylene group attached to oxygen-free nitrogen; the difference is nearly 1 ppm. Our findings are in agreement with those of *Freeman* [12], who examined the structures of unsymmetrically substituted aliphatic azoxy compounds. In fact, the compound **22** [12], obtained from the reaction of peracetic acid with cyclohexanone methylhydrazone, is an analog of the compounds reported in this paper; the methyl signal appears at δ 3.15.

The chemical shift of the methine proton in compound **11** is also in accordance with the postulated structure by comparison with the chemical shift of the methine protons in the starting material **10**. In the trichloroazoxy compound **13** the addi-

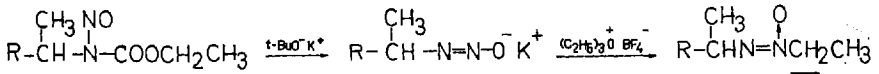
Table. *Chemical shifts,* δ ppm (CCl_4 or $DCCl_3$), *of signals of protons* α *to nitrogen in azoxy and related compounds*

Compound	Formula	$-CH_2N(\rightarrow O)=N(\rightarrow O)CH_2-$	$-CH_2N=NCH_2-$
2	$(CH_3)_2CHCH_2N(O)=N(O)CH_2CH(CH_3)_2$	4.07	
18	$(CH_3)_2CHCH_2N=NCH_2CH(CH_3)_2$		3.62
		$-CH_2N(\rightarrow O)=N-$	$-N(\rightarrow O)=NCH_2-$
19	$(CH_3)_2CHCH_2N(O)=NCH_2CH(CH_3)_2$	4.04	3.27
	$(CH_3)_2CHCHXN(O)=NCH_2CH(CH_3)_2$		
3	X = Cl		3.22
4	X = Br		3.18
20	$(CH_3)_2CHCH_2N(O)=NCHBrCH(CH_3)_2$	3.94	
	$(CH_3)_2CHCH(OOCR)N(O)=NCH_2CH(CH_3)_2$		
5	R = CH_3		3.21
6	R = 3,5-(NO_2)-C_6H_3		3.24
7	R = 1-(3-NO_2)-naphthyl		3.24
21	$(CH_3)_2CHCH_2N(O)=NCH(OOCCH_3)CH(CH_3)_2$	4.01	
		$-CH_2N(\rightarrow O)=N(\rightarrow O)CH_2-$	$-N(\rightarrow O)=NCH_2-$
12	$(CH_3)_2CClCH_2N(O)=N(O)CH_2CCl(CH_3)_2$	4.70	
13	$(CH_3)_2CClCHClN(O)=NCH_2CCl(CH_3)_2$		3.67
		$-CHN(\rightarrow O)=N(\rightarrow O)CH-$	$-N(\rightarrow O)=NCH-$
10		5.05	
11			3.92
22			3.15 (CH_3)
			$-CH_2N(\rightarrow O)=N-$
23	$(CH_3)_2CHCH_2N(\rightarrow O)=N-OTs$ [14]		3.87
24	$CH_3(CH_2)_3N(\rightarrow O)=N-OTs$ [13]		4.05
25	 [13 [14]		—

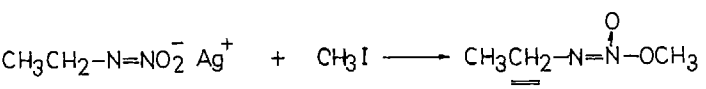
tional deshielding effect of the $-CCl(CH_3)_2$ group must be responsible for the lower shift ($\delta = 3.67$ ppm) of the methylene protons. The same trend is found by comparison of the chemical shifts of the methylene protons in the nitroso compounds **2** and **12**.

The above argument, based on NMR., is supported by the chemical shifts of the methylene protons in compounds **23** and **24** synthesized by the method of *Stevens* [13] from the N-alkyl-N-nitroso-hydroxylamines and *p*-toluenesulfonyl chloride. The structure of these compounds was verified by X-ray analysis of the aromatic analog **25** by *Dickerson* & *Bordner* [14].

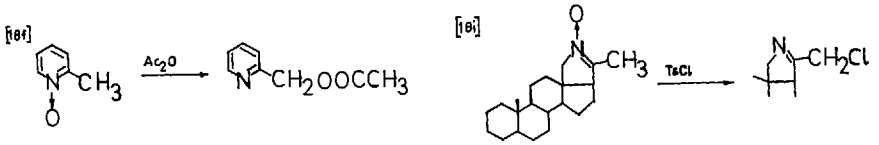
Moss et al. [11c] [15] and also *McGahren* & *Kunstmann* [16] described the successful alkylation of alkane diazoates (one example outlined below) to give unsymmetrically substituted aliphatic azoxy compounds. The chemical shift of $-CH_2-N(O)=N-$, $\delta = 4.08$ ppm, established the structure.



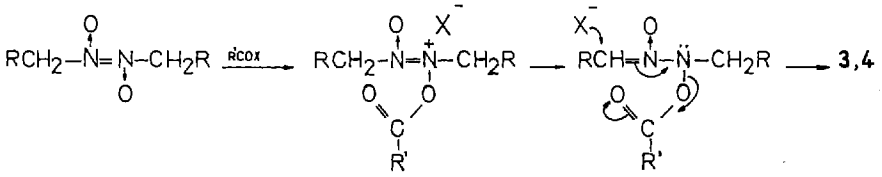
The methylene proton resonance at $\delta = 3.49$ ppm of O,N-dialkylnitrimides described by *Lamberton* & *Yusuf* [17] should be noted.



Comparison with nitrones. The reactions discussed above can be compared with a similar type of reaction in the nitrone series [18], as illustrated in the two examples [18f, i]:



The mechanism of the rearrangement of 2-alkylpyridine 1-oxides into 2-(α-acetoxy-alkyl)-pyridines has been the subject of considerable controversy since its discovery in 1953 [18], and the bulk of the evidence favors an ionic mechanism [18j, k]. This is likely to be the case also for the nitroso dimer reaction in view of the lower temperatures used, which would then follow the reaction pathway:



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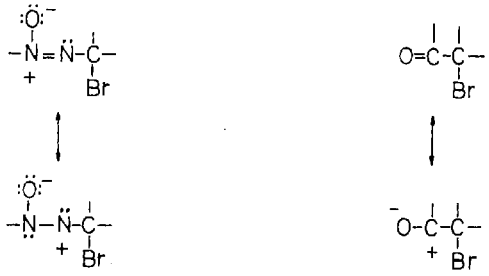
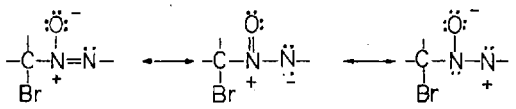
In the presence of silver carbonate, the halide ion concentration is low, and RCO_2^- can bring about an S_N2' chain reaction yielding **5–7**; alternatively, an allylic ester rearrangement may be involved, either concerted or involving ion pairs [19]. Treatment of **3** with silver acetate or silver 3,5-dinitrobenzoate did not yield compounds **5** and **6**, and reaction of the acyloxy compounds **5** and **6** with hydrogen chloride did not yield the halogeno analog **3**, thus suggesting that intermediate **26** is the species undergoing rearrangement.

The facile conversion of compound **20** → **21** is an *apparent* violation of the above observations. The halogen in **20** is in an environment similar to that in α-halogenoketones, however:



The latter compounds undergo rapid substitution reactions believed to involve interaction of the entering nucleophile with the adjacent positive center [20]. The environment of the halogen in compound **3** does not offer this type of stabilization:



Experimental Part

General Remarks. Melting points (m.p.) and boiling points (b.p.) (°C) are not corrected. Results for IR. are given in cm^{-1}; for UV.: λ_{max} in nm (log ε). The chemical shift in NMR. is given in ppm relative to tetramethylsilane as internal standard ($\delta = 0$). *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet, br. = broad signal. Silica gel PF_{254} *Merck* was used for preparative thick-layer chromatography (prep. TLC.). The fractions were recognized by UV. (254 nm). Molecular weights (MW.) were measured by vapor pressure method. Abbreviations: THF = Tetrahydrofuran, NBS = N-bromosuccinimide.

trans-*1-Nitrosoisobutane dimer* (**2**) was synthesized after the method of *Baldwin et al.* [7] from isobutylamine by oxidation with *m*-chloroperbenzoic acid. Yield: 81%. M.p. 38–40° was in agreement with those reported [3–5]. – IR. (CCl_4): 1206.

1-Chloro-1,1'-NNO-azoxyisobutane (**3**). Freshly sublimed 3,5-dinitrobenzoyl chloride, 5.2 g (0.023 mol), dissolved in 30 ml of alcohol-free methylene chloride was added dropwise to a solution of 4 g (0,023 mol) of *trans*-1-nitrosoisobutane dimer (**2**) in 30 ml of methylene chloride over a period of 20 min at room temp.; the mixture was kept in a closed flask at 20° in the dark for 16 h. After filtering from precipitated crystalline 3,5-dinitrobenzoic acid (identified by m.p. and IR.), methylene chloride was distilled from the filtrate and the residue extracted with *n*-hexane. Bulb to bulb distillation of the hexane extract (air-bath 80–100°/10 Torr) gave 2.90 g (65%) of the azoxy compound **3**. – IR. (CCl_4): 1510. – UV. (EtOH): *222* (3,75). – NMR. ($DCCl_3$): 0,98 and 1.08 (3 H each, *d*, 6.5 Hz, non-equivalent $(CH_3)_2CH$—); 0.98 (6 H, *d*, 6.5 Hz, equivalent $(CH_3)_2CH$—);

2.05 (1 H, *m*, $(CH_3)_2CH$—); 2.50 (1 H, *m* $(CH_3)_2CH$—); 3.22 (2 H, *d*, 6.5 Hz, —CH_2—N=N(O)—); 5.45 (1 H, *d*, 8 Hz, —CHCl—N(O)=N—).

$C_8H_{17}ClN_2O$	Calc.	C 49.8	H 8.8	Cl 18.7	N 14.5%
(192.68)	Found	,, 50.0	,, 8.6	,, 18.1	,, 14.7%

1-Bromo-1,1'-NNO-azoxyisobutane (**4**). 1.58 g (5.75 mmol) of 3,5-dinitrobenzoyl bromide (freshly prepared from 3,5-dinitrobenzoic acid and phosphorus tribromide) dissolved in 20 ml of THF were dropped into a solution of 1 g (5.75 mmol) of *trans*-1-nitrosoisobutane dimer (**2**) in 20 ml of THF over a period of 10 min at 20°; the reaction mixture was kept at 20° over night in the dark. THF was distilled off, the residue extracted with diethyl ether/petroleum ether 1:1, and the extract purified by prep. TLC. (diethyl ether/petroleum ether 1:1). Bulb to bulb distillation of the main fraction (Rf = 0.65) (air-bath temp. 90–110°/10 Torr) gave 0.562 g (41%) of azoxy compound **4**. – IR. (CCl_4): 1500. – NMR. ($DCCl_3$): 0.97 and 1.12 (3 H each, *d*, 6.5 Hz, non-equivalent $(CH_3)_2CH$—); 0.97 (6 H, *d*, 6.5 Hz, equivalent $(CH_3)_2CH$—); 2.02 (1 H, *m*, $(CH_3)_2CH$—); 2.50 (1 H, *m*, $(CH_3)_2CH$—); 3.18 (2 H, *d*, 6.5 Hz, —CH_2—N=N(O)—); 5.55 (1 H, *d*, 9 Hz, —CHBr-N(O)=N—).

$C_8H_{17}BrN_2O$	Calc.	C 40.52	H 7.23	Br 33.70	N 11.81	O 6.75%	M.W. 237.15
	Found	,, 40.50	,, 7.10	,, 33.10	,, 11.30	,, 6.80%	,, 242 (acetone)

Silver carbonate. 20.4 g (0.12 mol) silver nitrate dissolved in 50 ml of water were added to a solution of 6.4 g (0.4 g (0.06 mol) of sodium carbonate in 100 ml of water. The precipitate of silver carbonate was filtered, successively washed with water, methanol and diethyl ether, dried under vacuum at 20° and kept in the dark and under nitrogen.

1-Acetoxy-1,1'-NNO-azoxyisobutane (**5**). To 1.0 g (5.75 mmol) of *trans*-1-nitrosoisobutane dimer **2** and 3.2 g (11.5 mmol) of freshly prepared dry silver carbonate in 20 ml of methylene chloride a solution of 450 mg (5.75 mmol) of acetyl chloride in 10 ml of methylene chloride was added dropwise under stirring and under nitrogen at 20°. The reaction mixture was stirred in a closed flask at 20° for 16 h in the dark. Addition of the same amounts of acetyl chloride and silver carbonate were repeated twice, followed each time by refluxing for 18 h. The mixture was filtered and the filtrate purified by prep. TLC. (petroleum ether/diethyl ether 2:1). According to decreasing Rf-values 84 mg of azoxy compound **3** and then 269 mg (21%) of the title compound **5** were isolated; the latter was further purified by bulb to bulb distillation (80–100° air-bath temp./10 Torr.). – IR. (CCl_4): 1765, 1510, 1215. – UV. (EtOH): 217 (3.84). – NMR. ($DCCl_3$): 0.97 and 0.95 (each 3 H, *d*, 6.5 Hz, non-cquivalent $(CH_3)_2CH$—); 0,95 (6 H, *d*, 6.5 Hz, equivalent $(CH_3)_2CH$—); 2.00 (1 H, *m*, $(CH_3)_2CH$—); 2.14 (3 H, *s*, CH_3CO—); 2.43 (1 H, *m* $(CH_3)_2CH$—); 3.22 (2 H, *d*, 6.5 Hz, —CH_2N=N(O)—); 5.90 (1 H, *d*, 5 Hz, —CH(OOR)—N(O)=N—).

$C_{10}H_{20}N_2O_2$	Calc.	C 55.53	H 9.32	N 12.95	O 22.19%
(216.28)	Found	,, 55.10	,, 9.30	,, 12.80	,, 22.10%

The bromide **4** could not be converted to **5** with silver acetate by the method used for the conversion of **20** → **21**.

1-(3,5-Dinitrobenzoyloxy)-1,1'-NNO-azoxyisobutane (**6**). To 70 mg (0.40 mmol) of *trans*-1-nitrosoisobutane dimer (**2**) and 165 mg (0.60 mmol) of silver carbonate in 5 ml of methylene chloride a solution of 94 mg (0.40 mmol) of 3,5-dinitrobenzoyl chloride in 5 ml of methylene chloride was added dropwise with stirring and under nitrogen at 20°. After stirring the mixture at 20° in a closed flask for 16 h in the dark, the solvent was evaporated with dry nitrogen and the crude material was further purified by prep. TLC. (cyclohexane/diisopropyl ether 1:1). Crystallization of the main fraction from pentane gave 77 mg (52%) of the pure title compound **6**, m.p. 59–60°. – IR. (CCl_4): 1755 (C=O), 1548 and 1340 (—NO_2), 1510 (azoxy). – NMR. ($DCCl_3$): 0.92 and 0.94 (3 H each, *d*, 6.5 Hz, non-equivalent $(CH_3)_2CH$—); 1.12 (6 H, *d*, 6.5 Hz, equivalent $(CH_3)_2CH$—); 2.00 (1 H, *m*, $(CH_3)_2CH$—); 2.65 (1 H, *m*, $(CH_3)_2CH$—); 3.18 (2 H, *d*, 6.5 Hz, —CH_2—N=N(O)—); 6.10 (1 H, *m*, —CH(OOR)—N(O)=N—); 9.10 (2 H aromat, *d*, 2 Hz); 9.20 (1 H aromat, *t*, 2 Hz).

$C_{15}H_{20}N_4O_7$ (368.3) Calc. C 48.91 H 5.47 N 15.21% Found C 49.12 H 5.52 N 15.01%

28 mg of impure *trans*-1-nitrosoisobutane dimer (**2**) (m.p., IR.) were recovered from the reaction products.

The title compound **6** was not formed from **2** and 3,5-dinitrobenzoic anhydride in methylene chloride during 50 h at 20° and 4 h under reflux; only starting material was recovered (TLC. IR.). Compound **3** could not be converted into the title compound **6** by treatment with silver 3,5-dinitrobenzoate in boiling methylene chloride for 48 h.

3-Nitro-1-naphthoic acid was prepared from 3-nitro-1,8-naphthalic anhydride by decarboxylation with mercuric oxide [21] and used for the preparation of *3-nitro-1-naphthoyl chloride* by reaction with thionyl chloride [22].

1-(3-Nitro-1-naphthoyloxy)-1-,1'-NNO-azoxyisobutane (**7**). To 520 mg (3 mmol) of *trans*-1-nitrosoisobutane dimer (**2**) and 1.25 g (4.5 mmol) of silver carbonate in 15 ml of THF a solution of 720 mg (3 mmol) of 3-nitro-1-naphthoyl chloride in 15 ml of THF was added dropwise under stirring at 20°. The reaction mixture was stirred at 30° in the dark for 16 h and then purified by prep. TLC. (petroleum ether/diethyl ether 1:1). The fraction with the highest Rf-value was identified as the title compound **7**: 170 mg (15%) of colourless crystals from petroleum ether/diethyl ether, m.p. 81–82°. – IR. (CCl_4): 1748 (C=O), 1506 (azoxy), 1538, 1339, 1235, 1182, 1151, 1138. – NMR. (CCl_4): 0.94, 0.97, 1.10 and 1.13 (3 H each, 4 *d*, 6.5 Hz, two non-equivalent (CH_3)$_2$CH—); 2.03 (1 H, *m*, (CH_3)$_2$C*H*—); 2.68 (1 H, *m*, (CH_3)$_2$C*H*—); 3.24 (2 H, *d*, 6.5 Hz, —CH_2—N=N(O)—); 6.17 (1 H, *d*, 5 Hz, —C*H*(OOR)N(O)=N—); 7.50–8.05 (3 H aromat, *m*); 8.85–9.05 (3 H aromat, *m*).

$C_{19}H_{23}N_3O_5$	Calc.	C 61.11	H 6.21	N 11.25	O 21.42%	M.W. 373.40
	Found	,, 61.00	,, 6.20	,, 11.20	,, 22.00%	,, 360 (benzene)

Nitrosocyclohexane dimer (**10**) [23] was synthesized in 90% yield from cyclohexylamine by oxidation with *m*-chloroperbenzoic acid, using the method of *Baldwin et al.* [7].

1-Chloro-NNO-azoxycyclohexane (**11**). 461 mg (2 mmol) of 3,5-dinitrobenzoyl chloride and 452 mg (2 mmol) of nitrosocyclohexane dimer (**10**) were mixed together in 20 ml of methylene chloride at 20° and the reaction mixture kept in a closed flask for 5 days at 20° in the dark. After purification by prep. TLC. (cyclohexane/diethyl ether 8:2), the fraction with the highest Rf-value was identified as the title compound **11** and further purified by distillation: b.p. 80°/0.1 Torr. Yield: 125 mg (25%). – IR. (CCl_4): 1485. – NMR. (CCl_4): 1.3–2.0 (16 H, *m*); 2.1–2.6 (4 H, *m*); 3.92 (1 H, *m*, tert. H).

$C_{12}H_{21}ClN_2O$	Calc.	C 58.89	H 8.65	Cl 14.49	N 11.45	O 6.54%
(244.76)	Found	,, 59.35	,, 8.95	,, 14.34	,, 11.44	,, 6.46%

A more polar fraction was identified as *cyclohexanone oxime 3,5-dinitrobenzoate*. – IR. (KBr): 1761, 1639, 1550, 1346. – NMR. ($DCCl_3$): 1.3–2.0 (6 H, *m*); 2.45–2.80 (4 H, *m*); 9.17 (2 H aromat, *d*, 2 Hz), 9.25 (1 H aromat, *t*, 2 Hz).

1,2,2'-Trichloro-1,1'-NNO-azoxyisobutane (**13**). – *a*) 37 g (0.164 mol) of 3,5-dinitrobenzoyl chloride dissolved in 100 ml of THF were added dropwise during 20 min to a solution of 40 g (0.164 mol) of 2-chloro-2-methyl-1-nitroso-propane dimer (**12**) [8] in 100 ml THF. After 2 h, the THF was distilled off at 20° in vacuum and the residue extracted with diethyl ether, leaving insoluble 3,5-dinitrobenzoic acid (identified by m.p., IR.). The diethyl ether extract was washed twice with 1N sodium carbonate, twice with water and then dried over sodium sulfate. Distillation gave 31.9 g (74%) azoxy compound **13**, b.p. 78–82°/0.2 Torr; must be stored at −10 to −20°. – IR. (CCl_4): 1512 (azoxy), 1460, 1390, 1370, 1220, 1120. – UV. (EtOH): 221 (3.83). – NMR. ($DCCl_3$): 1.70 and 1.80 (each *s*, two (CH_3)$_2$CCl—); 3.68 (2 H, *s*, —CH_2—N=N(O)—); 6.07 (1 H, *s*, —C*H*Cl—N-(O)=N—).

$C_8H_{15}Cl_3N_2O$	Calc.	C 36.74	H 5.78	Cl 40.66	N 10.71	O 6.12%
(261.58)	Found	,, 36.74	,, 5.74	,, 40.40	,, 10.73	,, 6.39%

b) 840 mg (4 mmol) of 3,4-dichlorobenzoyl chloride and 972 mg (4 mmol) of 2-chloro-2-methyl-1-nitroso-propane dimer (**12**) were mixed together in 20 ml of THF. After 20 h, the THF was distilled off at 20° in vacuum and the residue purified by prep. TLC. (benzene). Besides 685 mg (65%) of azoxy compound **13**, 95 mg (8%) of *2-chloro-2-methyl-propanal oxime 3,4-dichlorobenzoate* (**14**), m.p. 69–71°, were isolated. – IR. (KBr): 1754. – NMR. ($DCCl_3$): 1.82 (6 H, *s*, (CH_3)$_2$CCl—); 7.61 (1 H aromat, *d*, 8 Hz), 7.91 (1 H aromat, *d* × *d*, 8 Hz and 2 Hz); 8.11 (1 H aromat, *d*, 2 Hz); 8.15 (1 H, *s*, —C*H*=N—).

c) The reaction described under *a*), with 3,5-dinitrobenzoyl chloride, was carried out in different solvents and followed by TLC. (benzene). In THF the reaction was fast, in acetonitrile

less, in methylene chloride still less fast, and in toluene practically no reaction took place in 14 h. Methylene chloride has the disadvantage of containing traces of ethyl alcohol. The reaction rate of different acid halides in THF appears to be in the order: 3,5-dinitrobenzoyl chloride > acetyl chloride > 3,4-dichlorobenzoyl chloride ≅ benzoyl chloride.

3-Chloro-bicyclo[2.2.1]heptan-2-one oxime 3,5-dinitrobenzoate (**15**). 4.61 g (0.02 mol) of 3,5-dinitrobenzoyl chloride dissolved in 20 ml of THF were added dropwise to a suspension of 6.38 g (0.02 mol) of 3-chloro-2-nitroso-bicyclo[2.2.1]heptane dimer [8] in 60 ml of THF at 20°. The reaction mixture was stirred 4 days at 20° and then refluxed for 3 h, at which point a clear solution resulted. The THF was distilled off and diethyl ether added: 4.72 g (67%) of the oxime ester **15** crystallized out, m.p. 170–172°. – IR. (KBr): 1761, 1631, 1546, 1344, 1258, 1130.

$C_{14}H_{12}ClN_3O_6$	Calc.	C 47.54	H 3.42	Cl 10.02	N 11.88%
(353.72)	Found	,, 47.20	,, 3.40	,, 10.50	,, 11.60%

Isobutyraldehyde azine (**16**) [24], b.p. 49–50°/13 Torr (Lit. [25]: 63°/17 Torr). – IR. (CH_2Cl_2): 1653. – NMR. ($DCCl_3$): 1.14 (12 H, *d*, 7 Hz, two $(CH_3)_2CH$–); 2.50 (2 H, *m*, two $(CH_3)_2CH$–); 7.68 (2 H, *d*, 5 Hz, two –CH=N–).

N,N'-Diisobutylhydrazine (**17**) [25]. Isobutyraldehyde azine **16**, in an equivalent of glacial acetic acid dissolved in ethanol, was hydrogenated in presence of platinum oxide. **17**: b.p. 62–63°/10 Torr (Lit. [25]: 72°/16 Torr). – NMR. ($DCCl_3$): 0.96 (12 H, *d*, 7 Hz, two $(CH_3)_2CH$–); 1.50–2.30 (2 H, *m*, two $(CH_3)_2CH$–); 2.65 (4 H, *d*, 6.5 Hz, two $-CH_2-$N); ~3.30 (2 H, *b*, two >N–H).

1,1'-Azoisobutane (**18**) was obtained from **17** by oxidation with a 10% excess of 30% hydrogen peroxide in an excess of saturated sodium hydrogen carbonate [26]; b.p. 35–36°/10 Torr (Lit. [25]: 55–56°/29 Torr). – NMR. ($DCCl_3$): 1.00 (12 H, *d*, 7 Hz, two $(CH_3)_2CH$–); 2.27 (2 H, *m*, two $(CH_3)_2CH$–); 3.62 (4 H, *d*, 6.5 Hz, two $-CH_2-$N=N–).

1,1'-Azoxyisobutane (**19**) was obtained from **18** by oxidation with *m*-chloroperbenzoic acid in methylene chloride [27]: b.p. 71°/10 Torr (Lit. [27]: 85°/15 Torr). – IR. (CCl_4): 1500. – NMR. ($DCCl_3$): 1.00 (12 H, *d*, 6.5 Hz, two $(CH_3)_2CH$–); 1.75–2.80 (2 H, *m*, two $(CH_3)_2CH$–); 3.27 (2 H, *d*+*t*, 7 Hz + 1 Hz, $-CH_2-$N=N(O)–); 4.04 (2 H, *d*+*t*, 7 Hz + 1 Hz, $-CH_2-$N(O)=N–).

1-Bromo-1,1'-ONN-azoxyisobutane (**20**). 4 g (0.026 mol) of 1.1'-azoxyisobutane (**19**), 4.65 g (0.026 mol) of NBS and 0.75 g (0.003 mol) of dibenzoyl peroxide were dissolved in 30 ml of carbon tetrachloride and the mixture was refluxed for 2.5 h. After filtration, the carbon tetrachloride was evaporated and bulb to bulb distillation (40–80° air-bath/~1 Torr) gave 2.6 g of the not quite pure, oily, unstable compound **20**. – IR. (CCl_4): 1495. – NMR. ($DCCl_3$): 3.94 (2 H, *d*, 7 Hz, $-CH_2-$N(O)=N–); 5.66 (1 H, *d*, 5.5 Hz, –CHBr-N=N(O)–). – Rf (**4**) > Rf (**20**) (silica gel, petroleum ether/diethyl ether 5:1). Decomposition was observed with loss of hydrogen bromide during distillation and storage.

1-Acetoxy-1,1'-ONN-azoxyisobutane (**21**). 810 mg (3.4 mmol) of impure bromide **20** and 2.3 g (13.6 mmol) of silver acetate were stirred together in 10 ml of carbon tetrachloride at 20° for 16 h in the dark. The reaction mixture was filtered and the filtrate purified by prep. TLC. (petroleum ether/diethyl ether 5:1). The main fraction (300 mg) was identified as the title compound **21** after further purification by bulb to bulb distillation (air-bath 60°/0.1 Torr). – IR. (CCl_4): 1754 (C=O), 1511 (azoxy). – UV. (EtOH): 222 (3.83). – NMR. ($DCCl_3$): 0,99 and 1.01 (each *3* H, *d*, 6.5 Hz, non-equivalent $(CH_3)_2CH$–); 1.01 (6 H, *d*, 6.5 Hz, equivalent $(CH_3)_2CH$–); 2.13 (3 H, *s*, CH_3CO–); 2.0–2.7 (2 H, *m*, two $(CH_3)_2CH$–); 4.01 (2 H, *d*, 7 Hz, $-CH_2-$N(O)=N–); 6.20 (1 H, *d*, 4 Hz, –CHOOR–N=N(O)–). – Rf (**5**) > Rf (**21**) (silica gel, petroleum ether/diethyl ether 5:1).

$C_{10}H_{20}N_2O_3$	Calc.	C 55.53	H 9.32	N 12.95	O 22.19%	M.W. 216.28
	Found	,, 55.70	,, 9.50	,, 12.80	,, 22.10%	,, 220 (dioxane)

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16. Contribution à la phytochimie du genre *Gentiana*. X [1])
Etude des composés flavoniques et xanthoniques dans les feuilles de *Gentiana verna* L.

(2ème communication)

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(23. XII. 74)

Summary. One new (**1**) and one previously identified (**2**) flavone-C-glycosides were isolated from leaves of *Gentiana verna* L. by means of column chromatography. The columns used were polyamid and cellulose. The structure of the new compound was established as iso-orientin-2″-O-

[1]) Partie IX, v. Helv. *57*, 2557 (1974).