# On the lead tetraacetate and related oxidations of aromatic ketoximes<sup>1</sup>

M. M. Frojmovic<sup>2</sup> and G. Just

Department of Chemistry, McGill University, Montreal, Quebec

Received March 14, 1968

Fluorenone and benzophenone oxime react in glacial acetic acid with lead tetraacetate to give parent ketones, geminal dinitromethanes, iminyl ketal derivatives (9,9-difluorenylideniminoxylfluorene and 1,1-bis(diphenylmethylideniminoxyl)-diphenylmethane), and minor amounts of oxime O-acetate. Benzophenone nitrimine is also formed but only in the absence of oxygen. Side reactions due to nitric oxide, oxygen, and nitrogen dioxide take place. Separate studies with these oxidizing agents have therefore been conducted. The lead tetraacetate oxidation of these oximes in methylene chloride (or any other solvent) is complete with a half-mole equivalent of lead tetraacetate, is insensitive to molecular oxygen, and affords mainly parent ketone and ketazinemonoxides. No ketazine-bis-N-oxides, obtained from the ferricyanide oxidation of these oximes, are formed. The model oximes, benzil anti-monoxime, xanthone oxime, and indanone oxime have been studied in the light of these observations. Mechanisms involving iminoxyl radicals have been postulated for all reactions studied.

Canadian Journal of Chemistry, 46, 3719 (1968)

#### Introduction

It has been shown by electron spin resonance (e.s.r.) measurements that iminoxyl radicals formed by lead tetraacetate oxidations of bisarylketoximes are very stable, with half lives ranging from 0.5 to 5.5 min (1). No reports have been published on the chemistry of these oxidations, except for the ferricyanide oxidation of benzophenone oxime (2), which gives benzophenone, benzophenone azine monoxide, and benzophenone anhydride N-oxide (2b), probably better formulated as azine-bis-N-oxide (3b). Similar oxidations of aliphatic ketoximes and substituted acetophenone oximes generate much shorter-lived radicals (1), with gem-nitrosoacetates generally produced as final products (3, 4); hindered and strained ketoximes generally lead to hydroxamic acids (5). In the following, the lead tetraacetate and related oxidations of fluorenone, benzophenone, xanthone, indanone, and benzil anti-monoxime (1a-e) in glacial acetic acid and methylene chloride will be described.

The products obtained in these oxidations depended on the nature of the oxime and the oxidizing agent used, the solvent, the ratio of oxidizing agent to substrate and the presence of oxygen. Compounds isolated or detected were gem-dinitro compounds (4), iminylketals (5), azine monoxides (6) and bis-oxides (3), oxime-O-acetates (7), parent ketones, and a nitrimine (8). In order to simplify the discussion, structure proofs of products obtained will be first given.

Structure and Properties of Products Gem-dinitro Compounds (4)

The molecular formula of 9,9-dinitrofluorene (4),  $C_{13}H_8N_2O_4$ , was confirmed by mass spectroscopy (M<sup>+</sup> = 256). Its ultraviolet (u.v.) spectrum showed maxima at 246 ( $\epsilon$  26 000) and 276 ( $\epsilon$  6800) mµ which are typical of the fluorenylidene skeleton. The infrared (i.r.) spectrum contained peaks at 1567 and 1350 cm<sup>-1</sup>, characteristic of the NO<sub>2</sub>-stretching vibrations. Although stable to acid, compound 4a decomposed with evolution of nitrous fumes and formation of fluorenone upon heating to its m.p. at 130°, Dinitrodiphenylmethane (4b) and 1,1-dinitroindane (4d) had similar chemical and spectroscopic properties.

### Iminoxyl Ketals (5)

9,9-Difluorenylideniminoxylfluorene (5*a*),  $C_{39}$ - $H_{24}N_2O_2$ , had a molecular weight of 597 (osmometry). Its i.r., u.v., and mass spectra (Table I) were consistent with the structure assigned. Hydrolysis of ketal 5*a* gave two equivalents of oxime and one equivalent of ketone. This ketal was synthesized in low yield by reaction of 9,9-dichlorofluorene with two equivalents of the sodium salt of fluorenone oxime in dimethyl sulfoxide. The analogous ketal 5*b*, derived from benzophenone, was characterized in a similar manner.

### Fluorenone Azinemonoxide (6a)

Compound  $C_{26}H_{16}N_2O$  had an u.v. (255 ( $\varepsilon$  53 000) and 261 ( $\varepsilon$  65 000) mµ) and an i.r.

<sup>&</sup>lt;sup>1</sup>Abstracted from the Ph.D. thesis of M. M. Frojmovic. Present address: Department of Physiology, McGill University, Montreal, Quebec.

<sup>&</sup>lt;sup>2</sup>Holder of a National Research Council of Canada Bursary, 1963–1964, and Studentships, 1964–1966.

CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968



(1540 and 1268  $\text{cm}^{-1}$ ) spectrum consistent with the structure 6a. Its mass spectrum contained peaks at m/e 356 and 180 due to loss of oxygen and nitrogen, respectively (Table I). Reduction of 6a with triphenylphosphine gave fluorenonazine, which was independently synthesized by the autoxidation of fluorenone hydrazone in glacial acetic acid. Hydrolysis of 6a in glacial acetic acid containing concentrated hydrochloric acid gave fluorenone (63%) and 9-chlorofluorene (33%). The formation of 9-chlorofluorene is somewhat surprising since a similar hydrolysis of aldazine monoxides was reported (6) to give the corresponding aldehyde and primary acetate. 9-Diazofluorene, suspected to be the intermediate in the hydrolysis of 6a, gave 9-chlorofluorene in acetic acid – hydrochloric acid, and 9-fluorenyl acetate in pure acetic acid. Benzophenonazinemonoxide (6b) had similar spectral and chemical properties. It was synthesized independently from benzophenone oxime and potassium ferricyanide (2).

## Fluorenone Azine bis-N-Oxide (3a)

The compound  $C_{26}H_{16}N_2O_2$  had i.r. and u.v. spectra similar to that of azine monoxide **6***a*. Acid hydrolysis gave a 1:1 mixture of fluorenone and its oxime. Pyrolysis gave fluorenone and the

azinemonoxide 6a. These data do not permit differentiation of the azine bis-oxide structure 3a from the anhydride N-oxide structure 2a. The i.r. spectrum of 3a does not correspond to the published spectra of other oxime anhydride Noxides and furoxans (7). The  $R_f$  value of 2awould be expected to be equal or less than that of azinemonoxide 6a. The observed  $R_f$  value was greater than that of 6a. The mass spectrum (Table II) showed a peak at M-16, while further fragmentation was strikingly similar to that of azinemonoxide 6a. Based on these criteria, structure 3a is preferred to 2a.



## Benzophenone Nitrimine (8)

Compound  $C_{13}H_{10}N_2O_2$  gave a mass spectrum consistent with the nitrimine structure 8. Of note was the weak parent peak at mass 226 and the base peak at mass 30 (NO<sup>+</sup>) which has been observed for other nitro compounds (8). Independent synthesis of 8 was effected from diazodiphenylmethane and nitric oxide (9).

Can. J. Chem. Downloaded from www.mrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

## FROJMOVIC AND JUST: LEAD TETRAACETATE AND RELATED OXIDATIONS

TABLE I

Mass spectral data of fluorenone derivatives

	Relative Intensity					
Mass-	5a		<b>6</b> a		3 <i>a</i>	
ratio <i>m/e</i>	70 eV	10 eV	70 eV	12 eV	- 70 eV	
358 357 356 355 328	7.3 25.9 9.0 4.0 11.6	4.2 13.0 3.0 0.6 4.0	0.3 1.7 6.2 5.5 2.4	0.9 6.4 20.0 0.0 1.3	1.0 2.7 4.4 3.7 1.9	
327 180 179	7.1 51.2 45.1	0.0 100.0 96.0	4.0 78.2 100.0	4.0 70.0 100.0	2.3 100.0 28.6	
Vapor temp. (°C) V <sub>A</sub> V <sub>M</sub>	200 (I 17: 240	Direct) 50V 00V	250 (Indi 1750) 2000	rect) 20 V V	00 (Direct) 1750V 2000V	

### Mass Spectrometry of Fluorenone Derivatives

The data shown in Table I for the mass spectra of compounds 3a, 5a, and 6a indicate that loss of an aromatic radical constitutes an important if not predominating process in the fragmentation of these compounds. This process probably occurs through abstraction of a hydrogen radical by a departing fragmented radical, since no metastable peaks corresponding to M to M-1 conversions were observed.

### Product Distribution

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

The results of the oxidation of fluorenone oxime (1a) and benzophenone oxime (1b) under a variety of conditions are shown in Table II. Lead tetraacetate oxidations of these ketoximes in glacial acetic acid [entries 1, 2, and 9] led to products which could be independently formed by analogous reactions with molecular oxygen [6 and 11] and nitrogen dioxide [7, 8, and 12]. The corresponding oxidation in methylene chloride (representative of other solvents ranging from dimethyl sulfoxide to ether) led to different products whose distribution [3, 4, and 10] was now insensitive to oxygen and required only a half-mole equivalent of lead tetraacetate for complete reaction. It must be noted that the distinct difference described above was not reflected in the e.s.r. spectra of iminoxyl radicals, which, in the case of aromatic ketoximes, have been reported to be relatively solvent independent (10).

The products of oxidation of benzil-antimonoxime (1e) were very different from those observed for the above bis-arylketoximes. The rapid ( $\ll 1$  min) lead tetraacetate oxidation of 1*e* in glacial acetic acid was only slightly oxygen sensitive and gave mainly a single, uncharacterized compound with spectral properties similar to that of an azine dioxide (3). In addition, a minor amount of ketone (only in the presence of oxygen) and of oxime-O-acetate (7) was formed. The corresponding rapid oxidation in methylene chloride was O<sub>2</sub>-insensitive, required only a halfmole equivalent of lead tetraacetate, and gave 50% of ketone as sole identifiable product. Finally, no autoxidation of oxime 1*e* took place.

Xanthone oxime (1c) and indanone oxime (1d)both behaved very similarly to aliphatic ketoximes (3-5). They underwent no autoxidation reactions. The lead tetraacetate oxidation of 1din oxygen-free acetic acid led to 50% gemnitrosoacetate and 50% parent ketone. All other lead tetraacetate oxidations of 1c and 1d in various solvents were insensitive to oxygen and led to parent ketone only. The nitrations of these oximes with NO<sub>2</sub>, as described for 1a and 1b, led to 70% yield of a nitrated product similar to 4 and 8% yield of 4d, respectively.

### Discussion

It is obvious from the above results that the oxidations of aromatic ketoximes do not proceed via a single pathway, and that, in addition to the primary oxidation step, many secondary reactions involving oxygen and nitrogen dioxide take place. Although by no means proved, the following schemes may account for the formation of various products described above.

#### Gem-dinitro Compounds

The most probable scheme for the formation of *gem*-dinitro compounds from the reaction of ketoximes with nitrogen dioxide may best be represented as shown in Scheme 1. A few reactions of this type have been described in the literature (11), but no mechanism has been given to describe in detail the course of the reaction.

Ionic reaction of dinitrogen tetroxide with fluorenone oxime was ruled out since the latter was inert to  $NO^+$  (12). Dimerization between the iminoxyl radical and the  $NO_2$  radical is expected to be very facile since the electronic and geometric properties of these two radicals have been reported to be strikingly similar (13). The above scheme will readily explain the formation

3722

TABLE II Oxidations of bis-aryl ketoximes

## CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968

					]			Prod (% y	lucts ield)		
Substrate (S)	Oxidizing agent	Ratio S/O	Solvent	Atmosphere	Time (min)	Dinitro 4	Ketal 5	Azine- monoxide 6	Oxime- <i>O</i> - acetate 7	Nitrimine 8	Ketone
F=NOH 1a	Pb(OAc)4	1:1	HOAc	$_{b){\rm O}_{2}}^{a){\rm N}_{2}}$	30 5	20 25	25 0	00	<u>کې</u>	00	> 50 > 50
	Pb(OAc)4	1: <del>1</del>	HOAc	$a)N_2$ $b)O_2$	30 5	3 15	25 3	00	ĩĩ	00	> 50 > 50
	Pb(OAc)4	1:}	CH <sub>2</sub> Cl <sub>2</sub>	O <sub>2</sub> or N <sub>2</sub>	90	1	ы	15	0	0	> 50
	Pb(OAc)4	1:}	1% HOAc- CH <sub>2</sub> Cl <sub>2</sub>	$N_2$	25	7	2	15	0	0	> 50
	K <sub>3</sub> Fe(CN) <sub>6</sub> *	1:1.7	KOH-H <sub>2</sub> O -5°	Air	60	0	× 1	15	0	0	> 50
	02	a) saturated	HOAc	02	24 h	25	13	0	0	0	65
		b) $O_2$ blown through	HOAc	02	24 h	30	0	0	0	0	65
	NO <sub>2</sub>	Excess	HOAc or CH <sub>2</sub> Cl <sub>2</sub>	NO2	<1	95+	0	0	0	0	1
-	$NO_2$	1:1	HOAc†	$N_2$	30	30	4	0	0	0	15
HON	Pb(OAc)4	1:1	HOAc	$a)N_2$ $b)O_2$		9 OE	ოო	00	ŝŠ	11 0	99 99
1b	Pb(OAc) <sub>4</sub>	1:ځ	CH <sub>2</sub> Cl <sub>2</sub>	$\mathbf{N}_{2}^{2or}$	I	0	0	35	ŝ	0	50
	02	Saturated solution	HOAc	02	24 h	30	0	0	0	0	70
	NO2	Excess	HOAc or CH <sub>2</sub> Cl <sub>2</sub>	Air	1	77	0	0	0	0	15
*Azine dioxide 3 v †Dropwise additio	vas obtained in 18% 3 n of Pb(OAc) <sub>4</sub> (50%	vield for reaction a oxime remained).	t –5°.		)					•	

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

nana, papit part

FROJMOVIC AND JUST: LEAD TETRAACETATE AND RELATED OXIDATIONS





Scheme 1. Gem-dinitro compounds.

of pseudonitroles 13 reported for aliphatic ketoximes (14) and aromatic aldoximes (15). For bis-aryl-pseudonitroles (never detected), radical displacement of NO by NO<sub>2</sub> most likely occurs as shown in step (d) above. It should be noted that an intermediate similar to nitrito-nitrone 12 has previously been postulated (16, 17).

### Auto-oxidations

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

Ionic reactions of organic compounds with oxygen have been reported (18). This type of mechanism may be ruled out since the sodium salt of fluorenone oxime was inert to oxygen. It is postulated that the auto-oxidation of fluorenone oxime is similar to the nitrogen dioxide oxidation depicted in Scheme 1. The iminoxyl radical initially formed can react with hydroperoxyl radicals to form ketone and nitrous acid. Nitrogen dioxide, generated from the latter, can then lead to *gem*-dinitro products (Scheme 1).

Auto-oxidations of the bis-aryl-ketoximes occurred *only* in glacial acetic acid and were totally quenched by catalytic amounts of water or acid. The latter phenomenon probably arises from the prohibitive activation energy required to form an iminoxyl radical whose unpaired electron cannot delocalize over both the iminoxyl oxygen and nitrogen (13).

#### Lead Tetraacetate Oxidations

Iminoxyl radicals produced in the lead tetraacetate oxidations of the oximes studied may recombine with lead triacetate and/or acetoxyl radicals to form *gem*-nitrosoacetates which, in the case of aromatic ketoximes, can be expected to decompose to parent ketone and nitric oxide (3). Nitric oxide was in fact isolated from the lead tetraacetate oxidation of fluorenone oxime in glacial acetic acid. Subsequent formation of gem-dinitro products (4) can proceed as shown in Scheme 1.

#### Iminyl Ketals (5)

These may be formed by Scheme 2 represented for the oxidation of fluorenone oxime. The *N*nitroso-nitrone **14** may behave as a radical trap in analogy with the similar behavior of nitroso compounds (19).



Scheme 2. Iminyl ketal formation.

### Benzophenone Nitrimine (8)

The formation of benzophenone nitrimine probably occurred via reaction of the iminoxyl radical of benzophenone oxime with nitric oxide<sup>3</sup>

<sup>&</sup>lt;sup>3</sup>Benzophenone oxime underwent rapid reaction with NO in glacial acetic acid to give unidentified products, while fluorenone oxime was inert.

## CANADIAN JOURNAL OF CHEMISTRY, VOL. 46, 1968

which has independently been shown to lead to parent ketone and nitrimine 8(9, 20).

#### Azine-bis-N-oxides (3)

These have been obtained only in ferricyanide oxidations of bis-arylketoximes and probably arose as shown in Scheme 3. The intermediate 16 has been proposed since similar radicals have been observed (21) in the oxidations of aromatic aldoximes which lead mainly to corresponding aldazine-bis-N-oxides (5, 7, 16). This intermediate 16 has not been observed in lead tetra-acetate oxidations of bis-arylketoximes, nor has the expected product 3 been detected in these oxidations.



Scheme 3. Fluorenonazine-bis-N-oxide formation.

### Azinemonoxide(6)

The formation is not understood. No intermediates, including azine-bis-*N*-oxides, were ever detected in the reactions leading to **6** [3, 5, and 10 in Table II], including those conducted at temperatures from  $-70^{\circ}$  to room temperature.

#### Experimental

#### General

The lead tetraacetate used in all experiments was obtained from Fisher Scientific. It was crystallized from glacial acetic acid, filtered, covered with a sheet of polystyrene and briefly kept under vacuum. It was then dried in an Abderhalden (refluxing methanol and 0.1 mm pressure). This compound was stored in the dark *in vacuo* for a few days with no decomposition. Solvents were obtained oxygen-free by distilling them in a stream of helium. Mass spectra were taken on a Hitachi Perkin-Elmer RMU6D mass spectrometer by Morgan and Schaffer Corporation, Montreal. Low temperature infrared (i.r.) spectra were taken of solutions in 0.1 mm Amalgam FT cells (IRT-2) from Barnes Engineering Co.

#### Fluorenonazine-bis-N-oxide (3a)

Fluorenone oxime (2.34 g) and potassium hydroxide (680 mg) in ethanol (40 ml) were added (16 min) to a vigorously stirred solution of potassium ferricyanide (6.8 g) and potassium hydroxide (13.6 g) in distilled water (300 ml) kept at -3 to  $-7^{\circ}$ . The resulting suspension was allowed to warm up overnight to give a red oily precipitate which was filtered. Addition of ether to the red oil gave 410 mg of light-yellow microcrystals of 3a, m.p. 210° (decomposed). Two crystallizations from benzenemethylene chloride (7:1) gave an analytical sample of 3a (70 mg), m.p. 212.5° (decomposed),  $v_{KBr}$  1620, 1520, and 1235 cm<sup>-1</sup>.

Anal. Calcd. for C<sub>26</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 80.4; H, 4.15; N, 7.21; O, 8.24. Found: C, 81.8; H, 3.18; N, 7.00; O, 8.08.

## Oxidation Products from Fluorenone Oxime (1a)

#### 9,9-Dinitrofluorene (**4**a)

Lead tetraacetate (1.4 g) in glacial acetic acid (3 ml) was added in 20 min to a stirred solution of 1*a* (585 mg) in glacial acetic acid (25 ml). Reaction was complete at the end of the addition.<sup>4</sup> The insoluble lead diacetate was removed by filtration. Water was added to the filtrate to give a yellow precipitate which was dissolved in methylene chloride, washed with saline water and NaHCO<sub>3</sub> solution (5%), and dried (MgSO<sub>4</sub>). Crystallization from hexane gave 150 mg of 9,9-dinitrofluorene (4*a*) as pale-yellow needles, m.p. 129.5–131° (decomposed, NO<sub>2</sub> evolved). Recrystallization gave an analytical sample with m.p. 131–133° (decomposed) (reported m.p. 130–131.5° (decomposed) (16)).

Anal. Calcd. for  $C_{13}H_8NO_2$  (mol. wt., 256): C, 60.94; H, 3.15; N, 10.93; O, 24.98. Found (mol. wt., mass spectrometry, 256): C, 60.76; H, 3.53; N, 10.67; O, 25.20.

9,9-Difluorenylideniminoxylfluorene (5a)

(i) Lead tetraacetate (1.2 g) was added to glacial acetic acid (50 ml) which was purged with dry nitrogen for 1 h. To this vigorously stirred solution was added fluorenone oxime (1 g). After 4 h the suspension was filtered to give 290 mg of 5a, slightly contaminated by 1a (shown by thin-layer chromatography (t.l.c.)), m.p. 264.5-265.5 (decomposed). Three recrystallizations from methylene chloride – ethanol gave an analytical sample of 5a, m.p. 267° (decomposed).

Anal. Calcd. for  $C_{39}H_{24}N_2O_2$  (mol. wt., 552): C, 84.60; H, 4.34; N, 5.06; O, 5.78. Found (mol. wt., osmometric-CHCl<sub>3</sub>, 597): C, 84.46; H, 4.26; N, 5.16; O, 5.96.

(*ii*) Fluorenone oxime (975 mg) was added to a solution of sodium hydride (480 mg of 50% NaH-oil suspension) in dimethyl sulfoxide. After 10 min, 9,9-dichlorofluorene, prepared according to ref. 22, was added. The solution was stirred overnight in a nitrogen atmosphere. Addition of water gave a precipitate which was filtered to give ketal 5a (150 mg).

#### Fluorenonazinemonoxide (6a)

Lead tetraacetate (1.4 g) was added to a stirred solution of 1a (1.17 g) in oxygen-free CH<sub>2</sub>Cl<sub>2</sub> (200 ml). An opaque

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

· 2

 $<sup>^{4}</sup>$ An aliquot (0.5 ml) was shaken with 0.1 N potassium iodide solution (2 drops). Addition of starch solution gave a purple color only when unreacted lead tetra-acetate remained.

## FROJMOVIC AND JUST: LEAD TETRAACETATE AND RELATED OXIDATIONS

chocolate brown suspension immediately formed. After 4 h, lead acetate was removed by filtration. The CH<sub>2</sub>Cl<sub>2</sub> filtrate was washed with water, dried and evaporated in vacuo to give a red oil (1.55 g). Elution on silica gel (30 g) with hexane followed by hexane-benzene (1:1) yielded ketal 5a (36 mg) and dinitro compound 4a (20 mg). Elution with benzene gave initial fractions containing azinemonoxide 6a and further fractions containing both the latter and starting oxime. Crystallizations of the initial benzene fractions from MetOH gave red rosettes of 6a (141 mg), homogeneous by t.l.c. A recrystallization from  $CH_2Cl_2$  - petroleum ether (90–120°) gave an analytic sample with m.p. 178°.

Anal Calcd. for C<sub>26</sub>H<sub>16</sub>N<sub>2</sub>O: C, 83.85; H, 4.33; N, 7.52; O, 4.30. Found: C, 83.60; H, 4.43; N, 7.80; O, 4.38.

## Dinitrodiphenylmethane (4b), 1,1-bis(Diphenylmethylideniminoxyl) diphenylmethane (5b), and

Benzophenone Nitrimine (8)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

eanath bhaile bhaile aire an an ann. Is fan air an airte an an Anna an Anna an Anna an Anna an Anna an Anna an

Lead tetraacetate (4.48 g) was added to a rapidly stirred solution of benzophenone oxime (2 g), m.p. 143-144°, (lit. 142° (23)) in oxygen-free acetic acid in a nitrogen atmosphere. After 20 min, the reaction was complete.<sup>4</sup> The acetic acid solution was evaporated in vacuo at 30°. Methylene chloride (10 ml) was added, the lead acetate was filtered off, and the solution evaporated. The resulting oil (1.84 g) was crystallized from methanol at  $-10^{\circ}$  overnight to give colorless flakes (60 mg). Two crystallizations from methanol - methylene chloride gave an analytic sample with m.p. 170.5-171.5°.

Anal. Calcd. for  $C_{39}H_{30}N_2O_2$  (mol. wt., 558.6): C, 83.84; H, 5.41; N, 5.01; O, 5.73. Found (mol. wt., 547, osmometric-CHCl<sub>3</sub>): C, 84.05; H, 4.93; N, 5.29; O, 6.07.

The mother liquor from the above reaction was evaporated. The yellow oil was dissolved in hexane and poured onto a column of silica gel (60 g). Elution with hexane-benzene (7:3) gave 226 mg of 6b, m.p. 78.5-79°, homogeneous by t.l.c. Crystallization from hexane gave an analytic sample of 6b, m.p. 80.5-81° (decomposed, 100° with NO<sub>2</sub> evolution).

Anal. Calcd. for C13H10N2O4 (mol. wt., 258.2): C, 60.46; H, 3.90; N, 10.85; O, 24.78. Found (mol. wt., 260, osmometric-CHCl<sub>3</sub>): C, 60.22; H, 4.79; N, 10.60; O, 24.58.

Further elution with hexane-benzene gave crystals of compound 8 (245 mg), m.p. 62-66°, homogeneous by t.l.c. Crystallization from hexane gave an analytic sample of 8, m.p. 70-71° (decomposed, 165° with NO<sub>2</sub> evolution),  $vNO_2/KBr$  1540 and 1270 cm<sup>-1</sup> (s).

Anal. Calcd. for  $C_{39}H_{10}N_2O_2$  (mol. wt., 226): C, 69.01; H, 4.46; N, 13.48; O, 14.14. Found (mol. wt., 233, osmometric-CHCl<sub>3</sub>): C, 69.15; H, 4.55; N, 12.37; O, 14.16,

Further elution with benzene afforded benzophenone (1.15 g) and elution with ether gave an oil (35 mg) probably corresponding to benzophenone oxime-O-acetate (7b) (i.r. 1765 cm<sup>-1</sup> and  $R_f$  value = that of 1b).

#### Geminal Dinitromethanes (4)

The following general method was used: methylene chloride (25 ml) was briefly purged with nitrogen dioxide to give a light brown solution. The oxime (ca. 100 mg) was added all at once to the stirred solution. Immediate reaction occurred. The light-green solution was evaporated at room temperature in vacuo. Work-up was continued as follows.

(i) 9,9-Dinitrofluorene (4a) was obtained directly as pure crystals, m.p. 129.5-131°

(ii) Pale-yellow crystals (174 mg) were obtained from oxime 1b (150 mg), treated as above, consisting of 4b and minor amounts of ketone. Crystallization from hexane gave pure 4b (115 mg), m.p. 79-79.5°.

(iii) The yellow oil (277 mg) obtained from indanone oxime (250 mg; prepared as in ref. 24) consisted mainly of indanone (t.l.c.). Elution on silica gel with hexanebenzene (1:1) gave a yellow oil (31 mg) whose i.r. spectrum in CHCl<sub>3</sub> contained bands characteristic of gemdinitromethanes (1570 (s) and 1360 (m) cm<sup>-1</sup>). These absorption bands and the  $R_{\rm f}$  value indicated that this product was probably 1,1-dinitroindane (4d).

#### Entries to Table II

The experimental runs were conducted as previously described. All solids used in the oxygen-free experiments were degassed in the reaction flask prior to reaction. In order to simplify analysis of crude reaction mixtures, the following graphical technique was used.

An aliquot was removed from the reaction mixture and analyzed by i.r. in 0.1 mm IRT cells. Bands at 3565, 1765, 1720, and 1570 cm<sup>-1</sup> could be empirically related to the amounts of oxime, oxime-O-acetate, ketone, and azinemonoxide, respectively for the cases of 1a and 1b. Workup led to actual isolation of the above compounds, except for oxime-O-acetates (10), which had  $R_{\rm f}$  values identical to parent oximes. Actual amounts of products 10 were empirically calculated from i.r. and nuclear magnetic resonance ( $\delta_{CDC1_3}$  2.35 p.p.m.) spectra of the crude reaction mixtures.

#### Acknowledgments

This work was supported by the National Research Council of Canada and by Bristol Laboratories, Syracuse, New York.

- 1. B. C. GILBERT and R. O. C. NORMAN. J. Chem. Soc. B. No. 1, 86 (1966). W. M. LAUER and W. S. DYER. J. Am. Chem. Soc.
- 2.
- Ind., London, 176 (1956). 5. K. DAHL and G. JUST. Tetrahedron Letters, 22,
- 2441 (1966). 6. L. HORNER and W. KIRMSE *et al.* Ber. **94**, 279 (1961). 7. H. KROPF and R. LAMBECK. Ann. Chem. To be
- published.
- J. COLLIN. Bull. Soc. Roy. Sci. Liege, 23, 201 (1954). 8.
- 9. L. HORNER et al. Ber. 94, 290 (1961). 10. B. C. GILBERT. Oxford University, England. Private communication.
- J. CANE. Chem. Rev. 64, 473 (1964). A. I. TITOV. Tetrahedron, 19, 557–580 (1963). L. I. KHMELNITSKI et al. Chem. Abstr. 55, 19, 833c (1961).
  O. TOUSTER. Organic reactions. Vol. VII. John Wiley and Sons, Inc., New York. 1953, p. 349.
  M. C. B. SINGUR, J. Chem. Soc. 1189. (1962). 11.
- 12
- M. C. R. SYMONS. J. Chem. Soc. 1189 (1963); M. C. R. SYMONS. Advan. Phys. Org. Chem. 1, 283 (1963). 13.

## CANADIAN JOURNAL OF CHEMISTRY. VOL. 46, 1968

- R. SCHOLL. Ber. 21, 506 (1888).
   L. I. KHMELNITSKI et al. Chem. Abstr. 55, 23, 389c (1961).
   H. SCHECHTER and R. B. KAPLAN. J. Am. Chem. Soc. 83, 3535 (1961).
   O. L. CHAPMAN and D. C. HECKERT. J. Am. Chem. Soc. To be published.
   G. A. RUSSELL. J. Chem. Educ. 36, 111 (1959).
   A. K. HOFFMAN, A. M. FELDMAN, and E. GELDBLUM. J. Am. Chem. Soc. 87, 6461 (1964).
   O. L. CHAPMAN and D. C. HECKERT. Chem. Commun. 8, 242 (1966).

- A. RASSAT et al. Bull. Soc. Chim. France, 1485, 1985 (1964).
   F. J. MOORE and E. H. HUNTRESS. J. Am. Chem. Soc. 49, 2618 (1927).
   A. I. VOGEL. Practical organic chemistry. 3rd ed. Longmans, Green and Co., Inc., New York. 1961, p. 741
- p. 741.
  24. W. UTERMARK and W. SCHICKE. Melting point tables of organic compounds. John Wiley and Sons, Inc., New York. 1963. pp. 719.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 132.174.255.116 on 11/10/14 For personal use only.

\* · .