

TABLE IV  
 YIELDS AND PHYSICAL DATA FOR THE SYNTHESIZED COMPOUNDS

Compd no.	Yield, %	Crystd from <sup>a</sup>	Mp, °C <sup>b</sup>	Empirical formula	Calcd, %			Found, % <sup>b</sup>		
					C	H	N	C	H	N
1a	77	A	183-234	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub>	86.63	5.59	7.77 <sup>c</sup>	86.50	5.54	7.97
1b	65.5	A	199-225	C <sub>26</sub> H <sub>18</sub> F <sub>2</sub> N <sub>2</sub>	78.77	5.48	7.07 <sup>d</sup>	78.86	4.86	6.78
1c	88	B <sup>e</sup>	190-240	C <sub>28</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub>	79.97	5.75	6.66	79.79	5.83	6.83
1d	70	B	250-280	C <sub>26</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	79.57	5.14	7.14	79.57	5.28	7.17
2b	63	C	273-275 dec	C <sub>26</sub> H <sub>16</sub> F <sub>2</sub> N <sub>2</sub> O	76.08	3.93	6.83	76.23	3.87	6.85
2c	34	D	295-297 dec	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>	77.40	5.10		77.43	5.28	
2e	63	B	260-267 dec	C <sub>30</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub>	73.46	4.52	5.71	73.78	4.57	5.67
3a	80 <sup>f</sup>	C	299-300	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub>	87.12	5.06	7.82	86.85	5.41	7.67
3b	88 <sup>g</sup>	C	275-280	C <sub>26</sub> H <sub>16</sub> F <sub>2</sub> N <sub>2</sub>	79.17	4.09	7.10	79.15	4.28	7.01
3c	100 <sup>h</sup>	C	288-290	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	80.35	5.30	6.69	80.30	5.14	6.85
6a	94	B	215-240	C <sub>28</sub> H <sub>22</sub> N <sub>2</sub> O	83.55	5.51	6.96	83.57	5.55	6.97
6c	73	B	203-213	C <sub>30</sub> H <sub>26</sub> N <sub>2</sub> O <sub>3</sub>	77.90	5.67	6.06	77.70	5.48	6.24
6e	76	B	195-222	C <sub>32</sub> H <sub>26</sub> N <sub>2</sub> O <sub>5</sub>			5.40			5.32
7	70	E	137-140	C <sub>19</sub> H <sub>16</sub> N <sub>2</sub>	83.79	5.92	10.29	84.01	5.89	9.99
9	85	C	159-160	C <sub>19</sub> H <sub>14</sub> N <sub>2</sub> O	79.70	4.93	9.78	79.91	5.03	9.97
10	88	E	220-221	C <sub>21</sub> H <sub>18</sub> N <sub>2</sub> O	80.23	5.77	8.91	79.97	5.77	9.11

<sup>a</sup> Solvent key: A (pyridine), B (*p*-dioxane), C (toluene), D (*o*-dichlorobenzene), E (ethanol). <sup>b</sup> Melting points were determined on a Fisher-Jones apparatus and are corrected to standards. The wide ranges indicate that melting depends on the temperature at which the substance is put on the plate. If put on within a degree of the top figure, the melting range is 1°. If put on at or below the lower figure, melting begins at the given point but spreads over a wider range. Microanalyses were determined by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and A. Bernhardt, Ellbach über Engelskirchen, West Germany. <sup>c</sup> Calcd: mol wt, 360. Found: mol wt, 365. <sup>d</sup> Calcd: F, 9.58. Found: F, 9.34. <sup>e</sup> Under N<sub>2</sub> atmosphere. <sup>f</sup> Obtained from Al<sub>2</sub>O<sub>3</sub> oxidation of 1a. <sup>g</sup> Obtained from the oxidation of 1b with an equivalent amount of *m*-chloroperoxybenzoic acid. <sup>h</sup> Obtained from the disproportionation reaction of 1c.

and dried giving 6a, 6c, or 6e.<sup>10</sup> Attempts to monoacetylate 1b or, by prolonged boiling, to diacetylate 1a produced the corresponding azo compound in each case.

**Reduction of 2,2'-Azoxyfluorene (2a) with Phenylhydrazine.**—A mixture of 1 g of 2a and 10 g of phenylhydrazine was heated to 225° for 30 min. At 165°, evolution of gas began. The resulting oil was cooled and poured into water to form a white precipitate, which was filtered off and dried to give 0.85 g (90%) of 4a, mp 125-127°.

**2-Fluorenylazobenzene (8).**—To a solution of 1.8 g (0.01 mol) of 4a in 40 ml of ethanol, 1.1 g (0.0103 mol) of nitrosobenzene and 2 ml of glacial acetic acid were added. The mixture was heated to 50° and allowed to cool. The precipitate was filtered off and recrystallized from ethanol giving 2.6 g (95%) of 8, mp 174-175° (lit.<sup>20</sup> mp 173-174°).

**N<sup>1</sup>-2-Fluorenyl-N<sup>2</sup>-phenylhydrazine (7).**—A solution of 1.35 g of 8 in 10 ml of pyridine was treated with 10 mg of Ru on C (5%) and 1 ml of hydrazine hydrate (100%) and boiled until the solution was decolorized (5 min). After filtration, the solution was concentrated to 5 ml. Addition of 30 ml of petroleum ether (bp 30-60°), brought out 0.95 g of 7, mp 137-139°.

**N<sup>1</sup>-Acetyl-N<sup>1</sup>-2-fluorenyl-N<sup>2</sup>-phenylhydrazine (10).**—Acetylation, as above, of 2.7 g of 7 gave 2.75 g of 10, mp, 318-321°.<sup>21</sup>

**N-2-Fluorenylazoxybenzene (9).**—A solution of 2 g (0.0074 mol) of 7 in 50 ml of toluene was treated with 2 g (0.01 mol) of *m*-chloroperoxybenzoic acid, boiled for 10 min, and cooled. The yellow precipitate was filtered off, washed with ethanol, and dried, giving 1.8 g of 9, mp 159-160°.

**Registry No.**—1a, 24247-79-8; 1b, 26319-77-7; 1c, 26319-78-8; 1d, 26319-79-9; 2a (*cis*), 26332-74-1; 2a (*trans*), 26332-70-7; 2b (*cis*), 26332-75-2; 2b (*trans*), 26395-33-5; 2c, 26319-80-2; 2e (*cis*), 26332-76-3; 2e (*trans*), 26347-40-0; 3a (*cis*), 26332-77-4; 3a (*trans*),

26332-71-8; 3b (*cis*), 26332-78-5; 3b (*trans*), 26332-72-9; 3c, 26347-41-1; 4a, 153-78-6; 4b, 363-16-6; 6a, 24225-71-6; 6c, 26319-84-6; 6e, 26319-85-7; 7, 26319-86-8; 8 (*cis*), 26332-79-6; 8 (*trans*), 26347-42-2; 9 (*cis*), 26332-80-9; 9 (*trans*), 26332-73-0; 10, 26319-87-9.

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#### Assignment of Ketoxime Stereochemistry by a Nuclear Magnetic Resonance Method

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The classical method for determining the stereochemistry of ketoximes is based upon the preferential migration of the group anti to the oximino hydroxyl group during the Beckmann rearrangement. The shortcomings of this method for stereochemical assignment are well known.<sup>1</sup> Recent nmr studies have provided alternate and more generally reliable techniques for assigning configuration. In the method of Karabatsos,<sup>2</sup> nmr spectra were obtained in carbon tetra-

(19) All of the mono-*N*-acetylhydrazo compounds were obtained analytically pure with respect to C, H, and N. However, in no case were values for *N*-acetyl correct or anywhere near correct. With 6a this was true for two different commercial analysts. However, we were able to analyze indirectly for *N*-Ac by reductive splitting, thus recovering an equivalent of *N*-acetylated amine within reasonable limits of theoretical values. As a check on this anomalous situation we made the known mono-*N*-acetylhydrazobenzene. *N*-acetyl values for this otherwise analytically pure compound also were abnormally low (Calcd: 19.03. Found: 14.26).

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TABLE I  
 EFFECT OF HYDROGEN CHLORIDE ON 60-MHZ NMR SPECTRUM OF

Ref	Compd no.	Registry no.	$\begin{array}{c} \text{N}-\text{OH} \\ \parallel \\ \text{R}_1-\text{C}-\text{R}_2 \end{array}$		$V_0$ , Hz from TMS	$V_0 - V_{\text{HCl}}$ , Hz <sup>a</sup>		
			R <sub>1</sub>	R <sub>2</sub>		2 ml	6 ml	10 ml
1b	I	26306-05-8	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	124.7	1.3	3.4	5.0
1b	II	26306-06-9	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	245.7	1.4	3.5	4.9
...	III	26306-07-0	C <sub>6</sub> H <sub>5</sub> CH(OCH <sub>3</sub> )	C <sub>6</sub> H <sub>5</sub>	308.7	-24.4	-49.5	-55.3
...	IV	26306-08-1	C <sub>6</sub> H <sub>5</sub> CHCH <sub>3</sub>	CH <sub>3</sub>	100.2	1.1	3.0	4.5
	IV		C <sub>6</sub> H <sub>5</sub> CHCH <sub>3</sub>	CH <sub>3</sub>	206.3	-3.4	-10.2	-17.0
	V	1188-11-0	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	136.6	...	2.2	3.3
	V		CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	118.6	...	-1.5	-3.1
1b	VI <sup>e</sup>	26306-10-5	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	102.8	...	1.7	2.2
	VI <sup>e</sup>	26306-11-6	CH <sub>2</sub>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	97.4	...	...	-2.0
	VII <sup>e</sup>	10048-64-3	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>3</sub>	99.4	3.5	6.5	10.3
	VII <sup>e</sup>		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>3</sub>	196.5	...	-6.7	-14.0
7	VII <sup>e</sup>	10048-65-4	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	215.8	3.2	7.3	10.7
	VII <sup>e</sup>		CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	93.4	...	-1.9	-5.1
	VIII <sup>f</sup>	100-64-1	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>		147.5	1.0	2.7	9.1
	VIII		CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub>		126.2	...	-2.2	-4.3
...	IX <sup>g</sup>	26358-61-2	CH=C(CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub>		367.5	-1.7	-4.5	-7.3
	IX		CH=C(CH <sub>3</sub> )CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub>		147.0	1.5	3.5	5.5

<sup>a</sup> Chemical shift in benzene solution minus chemical shift after treatment with the indicated volume of concentrated hydrochloric acid vapor. <sup>b</sup> R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962). <sup>c</sup> A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946). <sup>d</sup> Differences of less than 1 Hz were considered insignificant and, therefore, are not reported. <sup>e</sup> Where stereoisomeric mixtures were studied, the first entry is the principal isomer. <sup>f</sup> Cyclohexanone oxime. <sup>g</sup> R. H. Mazur, *J. Org. Chem.*, **26**, 1289 (1961). <sup>h</sup> *anti*-Isophorone oxime.

chloride and in benzene. The magnitude of the benzene-induced changes in chemical shifts were then taken as an indication of configuration. Correlation of <sup>15</sup>N-H coupling constants with stereochemistry has been accomplished, although the cost of <sup>15</sup>N-labeled hydroxylamine hydrochloride makes the method rather expensive.<sup>3</sup> Studies relating the chemical shift of the oximino hydroxyl proton to configuration have also been conducted.<sup>4</sup>

We wish to report an nmr method for assigning ketoxime stereochemistry which is simple and inexpensive. In addition, the procedure reported here obviates the need for comparing one's own experimental data with previously compiled values, which may or may not be applicable to the compound at hand.

Using benzene solutions of dialkyl, cycloalkyl, alkylphenyl, and  $\alpha,\beta$ -unsaturated ketoximes of known configuration, we observed that in *all* cases investigated, the addition of small amounts of concentrated hydrochloric acid vapor to an nmr sample caused the  $\alpha$  protons syn to the hydroxyl group to shift to higher field, while the anti  $\alpha$  protons were shifted to lower field. One of the more dramatic examples of this effect was provided by the spectrum of a stereoisomeric mixture of phenylacetone oximes, in which peak transposition occurred (Figure 1). In all cases examined, the changes in chemical shifts ( $V_0 - V_{\text{HCl}}$ ) produced by adding 10 ml of the reagent to approximately 1 ml of oxime solutions were large enough to be unambiguously recognized and measured (Table I). That hydrochloric acid vapor was observed to catalyze syn-anti isomerization in some instances (compounds III and VII, for example) is of no serious consequence, since stereochemical purity may be established<sup>2,5,6</sup> from the spectrum obtained before the addition of this reagent.

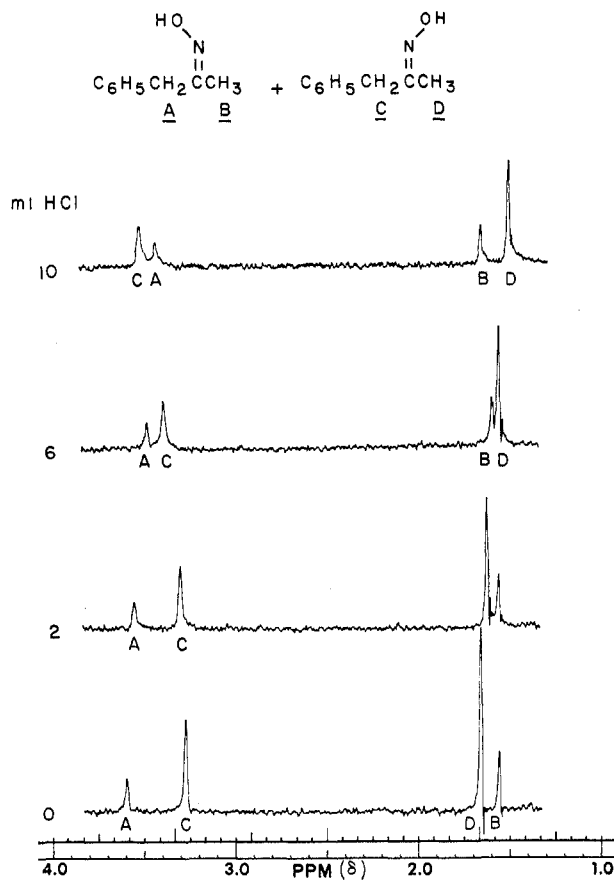


Figure 1.

The involvement of the aromatic solvent in causing this effect was deduced from a study of chloroform solutions of I, II, III, V, and VII. The hydrogen chloride induced spectral changes for I, II, and V were virtually zero (<1 Hz) in this solvent. The effects of hydrogen

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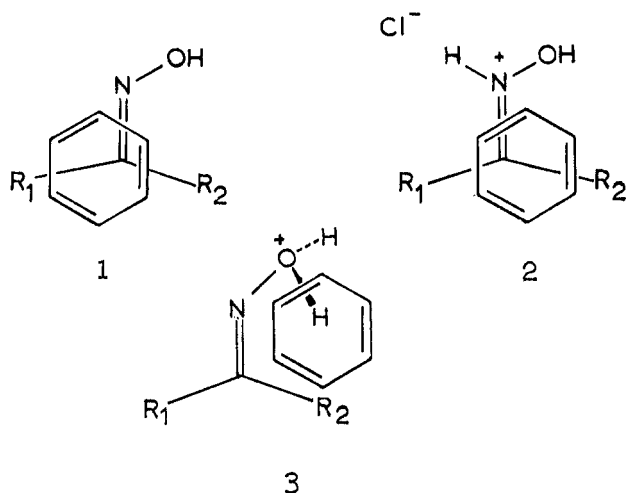
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chloride on the spectra of III and VII were similar in chloroform to those observed in benzene, but the magnitude of the changes was much smaller. These small changes may have been due to the presence of the aromatic rings in the oximes themselves.<sup>7</sup>

In agreement with previous reports,<sup>2,5,6</sup> the data in Table I demonstrate that for benzene solutions of ketoximes a given set of  $\alpha$  protons resonates at lower field when syn to the oximino hydroxyl group than when anti. This fact has been explained<sup>8</sup> in terms of complex formation between the oxime and the aromatic solvent. Such complexes (a preferential orientation of aromatic molecules with respect to the electric dipole in a polar solute) have been proposed in numerous cases to account for solvent-induced changes in chemical shifts.<sup>9-15</sup> The complex proposed<sup>8</sup> for oximes (1) satis-



factorily accounts for a large amount of experimental data<sup>2,5-7,16,17</sup> and, based on the currently accepted theory of complex formation, implies that the negative end of the dipole moment in oximes lies in the area of the oxygen atom.

We suggest that the effect of hydrogen chloride is due to the change in dipole moment produced by protonation of the oxime. Concomitant with this change in dipole moment, a reorientation of the solvent molecule<sup>18</sup> with respect to the oxime hydrochloride would be anticipated.

On the basis of spectral evidence, oxime hydrochlorides are believed to be protonated on nitrogen.<sup>19,20</sup> It has been suggested<sup>20</sup> that the dipole moment in these salts lies along the  $N^+-H$  bond. If this is the case in benzene solution, one would anticipate a complex (2)

having  $R_2$  closer to the diamagnetic region of the solvent molecule than was the case in 1. Likewise,  $R_1$  should be deshielded in 2 relative to 1. While such a model adequately explains the observed changes in chemical shifts, so would the oxygen protonated complex, 3. Since the addition of hydrogen chloride catalyzed chemical exchange of the hydroxyl proton as indicated by signal widths in the nmr spectra, we feel there is ample reason to consider both of the suggested species in explaining our data.

### Experimental Section

**Ketoximes.**—All of the ketoximes used in this study were prepared in our laboratories using standard techniques<sup>21</sup> and were of known configuration (see references in Table I).

**Nmr Spectra.**—Spectral data reported in this paper were recorded on a Varian HR60-IL (60 MHz) spectrometer. Similar results were also obtained from a Varian A-60-D spectrometer. The studies were carried out using approximately 10% (w/w) solutions in benzene or using saturated solutions where solubility was a problem (compound III).

**General Procedure.**—The nmr spectrum of the ketoxime was recorded, and the chemical shifts ( $V_0$ ) for the  $\alpha$  protons were measured. Hydrochloric acid vapor was withdrawn from the atmosphere in a concentrated hydrochloric acid reagent bottle using an eyedropper of sufficient length to reach to the bottom of an nmr sample tube. This gas was then slowly bubbled through the sample. The spectrum was recorded and chemical shifts were ( $V_{HCl}$ ) measured after each addition of hydrochloric acid vapor, made successively in 2-, 4-, and 4-ml portions. The foregoing volumes were based on the volume of the dropper bulb and must be regarded as approximate. Occasionally a precipitate began to form during the final addition but never became so voluminous that an acceptable spectrum could not be obtained.

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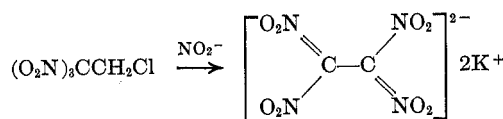
## Aliphatic Polynitro Compounds. II. Reactions of Substituted Polynitroalkanes<sup>1</sup>

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Following the discovery of the rearrangement of 2,2,2-trinitrochloroethane (1) to dipotassium tetranitroethane (2) in the presence of nitrite ion,<sup>2</sup> a program was



initiated to investigate the generality of this reaction with other substituted polynitro compounds and to obtain evidence pertinent to the mechanistic path of this rearrangement. The compounds investigated were  $X-C(NO_2)CH_2-Y$ , where  $X = -NO_2, -Cl, -CH_2-$

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(1) This work has been carried out as a part of the Lockheed Independent Research Program.

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