

TABLE I
SECOND-ORDER RATE CONSTANTS FOR TRITON
ABSTRACTION FROM *tert*-BUTYLMALONONITRILE-1-*t*

Base	pK _a	k ₂ , sec ⁻¹ M ⁻¹
H ₂ O ^a	-1.74	5.89 × 10 ⁻⁶
ClCH ₂ CO ₂ ^{-a}	2.85	3.25 × 10 ⁻³
HCO ₂ ^{-a}	3.75	2.52 × 10 ⁻²
CH ₃ CO ₂ ^{-a}	4.76	2.31 × 10 ⁻¹
OH ^{-a}	15.75	2.48 × 10 ⁶
Glycinamide	8.10	30.4
Hydrazine	8.16	46.6
2-Methoxyethylamine	9.43	184
Trifluoroethylamine	5.71	1.03
Methoxylamine	4.69	0.176
Trifluoroethanol	12.37	1.49 × 10 ⁵
Hydrogen peroxide	11.6	1.53 × 10 ⁶

^a F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, **93**, 2829 (1971).

tively, which supports the conclusion of a lack of an α effect. In contrast, from the relationship of β and the value of the α effect alluded to previously,¹² the ratio of $k_{\text{hydrazine}}/k_{\text{gl}}$ would be anticipated as *ca.* 40. Of the various rationales which have been put forth to explain the α effect, that of repulsive interaction of adjacent electron pairs¹⁷ appears most useful in explaining the relationship of the α effect to the Brønsted β constant as well as the finding of no α effect for proton abstraction. Thus, the more productlike the transition state the less available are the bonding electrons and the greater is the relief of repulsion. The lack of an α effect for proton abstraction from a carbon acid may be ascribed to the anticipated lessened perturbing influence of a proton upon the electron structure of a base.¹³

Registry No.—Glycinamide, 598-41-4; hydrazine, 302-01-2; 2-methoxyethylamine, 109-85-3; trifluoroethylamine, 753-90-2; methoxylamine, 67-62-9; trifluoroethanol, 75-89-8; hydrogen peroxide, 7722-84-1; *tert*-butyl malononitrile-1-*t*, 33407-05-5.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health.

(17) K. M. Ibne-Rasa and J. O. Edwards, *J. Amer. Chem. Soc.*, **84**, 763 (1962). This suggestion is very similar to that suggested by Ingold: C. K. Ingold, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, J. F. Norris Award Address.

(18) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

Stereochemistry of Iminoxy Radicals Derived from Some Benzohydroximoyl Chlorides

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The formation of iminoxy σ radicals by oxidation of oximes in organic solvents using ceric ion¹ or lead

(1) J. R. Thomas, *J. Amer. Chem. Soc.*, **86**, 1446 (1964); W. H. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965).

tetracetate^{2,3} is well established. The electron resonance spectra of these radicals are strongly dependent on their geometrical structure,^{2,3} since the transmission of spin density through space by direct overlap or through the framework of the molecule is greatly affected by the relative orientation of the σ orbital containing the unpaired electron and of the interacting nuclei. For instance, in the anti radical from benzaldoxime, a definite coupling constant of 1.4 G with the ortho protons of the aromatic ring is observed, whereas in the syn isomer there is no interaction with any of the phenyl protons;³ moreover, the splitting due to the hydrogen of the iminoxy group is considerably different in the two configurations, *viz.* 27 G in the syn and 6.5 G in the anti form.³ Consequently, the marked stereochemical dependence of the hyperfine splitting (hfs) constants of the coupled nuclei in the iminoxy radicals gives a means of obtaining information concerning their molecular geometry.

We wish to report the results of an esr study on iminoxy radicals derived from benzohydroximoyl chlorides (1-8). The aim of this investigation was to assign the molecular geometry of these radicals from hfs parameters. The configuration on the C=N bond and the conformation on the N-O bond of hydroximoyl chlorides have been recently investigated through the analysis of dipole moment data.⁴ Even though the results were less reliable than in studies of other oximino compounds⁵ and imidoyl chlorides,⁶ they favor the *E* ap (anti, trans) form. This assignment differs from that given by Lumbroso and coworkers, who preferred the *Z* ap (syn, trans) form.⁷



The radicals have been generated at room temperature by oxidation of the hydroximoyl chlorides with lead tetracetate in deoxygenated solutions of benzene or methylene chloride. Several compounds were examined, but in some cases the decay of the radical produced was so rapid that the esr spectrum could not be recorded. The compounds giving detectable concentrations of the radical for a sufficiently long time and their hyperfine splitting constants are listed in Table I. In each case the esr spectrum of the observed radical shows the presence of only one of the two geometric isomeric forms either in benzene or methylene chloride. This behavior differs from that of other oximino compounds, such as aldoximes and ketoximes, which usually give a mixture of syn and anti radicals in methylene chloride or other polar solvents.¹⁻³ The nature of the atom X in the CX=NOH group seems to be very important in determining the stability of the isomeric

(2) M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1985 (1964).

(3) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 86 (1966); 123 (1968).

(4) A. Battaglia, A. Dondoni, and O. Exner, *J. Chem. Soc., Perkin Trans. 2*, in press.

(5) O. Exner, *Collect. Czech. Chem. Commun.*, **30**, 652 (1965); D. Šnobl and O. Exner, *ibid.*, **34**, 3325 (1969); O. Exner, M. H. Benn, and F. Willis, *Can. J. Chem.*, **46**, 1873 (1968).

(6) A. Dondoni and O. Exner, *J. Chem. Soc., Perkin Trans. 2*, in press.

(7) J. Barassin, J. Armand, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 3409 (1969).

TABLE I
HFS CONSTANTS (GAUSS) OF IMINOXY RADICALS DERIVED
FROM BENZOHYDROXIMOYL CHLORIDES
ArC(Cl)=NOH

Ar	a_N	a_{Cl}	a_X^a	Solvent ^b
2,4,6-Trimethyl-3,5-dichlorophenyl (1)	30.9	1.71 ^c		B
		1.43 ^d		
2,4-Dichlorophenyl (2)	30.5	1.73 ^c		M
		1.44 ^d		
2,6-Dichlorophenyl (3)	32.0	1.89 ^e	1.89 ^e (1 Cl)	B
		32.2	1.76	2.15 (1 Cl)
2-Bromophenyl (4)	30.5	1.57		B
4-Nitrophenyl (5)	31.9	1.70	9.80 (1 Br)	B
2-Nitrophenyl (6)	30.0	1.30	0.70 (2 H)	B
3-Nitrophenyl (7)	30.0	1.33		B
4-Chlorophenyl (8)	30.4	Unresolved hyperfine structure		B
		Unresolved hyperfine structure		

^a Hfs constants of the nuclei X of the phenyl ring are indicated in parentheses. ^b B = benzene; M = methylene chloride. ^c Splitting due to ³⁵Cl. ^d Splitting due to ³⁷Cl. ^e Average values for the two coupled chlorine atoms.

radicals produced in the course of the oxidation; for instance, in the present case the chlorine atom greatly stabilizes one of the two configurations. By examining the hfs constants it was possible to decide in which form the observed radical was present.

The spectra⁸ were characterized by splittings due to nitrogen (a_N ca. 30 G) typical of σ -type iminoxy radicals,¹⁻³ and to chlorine. When the unpaired electron was not coupled with other nuclei, it was possible to resolve the lines due to isotopes ³⁵Cl and ³⁷Cl, which have different magnetogyric ratios. The splittings from nitrogen and chlorine are not very useful in assigning the preferred configuration of the radicals, since a_N is almost independent of the molecular geometry and the values due to chlorine in the syn and anti isomers are not known. However, considering the relative values of a_H on the two isomeric radicals derived from benzaldoxime,³ a large chlorine coupling constant would be expected for the syn configuration; the observed splitting of only 1.7 G may indicate that the anti isomer is the more stable.



The analysis of other hfs parameters supports this conclusion. The spectra of the radicals derived from **5** show the presence of coupling with the ortho aromatic protons, and those derived from **2** and **4** show ortho halogen splittings, the one resulting from bromine being very large. Also the lack of resolution in the spectra of the radicals derived from **7** and **8** may indicate that the unpaired electron is coupled with other nuclei, besides the chlorine, namely with the ortho aromatic protons. All these couplings should be

(8) The esr spectra of the radicals derived from compounds **1** (in methylene chloride) and **2** (in benzene) will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JOC-72-3564. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

absent in the syn isomers, since direct orbital overlap between the cited nuclei and the orbital containing the unpaired electron is prevented by the greater distance. No interaction has been detected with ortho nuclei on the phenyl ring placed in the opposite side with respect to the iminoxy oxygen.³ All these results confirm the anti isomer as the more stable geometrical form of these radicals.

The data obtained also allow some conclusions to be advanced on the conformation of the phenyl ring with respect to the Cl-C=N plane. A similar problem has been discussed for radicals derived from ortho-substituted acetophenone oximes.³ As mentioned above, the radicals from **2** and **4** show definite ortho halogen splittings ($a_{Cl} = 2.1$ G, $a_{Br} = 9.8$ G), whereas the coupling with the ortho aromatic proton is absent. Similarly, in the radical from 2-nitro derivative **6**, the splitting from the ortho proton was not observed. This indicates that the preferred arrangement of the phenyl ring is that which places the ortho substituent on the same side of the iminoxy oxygen, because of the steric overcrowding between the substituent and the aliphatic chlorine atom. However, full coplanarity of the phenyl ring with the Cl-C=N fragment seems unlikely for steric reasons, while a less crowded arrangement is that keeping the phenyl ring distorted at some angle from the Cl-C=N plane. This conclusion is supported by the greater values of ortho halogen hfs constants reported in iminoxy radicals where the coplanarity is granted by the rigid skeleton of the molecule.³

When radicals were generated from the ortho-disubstituted benzohydroximoyl chlorides **1** and **3**, the splittings from methyl protons or chlorine were not observed. In these cases the steric overcrowding appears to have held the phenyl ring in an arrangement almost perpendicular to the Cl-C=N plane, thus preventing any interaction between the ortho substituents and the unpaired electron.

The anti configuration of iminoxy radicals derived from benzohydroximoyl chlorides (**1-8**) has been established from their esr spectra. This constitutes evidence for the same configurational assignment for the radical as for its precursor,⁴ since, considering that only *one* isomer has been observed for both radical and precursor, it seems unlikely that the stability of syn and anti forms is completely reversed in the two cases.

Experimental Section

A Varian Model V-4502 spectrometer was used to obtain the esr spectra. Solutions of the reactants were deoxygenated by bubbling nitrogen through them before mixing. The spectra were recorded at room temperature under nitrogen.

Hydroximoyl chloride (**1**) was prepared by the literature method;⁹ compounds **2** and **4-8** were obtained as described.⁴ **2,6-Dichlorobenzohydroximoyl chloride (3)** was prepared by slow addition of dry hydrochloric acid to an ice-cooled solution of the corresponding nitrile oxide¹⁰ (1 g) in 75 ml of methylene dichloride. The reaction was completed within 1 hr. The solvent was removed *in vacuo* and the oily residue was treated with petroleum ether (bp 30-60°) to yield **3**, which after recrystallization from benzene-petroleum ether had mp 93-94°. Ir and nmr spectra were similar to those of the other compounds.

Anal. Calcd for C₇H₄Cl₂NO: C, 37.45; H, 1.79; Cl, 47.38; N, 6.24. Found: C, 37.49; H, 1.80; Cl, 47.24; N, 6.18.

(9) P. Beltrame, C. Veglio, and M. Simonetta, *J. Chem. Soc. B*, 867 (1967).

(10) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

Attempts to prepare this compound by chlorination of the corresponding oxime with chlorine or nitrosyl chloride were unsuccessful.

Registry No.—*anti*-1, 35623-67-7; *anti*-2, 35623-68-8; *anti*-3, 35623-69-9; *anti*-4, 35623-70-2; *anti*-5, 35623-71-3; *anti*-6, 35623-72-4; *anti*-7, 35623-73-5; *anti*-8, 35623-74-6.

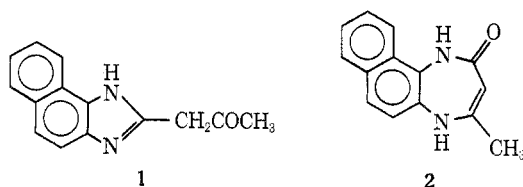
A Reexamination of the Reactions of 1,2-Diaminonaphthalene with Ethyl Acetoacetate and Crotonic Acid¹⁻³

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The direct condensation of 1,2-diaminonaphthalene with ethyl acetoacetate in boiling xylene has been reported⁴ to give a mixture of the two isomeric products, 2-acetonaphthimidazole (1) and the dihydrodiazepinone 2. Structure 2, rather than the alternate cycliza-



tion possibility 3, was assigned because, upon reduction, the product gave material isomeric with that obtained from the reaction of the naphthalenediamine with crotonic acid.⁴ However, the structure of the crotonic acid product was not established with certainty and, therefore, structure 2 has remained open to question.⁵ Furthermore, there is now reason in the literature^{6,7} to suspect that 1 is an erroneous assignment. A recent reinvestigation in our laboratory of the reactions of 1,2-diaminonaphthalene with ethyl acetoacetate and crotonic acid has revealed that all of the previous structural assignments for the reaction products are indeed incorrect.

The structures of the various products involved in this study are shown in Scheme I. The lower melting product from the reaction of the diamine with ethyl acetoacetate, previously thought to be 1, was found to be an isopropenylimidazolone on the basis of its ir

(1) This investigation was supported in part by Research Grant C6516 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service.

(2) This is part 4 of the series, "Application of a Thermal Rearrangement Reaction to Questions of Structure of Condensed Dihydrodiazepinones." For part 3, see M. Israel, L. C. Jones, and M. M. Joullié, *J. Heterocycl. Chem.*, **8**, 1015 (1971).

(3) A brief account of part of this work has appeared: M. Israel, L. C. Jones, and E. C. Zoll, Abstracts of Papers, Third International Congress of Heterocyclic Chemistry, Sendai, Japan, Aug 1971, p 550.

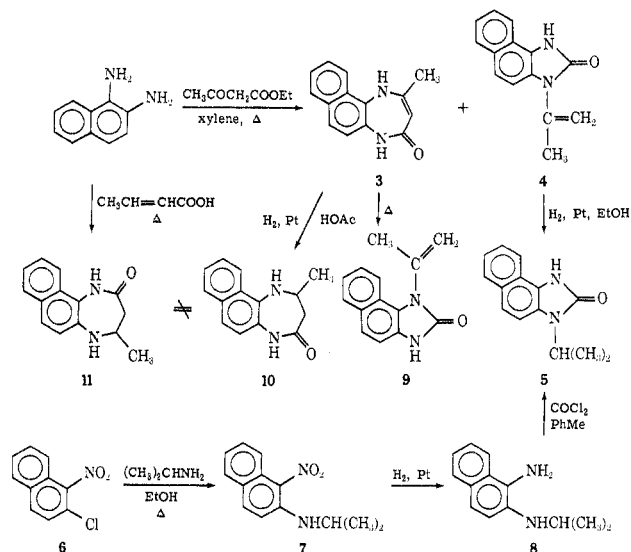
(4) W. Ried and W. Höhne, *Chem. Ber.*, **87**, 1801 (1954).

(5) The lack of certainty of Ried and Höhne's structure assignments has been noted by J. A. Moore in "Heterocyclic Compounds," Vol. 9, R. C. Elderfield, Ed., Wiley, New York, N. Y., 1967, pp 319 and 327.

(6) J. Davoll, *J. Chem. Soc.*, 308 (1960).

(7) M. Israel, L. C. Jones, and E. J. Modest, *Tetrahedron Lett.*, 4811 (1968).

SCHEME I



spectrum ($\lambda_{\text{max}}^{\text{KCl}} 5.85 \mu$) and nmr spectrum (CDCl_3) (methyl signal at δ 2.48 and two vinyl proton quartets at 5.53 and 5.65 ppm). Assignment of structure 4 to this material followed from the observation that, upon reduction, it afforded a product identical with a sample of 1,2-dihydro-3-isopropyl-3*H*-naphth[1,2-*d*]imidazol-2-one (5) prepared by unambiguous synthesis (6 \rightarrow 7 \rightarrow 8 \rightarrow 5). The isomeric product from the condensation reaction (reported⁴ mp 228°) had mp 228° when first isolated but this was raised to 246° upon purification. The nmr spectrum in various solvents showed, in addition to the aromatic ring protons, a methyl singlet, a methylene singlet, and a broad downfield NH signal, a pattern similar to that of other acetoacetic ester diazepinone products.⁷⁻¹¹

Often, but not always, the reaction of an *o*-diamine with a β -keto ester in boiling hydrocarbon solvent gives rise to a mixture of a diazepinone and an isomeric alkenylimidazolone.^{6-8,10-14} The imidazolone product is now known to arise in these reactions *via* thermal rearrangement of the diazepinone.⁷ Based upon previous experience,^{7,8,10,11} the presence of 4 in the naphthalenediamine-ethyl acetoacetate reaction mixture suggested that the diazepinone product was 2. However, all attempts to convert the diazepinone into 4 either by fusion⁷ or under conditions of base catalysis^{6,9} were unsuccessful. Thermal rearrangement of the diazepinone, under stronger conditions than normally required for this reaction, afforded instead an isomeric isopropenylimidazolone, mp 222°, the nmr spectrum (CDCl_3) of which showed the methyl quartet 0.18 ppm upfield from that of 4 and the two vinyl quartets at δ 5.43 and 5.60 ppm. This information identified the rearranged material as 9 and, since C-N bonds are not disrupted during the ring contraction process,⁷ the

(8) M. Israel, L. C. Jones, and E. J. Modest, *J. Heterocycl. Chem.*, **4**, 859 (1967).

(9) M. Israel, S. K. Tinter, D. H. Trites, and E. J. Modest, *ibid.*, **7**, 1029 (1970).

(10) M. Israel and L. C. Jones, *ibid.*, **8**, 797 (1971).

(11) Unpublished results from these laboratories.

(12) A. Rossi, A. Hunger, J. Kebrle, and K. Hoffmann, *Helv. Chim. Acta*, **43**, 1298 (1960).

(13) A. Rossi, A. Hunger, J. Kebrle, and K. Hoffmann, *ibid.*, **43**, 1046 (1960).

(14) R. Barchet and K. W. Merz, *Tetrahedron Lett.*, 2239 (1964).