THE JOURNAL OF Organic Chemistry®

Volume 22, Number 10 © Copyright 1957 by the American Chemical Society October 11, 1957

[Contribution from the Kedzie Chemical Laboratory, Michigan State University]

Iminotetrazolinium Salts. Identification of Sulfonic Acids

ROBERT M. HERBST and K. G. STONE

Received April 3, 1957

Tartrates of several 1-alkyl-4-benzyl-5-iminotetrazolines are described. Excepting 1-*n*-octyl-4-*p*-nitrobenzyl-5-iminotetrazoline which forms an acid tartrate, the bases combine with two moles of tartaric acid to form hydrated complex tartrates. A number of iminotetrazolinium alkane sulfonates and arylsulfonates are described. 1-*n*-Octyl-4-benzyl-5-iminotetrazolinium ditartrate monohydrate (OBIT) is suggested as a reagent for the qualitative identification of sulfonic acids or their sodium salts. The insolubility of most of the sulfonates in water suggests that they might be adaptable to quantitative estimations.

Recently the synthesis of a series of 1,4-disubstituted 5-iminotetrazolines was described.[1] The products were isolated as the rather insoluble hydrochlorides and screened for activity against various microorganisms. Because of the insolubility of the hydrochlorides and other salts with inorganic acids, the preparation of salts with organic acids was undertaken. Salts with tartaric acid could be prepared easily by treating the bases with tartaric acid in ethyl acetate solution containing a little water. Although the iminotetrazoline bases are monoacidic and form neutral salts with one equivalent of hydrochloric acid, they form, with one exception, complex ditartrate monohydrates even when treated with only an equimolar amount of tartaric acid. The complex tartrates are soluble not only in water but in ethanol, acetone, chloroform, benzene, and hot ethyl acetate. The complex formed from 1-*n*-octyl-4-benzyl-5-iminotetrazoline and tartaric acid is extremely soluble in water; 20% solutions in water could be prepared without difficulty. Only in one case, 1-*n*-octyl-4-*p*-nitrobenzyl-5-iminotetrazoline was an acid tartrate formed, and this even in the presence of two moles of tartaric acid per mole of base.

The composition of the tartrates was established by elemental analysis and by titration with Karl Fischer reagent.[2] The base content was estimated by precipitation of the insoluble chlorides and by titration of the tartrates with perchloric acid in glacial acetic acid.[3] Attempts to estimate tartaric acid by titration of the complexes in dimethylformamide with sodium methoxide in benzene-methanol solution[4] were successful in only one instance, the acid tartrate of 1-*n*-octyl-4-*p*-nitrobenzyl-5-iminotetrazoline. In the other instances the water in the hydrates interfered with the end point of the titration. It is interesting to note that the octyl-*p*-nitrobenzyliminotetrazoline acted as a self-indicator in the titration with sodium methoxide; an intense wine-red color developed at the equivalence point, possibly due to the involvement of the *aci* form of the nitro group.

In view of the insolubility of the inorganic acid salts of the iminotetrazolines, the solubility of salts with a number of sulfonic acids was investigated. A variety of amines, quaternary pyridinium bases, and other organic compounds have been suggested as reagents for the qualitative identification of sulfonic acids. The literature has been reviewed in some detail by Chambers and Watt,[5] Dermer and

---

[1] R. M. Herbst and C. F. Froberger, *J. Org. Chem.*, **22**, 1050 (1957).

[2] W. Seaman, W. H. McComas, Jr., and G. A. Allen, *Anal. Chem.*, **21**, 510 (1949).

[3] P. C. Markunas and J. A. Reddick, *Anal. Chem.*, **23**, 337 (1951).

[4] J. S. Fritz, *Anal. Chem.*, **24**, 306 (1952).

[5] E. Chambers and G. W. Watt, *J. Org. Chem.*, **6**, 376 (1941).

[6] O. C. Dermer and V. H. Dermer, *J. Org. Chem.*, **7**, 581 (1942).

Dermer,[6] and Shriner, Fuson, and Curtin.[7] A reagent which will form insoluble salts with either the free sulfonic acids or their sodium salts in dilute aqueous solutions still seems to be desirable. All the complex tartrates described in Table I will cause precipitation of iminotetrazolinium sulfonates from dilute aqueous solutions of the aromatic sulfonic acids or their sodium salts. Because of its great solubility in water 1-*n*-octyl-4-benzyl-5-iminotetrazolinium ditartrate monohydrate (OBIT) was chosen for extensive investigation. With the exception of methane- and ethanesulfonic acid, insoluble sulfonates were precipitated by the reagent from aqueous solutions of all the aliphatic and aromatic sulfonic acids, or their sodium salts, listed in Table III. The methane- and ethanesulfonates could also be obtained as well-crystallized solids after extraction from their aqueous solutions with chloroform. The various iminotetrazolinium sulfonates could be recrystallized from water, aqueous ethanol, aqueous acetone, ethyl acetate, ethyl acetate–cyclohexane, benzene, benzene–petroleum ether or benzene-hexane mixtures as indicated in Table III. Many of the salts with aromatic sulfonic acids are so insoluble in water that they might lend themselves to gravimetric estimations of the sulfonic acids. Disulfonic acids form neutral salts with two moles of the OBIT reagent. Sulfocarboxylic acids and hydroxysulfonic acids form salts with only a single equivalent of the OBIT reagent. Aminosulfonic acids or their sodium salts form water-insoluble OBIT salts that crystallize readily from the indicated solvents. The melting points of the various sulfonates show a wide spread. In instances where isomeric sulfonates melt in the same temperature range, mixture melting points show depressions of 20–30°. The presence of chlorides, sulfates, and nitrates may interfere with the usefulness of the reagent due to the insolubility of the iminotetrazolinium chlorides, sulfates, and nitrates. As already noted the chlorides are sufficiently insoluble to permit their use in estimating the base content of the tartrates, and conversely, their use in the gravimetric estimation of chloride ion could be of interest. Potassium salts of the sulfonic acids may also cause difficulty due to the rather low solubility in water of potassium acid tartrate.

EXPERIMENTAL[8]

1-n-Octyl-4-benzyl-5-iminotetrazolinium ditartrate monohydrate (OBIT). A mixture of 15 g. (0.076 mole) of 1-*n*-octyl-5-aminotetrazole[1] and 11.4 g. (0.09 mole) of benzyl chloride was heated in an oil bath at 120–130° for 7 hr. A clear, homogeneous melt formed and resolidified during the first hour of heating. The crude hydrochloride was taken up in 50 ml. of 95% ethanol, diluted with 500 ml. of water, and the mixture distilled to remove ethanol and excess benzyl chloride. The hydrochloride crystallizes from the residual aqueous solution on cooling. The base was liberated with excess 10% sodium hydroxide solution and extracted with several portions of benzene. After drying over potassium carbonate the solvent was removed from the combined benzene solutions on a water bath under reduced pressure. The residual oil (22.5 g.) was taken up in 150 ml. of dry ethyl acetate and to the solution was added 22.5 g. (0.15 mole) of tartaric acid and 5 ml. of water. The solution that resulted when the mixture was heated to boiling was treated with charcoal to remove a slight turbidity. On cooling the ditartrate monohydrate separated as colorless platelets, yield 41.5 g. (92%).

The 1-*n*-nonyl and 1-*n*-decyl-4-benzyl-5-iminotetrazolinium ditartrate monohydrates were prepared in similar manner and yield from the appropriate 1-alkyl-5-aminotetrazoles.[1] The *p*-chlorobenzyl analog was prepared similarly from 1-*n*-octyl-5-aminotetrazole and *p*-chlorobenzyl chloride in equally good yield. Physical constants and analytical data for the ditartrates are given in Tables I and II.

In the first attempt to prepare a tartrate from 1-*n*-octyl-4-benzyl-5-iminotetrazoline only slightly over the equimolar amount of tartaric acid was used in the expectation that an acid tartrate would be formed. Even under these conditions only the ditartrate monohydrate could be isolated.

1-n-Octyl-4-p-nitrobenzyl-5-iminotetrazolinium acid tartrate. The base obtained from the reaction of 10 g. (0.05 mole) of 1-*n*-octyl-5-aminotetrazole and 10 g. (0.058 mole) of *p*-nitrobenzyl chloride as described in the foregoing example was treated with 15 g. (0.1 mole) of tartaric acid in ethyl acetate under the previously described conditions. The tartrate crystallized rapidly on cooling the solution, crude yield 25 g., m.p. 119–125°. One recrystallization from ethyl acetate containing a little water gave the pure acid tartrate described in Table I, yield 21.5 g. (89%).

Elemental analyses were done on the hydrates because the salts softened on attempts at drying under reduced pressure over phosphorus pentoxide at 60–65° and hardened to glassy solids on cooling. Water content of the hydrates was also estimated volumetrically with the Karl Fischer reagent.[2] The base content was estimated by titration of the tartrates with perchloric acid in glacial acetic acid solution.[3] Precipitation of the almost insoluble chlorides from aqueous, or in the case of the *p*-chlorobenzyl derivative, 10% aqueous acetone, solution gave a gravimetric estimation of the base content of the tartrates. The results of these determinations are summarized in Table II.

Attempts to estimate the tartaric acid content of the salts in dimethyl formamide solution by titration with standard sodium methoxide in 10:1 benzene-methanol solution[4] were not successful due to interference by the water. Only in the case of 1-*n*-octyl-4-*p*-nitrobenzyl-5-iminotetrazolinium acid tartrate was an acceptable result obtained. The latter acted as a self-indicator by developing an intense wine-red color at the equivalence point. Titration of the *p*-nitrobenzyl derivative gave the following results: Calcd. for $C_{16}H_{24}N_6O_2.C_4H_6O_6$: tartaric acid, 31.1. Found: tartaric acid, 31.2.

Iminotetrazolinium sulfonates. The salts of the iminotetrazolines with most alkanesulfonic acids and the aromatic sulfonic acids precipitated from aqueous solutions of the sulfonic acids or their sodium salts on addition of a concentrated aqueous solution of the iminotetrazolinium ditartrate monohydrate. Only the salts with methane- and ethanesulfonic acid failed to precipitate and these could be extracted easily from their aqueous solutions with chloroform. In most instances commercially available sulfonic acids or their sodium salts were used without purification. The use of potassium salts may be complicated by precipitation of potassium acid tartrate. Several typical examples are described.

Reagent. A 0.25 molar solution of the reagent was prepared by dissolving 15.1 g. of 1-*n*-octyl-4-benzyl-5-imino-

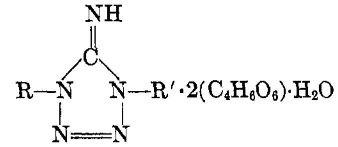
---

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Edition, John Wiley and Sons, Inc., New York, 1956, p. 269.

(8) Microanalyses were done by Micro-Tech Laboratories, Skokie, Ill.

TABLE I

1-ALKYL-4-BENZYL-5-IMINOTETRAZOLINIUM DITARTRATE MONOHYDRATES



Compound No.	R	R′	M.P., °C.	Formula	Analyses Calcd. C	H	N	Found C	H	N
I	n-C_8H_{17}	$C_6H_5CH_2$	78–79	$C_{24}H_{39}N_5O_{13}$	47.6	6.5	11.6	47.8	6.6	11.5
II	n-C_8H_{17}	p-$ClC_6H_4CH_2$	88–89	$C_{24}H_{38}ClN_5O_{13}$[a]	45.0	6.0	10.9	45.2	6.0	10.8
III	n-C_8H_{17}	p-$NO_2C_6H_4CH_2$	153–155	$C_{20}H_{30}N_6O_8$[b]	49.8	6.3	17.4	50.1	6.4	17.5
IV	n-C_9H_{19}	$C_6H_5CH_2$	80–82	$C_{25}H_{41}N_5O_{13}$	48.5	6.7	11.3	48.4	6.6	11.4
V	n-$C_{10}H_{21}$	$C_6H_5CH_2$	70–72	$C_{26}H_{43}N_5O_{13}$	49.3	6.8	11.1	49.9	6.9	11.0

[a] Calcd.: Cl, 5.5. Found: Cl, 5.5. [b] Acid tartrate.

tetrazolinium ditartrate monohydrate (OBIT) in water and diluting to 100 ml. Solutions of the reagent have been kept for several months without outward signs of deterioration.

Benzenesulfonate. A solution of 0.9 g. (0.005 mole) of sodium benzene-sulfonate in 150 ml. of warm water was treated with 20 ml. (0.005 mole) of cold OBIT reagent, added slowly with manual agitation. The benzene-sulfonate separated as a voluminous precipitate. Since the salt melts under boiling water, it is best precipitated in warm, not hot, solution. Should the sulfonate separate as an oil, it usually solidifies promptly on cooling. The benzenesulfonate crystallized from 50% ethanol as a cottony mass of fine needles, yield 82%.

TABLE II

FUNCTIONAL GROUP ANALYSES OF 1-ALKYL-4-BENZYL-5-IMINOTETRAZOLINIUM DITARTRATE MONOHYDRATES

Compound No.	Calculated H_2O	Base	Found H_2O[a]	Base[b]	Base[c]
I	2.98	47.5	2.99	47.7	47.5
II	2.82	50.3	2.83	50.5	50.6
III	—	68.9	—	—	69.1
IV	2.91	48.6	2.6[d]	48.2	48.7
V	2.84	49.8	2.91	49.4	50.0

[a] By titration with Karl Fischer reagent.[2] [b] By precipitation of the chloride. [c] By titration with perchloric acid in glacial acetic acid.[3] [d] By drying to constant weight at 65° under reduced pressure over phosphorus pentoxide.

p-Nitrobenzenesulfonate. A hot solution of 1.02 g. (0.005 mole) of p-nitrobenzenesulfonic acid in 75 ml. of water was treated with 20 ml. (0.005 mole) of OBIT reagent as just described. The salt was recrystallized from 30% ethanol from which it separated as pale, straw-colored needles, yield 95%.

Naphthalene-2,5-disulfonate. Sodium naphthalene-2,6-disulfonate (0.66 g., 0.002 mole) dissolved in 100 ml. of hot water was treated with 16 ml. (0.004 mole) of OBIT reagent as just described. A voluminous precipitate separated immediately but changed to a dense solid on standing overnight. It crystallized from 50% ethanol as dense, long prisms, yield 98%. Analysis showed the product to be the neutral salt, Table III.

Sulfanilate. A solution of 0.35 g. (0.002 mole) of sulfanilic acid and 0.30 g. (0.002 mole) of tartaric acid in 50 ml. of hot water was treated with 8 ml. (0.002 mole) of OBIT reagent. The product crystallized from the hot solution as colorless needles on cooling and was recrystallized from hot water, yield 65%. The same product was also obtained from hot aqueous solution without addition of excess tartaric acid.

5-Sulfosalicylate. A warm solution of 1.27 g. (0.005 mole) of 5-sulfosalicylic acid dihydrate in 50 ml. of water was treated with 20 ml. (0.005 mole) of OBIT reagent. The salt separated as an oil with the first addition of reagent. Cooling the solution slightly induced crystallization after which the balance of the reagent was added. The product crystallized from 50% ethanol as needles that melted partially at 150–151°, resolidified and remelted at 169–170°. When plunged into a bath preheated to 150°, the salt melted completely, resolidified and melted again at 169–170°. This was the only salt that behaved peculiarly on melting. Analysis showed the product to be a 1:1 combination of the sulfosalicylic acid and the base, Table III.

Methanesulfonate. A solution of 0.53 g. (0.006 mole) of technical methanesulfonic acid in 15 ml. of water was treated with 20 ml. (0.005 mole) of OBIT reagent. The sulfonate did not crystallize on chilling but was extracted completely with several small portions of chloroform. After drying the extracts over sodium sulfate and removing the solvent by distillation, the solid residue was crystallized twice from benzene by addition of petroleum ether, colorless needles, yield 74%.

The ethanesulfonate was also isolated by extraction from aqueous solution with chloroform. The other alkanesulfonates were prepared in similar volumes of solvent and crystallized from their cold aqueous solutions.

All the sulfonates prepared as just described are recorded in Table III where melting points, molecular formulas and and analytical data are given.

1-n-Octyl-4-p-chlorobenzyl-5-iminotetrazolinium methanesulfonate was prepared by adding 1.62 g. (0.005 mole) of 1-n-octyl-4-p-chlorobenzyl-5-iminotetrazoline base[1] to a solution of 0.48 g. (0.005 mole) of methanesulfonic acid in 10 ml. of water. A clear solution formed on warming from which the salt crystallized on cooling. The product was recrystallized from benzene by addition of hexane, colorless leaflets, m.p. 126–128°, yield 1.9 g. (91%).

Anal. Calcd. for $C_{17}H_{28}ClN_5O_3S$: Cl, 8.5; N, 16.8; S, 7.7. Found: Cl, 7.8; N, 16.6; S, 7.6.

1-n-Octyl-4-p-chlorobenzyl-5-iminotetrazolinium sulfanilate was prepared by adding with manual agitation a solution of 6.39 g. (0.01 mole) of 1-n-octyl-4-p-chlorobenzyl-5-iminotetrazolinium ditartrate monohydrate in 50 ml. of warm acetone to 1.73 g. (0.01 mole) of sulfanilic acid dissolved in 300 ml. of warm water. A clear solution resulted on heat-

TABLE III

1-*n*-OCTYL-4-BENZYL-5-IMINOTETRAZOLINIUM SULFONATES

Sulfonic acid	M.P., °C.	Formula	Analyses Calcd. C	H	N	S	Found C	H	N	S
Methane[a]	116–117	$C_{17}H_{29}N_5O_3S$	53.2	7.6	18.3	8.4	53.6	7.8	18.5	8.3
Ethane[a]	98–99	$C_{18}H_{31}N_5O_3S$	54.4	7.9	17.6	8.1	54.4	7.9	17.9	8.0
2-Propane[a]	108–110	$C_{19}H_{33}N_5O_3S$	55.4	8.1	17.0	7.8	55.9	8.0	17.3	7.8
1-Butane[b]	125	$C_{20}H_{35}N_5O_3S$	56.4	8.3	16.5	7.5	56.5	8.3	16.5	7.4
3-Methyl-1-butane[c]	132–133	$C_{21}H_{37}N_5O_3S$	57.4	8.5	15.9	7.3	57.3	8.7	16.0	7.3
Benzene[d]	129	$C_{22}H_{31}N_5O_3S$	59.3	7.0	15.7	7.2	59.3	6.9	16.0	7.1
p-Toluene[d]	172–173	$C_{23}H_{33}N_5O_3S$	60.1	7.2	15.2	7.0	60.0	7.1	15.3	6.9
2,4-Dimethylbenzene[a]	91–92	$C_{24}H_{35}N_5O_3S$	60.9	7.5	14.8	6.8	60.8	7.6	14.8	7.0
2,5-Dimethylbenzene[a]	102–103	$C_{24}H_{35}N_5O_3S$	60.9	7.5	14.8	6.8	61.0	7.5	14.8	7.0
p-Chlorobenzene[d,e]	159–160	$C_{22}H_{30}ClN_5O_3S$	55.0	6.3	14.6	6.9	55.2	6.5	14.7	6.8
2,4-Dichlorobenzene[d,f]	134–135	$C_{22}H_{29}Cl_2N_5O_3S$	51.4	5.7	13.6	6.2	51.3	5.7	13.4	6.0
p-Bromobenzene[d,g]	162–163	$C_{22}H_{30}BrN_5O_3S$	50.4	5.8	13.4	6.1	50.5	5.7	13.4	6.0
p-Phenol[d]	114–115	$C_{22}H_{31}N_5O_4S$	57.2	6.8	15.2	7.0	57.3	6.8	15.0	7.1
m-Nitrobenzene[d]	138–139	$C_{22}H_{30}N_6O_5S$	53.9	6.2	17.1	6.5	54.0	6.4	16.9	6.6
p-Nitrobenzene[d]	171–172	$C_{22}H_{30}N_6O_5S$	53.9	6.2	17.1	6.5	54.2	6.3	17.2	6.3
Orthanilic[d]	134–135	$C_{22}H_{32}N_6O_3S$	57.4	7.0	18.3	7.0	57.7	6.9	18.3	6.7
Metanilic[a]	107–108	$C_{22}H_{32}N_6O_3S$	57.4	7.0	18.3	7.0	57.7	7.1	18.2	6.7
Sulfanilic[h]	154–155	$C_{22}H_{32}N_6O_3S$	57.4	7.0	18.3	7.0	57.5	7.2	18.0	6.8
m-Sulfobenzoic[d]	200–201	$C_{23}H_{31}N_5O_5S$	56.4	6.4	14.3	6.6	56.4	6.5	14.3	6.6
5-Sulfosalicylic[d]	169–170[i]	$C_{23}H_{31}N_5O_6S$	54.6	6.2	13.9	6.3	54.8	6.2	13.6	6.4
m-Benzenedi-[j,k]	143–144	$C_{38}H_{56}N_{10}O_6S_2$	56.1	6.9	17.2	7.9	56.0	7.0	17.2	8.1
4,4′-Biphenyldi-[d,j]	244–245	$C_{44}H_{60}N_{10}O_6S_2$	59.4	6.8	15.8	7.2	59.4	6.6	16.0	7.3
dl-10-Camphor[b]	146–147	$C_{26}H_{41}N_5O_4S$	60.1	8.0	13.5	6.2	60.4	8.1	13.3	6.3
d-10-Camphor[b]	144–145	$C_{26}H_{41}N_5O_4S$	60.1	8.0	13.5	6.2	60.1	8.0	13.3	6.1
2-Naphthalene[d]	146–147	$C_{26}H_{33}N_5O_3S$	63.0	6.7	14.1	6.5	63.2	6.8	14.3	6.6
4-Amino-1-naphthalene[k]	131–132	$C_{26}H_{34}N_6O_3S$	61.2	6.7	16.5	6.3	61.1	6.8	16.6	6.1
4-Acetamido-1-naphthalene[d]	148–149	$C_{28}H_{36}N_6O_4S$	60.9	6.6	15.2	5.8	61.0	6.7	15.0	5.7
1,5-Naphthalenedi-[d,j]	213–214	$C_{42}H_{58}N_{10}O_6S_2$	58.5	6.8	16.2	7.4	58.5	6.7	16.2	7.5
2,6-Naphthalenedi-[d,j]	253–254	$C_{42}H_{58}N_{10}O_6S_2$	58.5	6.8	16.2	7.4	58.9	6.8	16.3	7.6
2,7-Naphthalenedi-[d,j]	210–211	$C_{42}H_{58}N_{10}O_6S_2$	58.5	6.8	16.2	7.4	58.3	6.7	16.3	7.7

[a] Recrystallized from benzene–petroleum ether or benzene-hexane [b] Recrystallized from ethyl acetate–cyclohexane [c] Recrystallized from ethyl acetate [d] Recrystallized from aqueous ethanol. [e] Calcd.: Cl, 7.4. Found: Cl, 7.4. [f] Calcd.: Cl, 13.8. Found: Cl, 13.9. [g] Calcd.: Br, 15.2. Found: Br, 15.3. [h] Recrystallized from water. [i] Melts partially at 150–151°, resolidifies and remelts at 169–170°. [j] Neutral salt. [k] Recrystallized from benzene.

ing the mixture to boiling. The product which separated in sheaf-like clusters of crystals on cooling was recrystallized from 30% aqueous acetone, yield 3.5 g. (72%), m.p. 159–161°.

Anal. Calcd. for $C_{22}H_{31}ClN_6O_3S$: Cl, 7.2; N, 17.0; S, 6.5. Found: Cl, 7.1; N, 17.0; S, 6.3.

EAST LANSING, MICH.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Apparent Acidic Dissociation of Some 5-Aryltetrazoles[1]

ROBERT M. HERBST AND KENNETH R. WILSON

Received February 27, 1957

An improved procedure has been developed for the preparation of 5-aryltetrazoles in which solutions of the aryl cyanides, sodium azide, and acetic acid in *n*-butyl alcohol are heated under reflux. The isomeric 5-chlorophenyl-, 5-bromophenyl-, and 5-methoxyphenyltetrazoles were prepared, their apparent acidic dissociation constants and ultraviolet absorption spectra determined and compared with those of the correspondingly substituted benzoic acids. With the exception of the *ortho* substituted compounds, the 5-aryltetrazoles appear to be stronger acids than the correspondingly substituted benzoic acids.

Tetrazole derivatives in which the hydrogen atom attached to the ring nitrogens has not been replaced generally behave as acidic substances.[2,3,4]

---

[1] Based on a thesis submitted by Kenneth R. Wilson to Michigan State University in 1955 in partial fulfillment of the requirements for the degree of Master of Science.

(2) J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, **15**, 1082 (1950).

(3) E. Oliveri-Mandalà, *Gazz. chim. ital.*, **44**, II, 175 (1914).

(4) W. L. Garbrecht and R. M. Herbst, *J. Org. Chem.*, **18**, 1023, 1269 (1953).