Experimental[13]

Cyclopropyl bromide was prepared according to the excellent procedure described by Professor J. S. Meek, University of Colorado.[14]

Tetracyclopropyllead.—The cyclopropylmagnesium bromide was prepared from 5.08 g. of magnesium, 25 g. of cyclopropyl bromide, and 175 ml. of tetrahydrofuran as solvent.[5] The reaction was allowed to cool to room temperature and 42 g. of lead dichloride was added with constant stirring over a period of 25 min. The reaction mixture appeared green-brown in color, turning deep black from lead deposition near the end of the reaction. The system was then refluxed in an oil bath at 70–80° for 90 min. The tetrahydrofuran was then removed under slightly reduced pressures at an oil bath temperature of 40–45°. After the tetrahydrofuran had been removed, the system was connected to a cold trap (−80°), the pressure was reduced to about 0.1 mm., and the oil bath temperature was raised to 90°. After 30 hr., 10.4 g. of crude product had collected. The crude product (mol. wt. calcd., 371.5; found, 398) was redistilled, yielding 7.54 g. (29.8% yield) of colorless liquid boiling at 57–58.5° (0.1 mm.). A middle cut boiling at 58° (0.1 mm.), $n^{24}\text{D}$ 1.5505, was taken for analysis.

Anal. Calcd. for $C_{12}H_{20}Pb$: C, 38.79; H, 5.44. Found: C, 38.70, 38.48; H, 5.73, 5.62.

Tricyclopropyllead Chloride.—To a clean, dry test tube was added 215 mg. of tetracyclopropyllead and an equivalent amount of concentrated hydrochloric acid. A white precipitate formed immediately. The reaction was allowed to stand for 1 hr. with frequent stirring. The crystals were then washed with *n*-hexane and filtered. The yield was 186 mg. (84% yield) of colorless crystals, m.p. 173–174°.

Anal. Calcd. for $C_9H_{15}ClPb$: C, 29.55; H, 4.13. Found: C, 29.57; H, 4.21.

Dicyclopropyllead Dichloride.—A solution of 57.5 mg. of tetracyclopropyllead in 5 ml. of *n*-hexane was saturated with chlorine gas during which time precipitation occurred. The mixture was allowed to sit for 1 hr. with occasional addition of chlorine. The precipitate was collected, washed with *n*-hexane several times, and dried under vacuum at room temperature leaving 44.8 mg. (81%) of dicyclopropyllead dichloride, m.p. 250° dec.

Anal. Calcd. for $C_6H_{10}Cl_2Pb$: C, 20.00; H, 3.00. Found: C, 20.34; H, 2.82.

Dicyclopropyllead Bisdichloroacetate.—Tetracyclopropyllead (200 mg., 0.54 mmole) and 70 mg. of dichloroacetic acid (0.54 mmole) were mixed in 5 ml. of ether. After about 3 hr., precipitation began. After 20 hr., the white needles were collected, washed several times with 5-ml. portions of ether, and dried under vacuum at room temperature. The yield was 130 mg., m.p. 179–180° dec.

Anal. Calcd. for $C_{10}H_{12}Cl_4O_4Pb$: C, 22.03; H, 2.22. Found: C, 21.89; H, 2.48.

Other lead salts reported in Table I were obtained by similar reactions. Products in these cases were impure or mixtures, and dithizone analyses for them are reported in Table I also.

Acknowledgment.—The authors gratefully acknowledge Mr. S. R. Henderson of Ethyl Corporation for analyses and to the Ethyl Corporation for samples of tetraethyllead used in these studies.

[13] Analyses were by Drs. G. Weiler and F. B. Strauss, Oxford, England.

[14] We are indebted to Mr. Dean Sinclair, Kansas State University, for bringing this excellent procedure to our attention.

Michael Addition of Hydroxylamines to Activated Double Bonds. A Convenient Synthesis of N,N-Dialkyl Hydroxylamines

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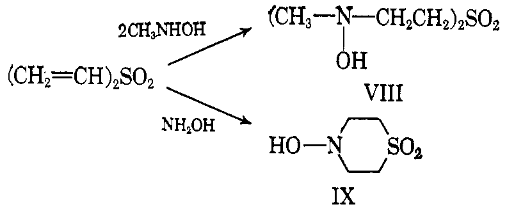
N,N-Dialkyl hydroxylamines have not been readily available, because attempts to synthesize them by dialkylation of hydroxylamine and by oxidation of secondary amines have given low yields, and the thermal decomposition of N-oxides have been restricted to the lower aliphatic members. We have found that a satisfactory route to these compounds lies in the addition of N-alkyl hydroxylamines to activated double bonds, a reaction not previously reported, although hydroxylamine itself has been used in addition reactions with methyl acrylate,[3] cinnamates,[4] mesityl oxide,[5] chalcones,[6] nitro olefins,[7,8] acrylonitrile,[9] 2-vinylpyridines,[10] diphenylmethylene carbamate,[11] and vinyl ketones.[12] In these cases, the products were generally the 1:1 adducts, which, on consideration of the difunctional character of the hydroxylamine, might not have been expected.

From the reaction of N-methylhydroxylamine with a number of vinyl compounds we obtained high yields of N-methyl-N-alkyl hydroxylamines (Table I). N,N-Dialkyl hydroxylamines were also produced by the reaction of hydroxylamine with vinyl sulfones and vinylpyridines (Table II), and in no case could the monosubstituted hydroxylamine, the 1:1 adduct, be isolated.

The expected product, bis(2-N-methylhydroxylaminoethyl) sulfone (VIII), was obtained when divinyl sulfone was allowed to react with N-methylhydroxylamine. However, in the reaction of divinyl sulfone with hydroxylamine, cyclization occurred and 4-hydroxytetrahydro-1,4-thiazine 1,1-dioxide (IX) was produced almost quantitatively. That IX is indeed the product, having arisen by intramolecular rather than intermolecular condensation, is indicated by the fact that it was also obtained, as the only product, from a high dilution experiment. Cyclic addition products have been isolated from the reaction of divinyl sulfones and primary amines.[13]



VIII

IX

Experimental[14]

Vinyl Compounds.—The acrylamide, 2-vinylpyridine, 4-vinylpyridine, and divinyl sulfone used were the commercially available materials. Vinyl ethyl sulfone, b.p. 69–70° (0.7 mm.), was synthesized from 2-chloroethyl ethyl sulfone and triethylamine,[15] rather than by the dehydration of 2-hydroxyethyl ethyl sulfone[16] which was unsatisfactory.

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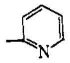
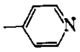
TABLE I

N-METHYL-N-ALKYL HYDROXYLAMINES

$$RCH{=}CH_2 + CH_3NHOH \longrightarrow RCH_2CH_2N(CH_3)OH$$

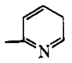
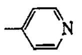
Compound No.	Compound R	Yield, %	Solvent	M.p., °C.	Empirical formula	Calcd., %	Found, %
I	$-CONH_2$	60.5	Methanol	94–95[a]	$C_4H_{10}N_2O_2$	N 23.71	23.41
II	$-SO_2C_2H_5$	49	Water	106[b]	$C_5H_{13}NO_3S$	C 35.91	36.50
						H 7.38	8.31
						N 8.37	8.30
III		79	c	108–109[d]	$C_9H_{15}IN_2O$[e]	C 36.73	36.88
						H 5.13	5.41
						N 9.52	9.82
IV		83.5	c	78[f]	$C_8H_{12}N_2O$	C 63.13	63.24
						H 7.95	8.05
						N 18.41	18.10

[a] Recrystallized from methanol. [b] Recrystallized from benzene. [c] No solvent was employed. [d] Boiling point at 1.8 mm.; n^{25}_D 1.5275. [e] Analyzed as the methiodide, m.p. 113–114°. [f] Recrystallized from ligroin.

TABLE II

N,N-DIALKYL HYDROXYLAMINES

$$2RCH{=}CH_2 + NH_2OH \longrightarrow RCH_2CH_2N(OH)CH_2CH_2R$$

Compound No.	Compound R	Yield, %	Solvent	M.p., °C.	Empirical formula	Calcd., %	Found, %
V	$-SO_2C_2H_2$	88.5	Water	134–135[a]	$C_8H_{19}NO_5S$	N 5.11	4.78
VI		61.5	b	110–111[c,d]	$C_{14}H_{17}N_3O$	N 17.27	16.88
VII		62	Methanol	148–149[c,e]	$C_{14}H_{17}N_3O$	N 17.27	17.26

[a] Recrystallized from methanol. [b] No solvent was employed. [c] Recrystallized from benzene. [d] Lit.[10] m.p. 105–106.5°. [e] Lit.[10] m.p. 143–144°.

N,N-Dialkyl Hydroxylamines (General Procedure).—To 0.2 mole of N-methylhydroxylamine hydrochloride or hydroxylamine hydrochloride in 100 ml. of methanol or water, as indicated (Tables I and II), was added 0.1 mole of anhydrous sodium carbonate, followed by 0.15 mole of the vinyl compound. The reaction proceeded quite rapidly and, in the case of I, the sodium chloride was removed by filtration after stirring for 30 min. Evaporation of the methanol gave the product. The water-insoluble sulfones II and V separated during the course of the reaction and were filtered off. To prepare compounds III, IV, VI, and VII, the hydroxylamine hydrochlorides were added either directly or to a methanolic solution of the vinylpyridines and the products were extracted with chloroform from the reaction mixture after it had been neutralized by the addition of aqueous sodium bicarbonate.

Reaction of Divinyl Sulfone and Methylhydroxylamine.—To 20 g. (0.24 mole) of N-methylhydroxylamine hydrochloride in 100 ml. of water was added 13 g. (0.12 mole) of anhydrous sodium carbonate with ice cooling. Then 11.8 g. (0.1 mole) of divinyl sulfone was added dropwise and the mixture was stirred for 30 min. The crude product which had separated was filtered off and recrystallized from ethanol, yielding 15.7 g. (74%) of bis-(2-N-methylhydroxylaminoethyl) sulfone (VIII), m.p. 166–167°; λ_{max} (KBr) 3.18 (OH), 7.83 and 8.7 (SO_2) μ.

Anal. Calcd. for $C_6H_{16}N_4OS$: N, 13.19. Found: N, 12.93.

Reaction of Divinyl Sulfone and Hydroxylamine.—Six grams (0.05 mole) of anhydrous sodium carbonate was added to a solution of 6.9 g. (0.1 mole) of hydroxylamine hydrochloride in 200 ml. of water. Then 11.8 g. (0.1 mole) of divinyl sulfone was added dropwise with vigorous stirring. The stirring was continued for 30 min. and the separated solid was then collected. This consisted of 12.9 g. (85.5%) of 4-hydroxytetrahydro-1,4-thiazine 1,1-dioxide (IX), m.p. 192–193° dec.; λ_{max} (KBr) 2.98 (OH), 7.85 and 8.88 (SO_2) μ.

Anal. Calcd. for $C_4H_9NO_3S$: C, 31.77; H, 5.99; N, 9.26. Found: C, 31.74; H, 6.19; N, 9.35.

In a high-dilution experiment using 1500 ml. of water, the same compound was obtained as the only product.

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The Rate of Reaction of Piperidine with Piperonal in Methanol

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Although secondary amines cannot react with aromatic carbonyl compounds to form uncharged aldimines or ketimines, cations of the type $\overset{-}{Ar}CH{=}\overset{+}{N}R_2$ (I) exist and may be intermediates in reactions catalyzed by piperidine or other secondary amines.[2] Having already studied the kinetics of ammonia[3] and primary amines[4] with aromatic aldehydes, we attempted to detect a reaction between piperidine and piperonal in methanol to form I or its tetrahedral precursor, ArCH-(OH)NR_2 (Ia).

The ultraviolet absorption at the λ_{max} of piperonal (312 mμ) did indeed decrease in the presence of piperidine. Since no peak appeared at the higher wave length expected for I (in analogy with a protonated Schiff base[5]), this species was not present in appreciable quantity, though it might be formed in more acidic solutions. Moreover, the reaction was readily reversed by water. These observations suggested that

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