ysis and from the infrared spectrum. While the ester band present in the spectrum of vincamine at 1755 cm.$^{-1}$ disappeared, a new band at 3510 cm.$^{-1}$ appeared which was assigned to a primary alcoholic group. There was no absorption in the region between 5 and 6 μ which would be expected if a keto group were present in the molecule as is the case with eburnamonine.[4] The ultraviolet spectrum of vincaminyl alcohol was quite similar to that of vincamine and many 2,3-substituted indole derivatives.[4]

A mononitrite of vincamine which could be reconverted into vincamine by treatment with hydrochloric acid has been made. Similarily, a mononitrite of yohimbine has been prepared.

Experimental

Vincaminyl Alcohol.—A solution of 200 mg. of vincamine[5] in 25 ml. of tetrahydrofuran which had been dried by sodium, was added dropwise in 15 min. with stirring to a suspension of 100 mg. of lithium aluminum hydride in 20 ml. of dry ether. Stirring was continued, while the reaction mixture was gently refluxed for 1 hr. After cooling in an ice bath, 5 ml. of water was gradually added to decompose the excess of lithium aluminum hydride. After addition of 40 ml. of 10% sodium hydroxide solution, the mixture was extracted three times with ether (50 ml. each). The ether extract was washed with water, dried over anhydrous sodium sulfate, and distilled. The yellowish, amorphous solid which remained (180 mg.), was crystallized from benzene in needles; m.p. 180° (dec.). For analysis the compound was dried at 100° *in vacuo* over phosphorus pentoxide.

Anal. Calcd. for $C_{20}H_{26}N_2O_2$: C, 73.60; H, 8.03; N, 8.59; 3 active H, 0.93. Found: C, 73.41; H, 7.99; N, 8.80; active H, 0.88.

Ultraviolet Spectrum.—Maxima at 232 mμ (ϵ 27300); 280 mμ (ϵ 7200); minimum at 250 mμ (ϵ 1670).

Infrared Spectrum.—Sharp band at 3510 cm.$^{-1}$ (due, apparently, to the primary alcohol group resulting from reduction of the carbomethoxy group), broad band at 3325 cm.$^{-1}$ (apparently the original associated OH), strong band at 738 cm.$^{-1}$, no ester nor amide band in the region 1650 cm.$^{-1}$ to 1900 cm.$^{-1}$.

Vincamine Nitrite.—To an ice-cooled solution of 100 mg. of vincamine in 7.0 ml. of 70% acetic acid was gradually added within 0.5 hr. a cold solution of 400 mg. of sodium nitrite in 10 ml. of water. The reaction mixture from which yellowish needles began to separate was kept in the refrigerator for 24 hr. The yellowish solid (50 mg.) was separated by filtration; an additional 20 mg. were obtained from the mother liquor on standing for a few days. Vincamine nitrite was recrystallized from methanol–ether as needles, m.p. 224–225° (dec.). For analysis the compound was dried at 100° *in vacuo* over phosphorus pentoxide.

Anal. Calcd. for $C_{21}H_{27}N_3O_5 \cdot H_2O$: C, 60.13; H, 6.97; N, 10.02. Found: C, 60.75, 60.46; H, 6.58, 6.44; N, 9.89.

Ultraviolet Spectrum.—Maxima found at 223 mμ (ϵ 29500), 275 mμ (ϵ = 7370); minimum at 243 mμ (ϵ 2060).

Infrared Spectrum.—Strong ester band at about 1725 cm.$^{-1}$, and strong band at about 1380 cm.$^{-1}$.

When vincamine nitrite was dissolved in dilute hydrochloric acid and then the solution made alkaline with ammonia, vincamine was obtained. It was characterized by its melting point, mixed melting point, and infrared spectrum.

Yohimbine Nitrite.—Yohimbine (100 mg.) was dissolved in 2 ml. of acetic acid; 2 ml. of water was then added, and the solution was cooled in an ice bath. A solution of 200 mg. of sodium nitrite in 2 ml. of water was gradually added in the course of about 30 min. The yellow solution was then kept in the refrigerator, when a yellow precipitate slowly separated. After 24 hr., the precipitate (25 mg.) was filtered. It crystallized from methanol in yellowish elongated plates, m.p. 290° (dec.). For analysis the compound was dried at 100° over P_2O_5 *in vacuo*.

Anal. Calcd. for $C_{21}H_{27}N_3O_5 \cdot H_2O$: C, 60.13; H, 6.97; N, 10.02. Found: C, 60.71; H, 6.31; N, 9.96.

Infrared Spectrum.—Strong ester band at about 1725 cm.$^{-1}$ and a strong band at about 1380 cm.$^{-1}$.

Acknowledgment.—This work was supported by a grant from the National Institute of Health, grant B-2142 (C-2). Analyses were made by Geller Laboratories, Bardonia, N. Y.

(4) N. Neuss, "Physical Data of Indole and Dihydroindole Alkaloids," 4th ed., Lilly Research Laboratories, Indianapolis, Ind., 1960.

(5) Prepared by a method for the isolation of vincamine from *Vinca minor* which was developed in this laboratory by Dr. Friedrich Dursch. Final separation of the alkaloid depended upon a 950 stage Craig distribution between ether and a buffer solution at pH 5.5.

A Convenient Synthesis of Phenyldiazomethane

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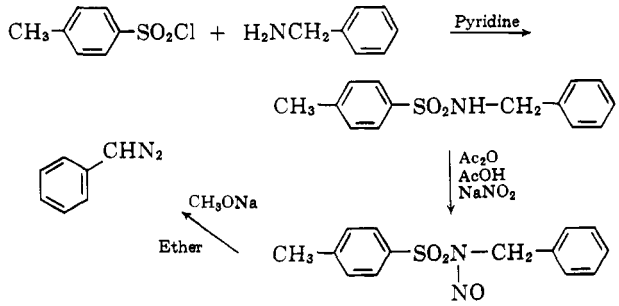
In connection with some other work, a convenient method for the preparation of phenyldiazomethane was desired. The available methods[1–3] are good but all require the use of somewhat unstable intermediates and long periods of time. We have therefore extended the procedure of de Boer and Backer[4] for diazomethane to phenyldiazomethane according to the following sequence of reactions. This procedure will supplement the already existing methods.



N-Benzyl-*p*-toluenesulfonamide was prepared essentially according to the procedure of Holmes and Ingold.[5] An 81% yield of the desired *N*-nitroso-*N*-benzyl-*p*-toluenesulfonamide[6] was achieved following a general procedure of White,[7] using a large excess of sodium nitrite. The nitrosoamide is indefinitely stable at room temperature; after six months, there was no change in its infrared spectrum or its melting point. Kirmse and Horner[8] had obtained the characteristic red color of phenyldiazomethane upon reaction of this nitrosamide with sodium methoxide. Indeed, by a modification of their procedure, an ethereal solution of phenyldiazomethane was obtained. The yield of the benzyl ester of 3,5-dinitrobenzoic acid formed from the reaction of this solution with a slight excess of the acid was 60%.

Experimental

***N*-Benzyl-*p*-toluenesulfonamide.**—An 87% yield of this compound was obtained by the procedure of Holmes and Ingold.[5]

(1) C. D. Gutsche and H. E. Johnson, *Org. Syntheses*, **35**, 91 (1955).
(2) C. D. Gutsche and E. F. Jason, *J. Am. Chem. Soc.*, **78**, 1184 (1956).
(3) P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958).
(4) T. J. de Boer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954).
(5) E. L. Holmes and C. K. Ingold, *J. Chem. Soc.*, **127**, 1800 (1925).
(6) T. Takizawa, *J. Pharm. Soc. Japan*, **70**, 490 (1950).
(7) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).
(8) W. Kirmse and L. Horner, *Chem. Ber.*, **89**, 1674 (1956).

The reaction was conveniently carried out in an Erlenmeyer flask by means of a magnetic stirrer. The infrared spectrum exhibited the characteristic strong N—H band at 3320 cm.$^{-1}$.

N-Nitroso-N-benzyl-p-toluenesulfonamide.—A solution of 10.5 g. (0.04 mole) of N-benzyl-p-toluenesulfonamide in 50 ml. of glacial acetic acid and 200 ml. of acetic anhydride, was prepared in a three-necked flask equipped with a stirrer, a thermometer, and a solid addition funnel. The flask was cooled to around 5°. Then 60 g. (0.85 mole) of powdered sodium nitrite was added in portions over a period of 6 hr. The temperature was kept below 10° at all times; the mixture turned green. After the addition of sodium nitrite was completed, the reaction mixture was stirred overnight. The mixture was then poured over an excess of ice water with vigorous stirring and cooled for 1 hr. in an ice bath. The pale yellow precipitate was filtered, washed several times with water, and dried overnight in vacuum. The crude product was then recrystallized from ethanol to give 9.4 g. (81%) of tiny yellow needles, m.p. 90–92° (m.p. 89–90° [6] by nitrosation in aqueous sodium nitrite) after drying in vacuum overnight; the infrared spectrum was free of N—H and showed a strong band at 1387 cm.$^{-1}$, assigned to the N–NO group. This nitrosation was carried out in much larger scale with comparable yields; it should be done in the hood because of the evolution of oxides of nitrogen.

Benzyl Ester of 3,5-Dinitrobenzoic Acid.—N-nitroso-N-benzyl-p-toluenesulfonamide (14.5 g., 0.05 mole) was added in portions over a period of 1 hr. to a stirred mixture of 2.7 g. (0.05 mole) of sodium methoxide, 10 ml. of methanol, and 60 ml. of ether. Within 5 min., a pinkish color was visible. After the addition was completed, the mixture was stirred under reflux for 15 or 20 min. After cooling the mixture, 100 ml. of water was added to dissolve the salts and the water layer discarded. The ethereal solution of phenyldiazomethane was washed three times with 75-ml. portions of water and dried for 30 min. over anhydrous sodium sulfate. It was then filtered and added dropwise with stirring to a suspension of 11 g. of 3,5-dinitrobenzoic acid in 50 ml. of ether. The disappearance of the red color was accompanied by a copious evolution of nitrogen. The mixture was stirred overnight and then enough ether was added to give a clear solution which was extracted with dilute base, then with water until neutral and dried over anhydrous sodium sulfate. The ether was removed under vacuum and 9.1 g. (60%) of the benzyl ester of 3,5-dinitrobenzoic acid, m.p. 111–113° [9] (mixed m.p. 111–112°) were obtained.

(9) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 572.

A Convenient Synthesis of Aromatic and Aliphatic Sodium Sulfinates

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Recent interest in aliphatic and aromatic sulfinic acids[1-3] has prompted us to report a simple method of converting readily available thiols to the corresponding sodium sulfinates in good yield.

Methods now available for the synthesis of these compounds include reduction of the appropriate sulfonyl chloride,[4] treatment of organometallic reagents with sulfur dioxide,[5] reaction of diazonium compounds with sulfur dioxide,[6] and cleavage of 1,2-disulfones with alkaline potassium cyanide.[7]

(1) E. Wellisch, E. Gipstein, and O. J. Sweeting, *J. Org. Chem.*, **27**, 1810 (1962).
(2) M. T. Beachem, *et al.*, *J. Am. Chem. Soc.*, **81**, 5430 (1959).
(3) J. L. Kice and K. W. Bowers, *ibid.*, **84**, 605 (1962).
(4) H. Gilman, E. W. Smith, and H. J. Oatfield, *ibid.*, **56**, 1412 (1934).
(5) H. Houlton and H. Tartar, *ibid.*, **60**, 544 (1938).
(6) L. Gatterman, *Ber.*, **32**, 1136 (1899).

The present method consists of adding the thiol to acrylonitrile,[8] oxidizing the resulting sulfide to its sulfone by means of hydrogen peroxide in glacial acetic acid,[8] followed by treating the β-sulfonylnitrile with an equivalent amount of the sodium salt of a thiol.

$$RSH + CH_2{=}CH{-}CN \xrightarrow{\text{base}} RSCH_2{-}CH_2CN \quad (I)$$

$$RSCH_2{-}CH_2{-}CN + H_2O_2 \xrightarrow{CH_3CO_2H} RSO_2CH_2CH_2CN \quad (II)$$

$$RSO_2CH_2CH_2CN + R'SNa \xrightarrow{C_2H_5OH} RSO_2Na + R'SCH_2CH_2CN \quad (III)$$

I, II, III: R = *n*-C_4H_9; R = *n*-C_3H_7; R = *p*-$CH_3C_6H_4$; R = *o*-$CH_3C_6H_4$

Other bases have been used to effect the elimination of the sulfinate but sodium thiolate also regenerates I which can be oxidized to II and thus serve as precursor for more III. The over-all yields for the transformation of thiol to sodium sulfinate are 70–75%.

The structure of each of the aromatic sulfinates was established by the isolation of the free sulfinic acid, melting point determination and determination of the infrared absorption spectrum (strong band at 1090 cm.$^{-1}$).[9]

Because of the instability of the free aliphatic sulfinic acids,[10] the sodium salts were treated directly with benzyl chloride to form the known alkyl benzyl sulfones.

In a similar fashion, aromatic and aliphatic sulfinic acids can be made by the action of RSNa on compounds of type V. The reaction sequence is outlined below. The yields are comparable.

$$RSH + HC{\equiv}C{-}CO_2C_2H_5 \xrightarrow[\text{cat.}]{\text{base}} RSCH{=}CHCO_2C_2H_5 \quad (IV)$$

$$RSCH{=}CHCO_2C_2H_5 + H_2O_2 \xrightarrow{CH_3CO_2H} RSO_2CH{=}CHCO_2C_2H_5 \quad (V)$$

$$RSO_2CH{=}CHCO_2C_2H_5 + R'SNa \xrightarrow{C_2H_5OH} RSO_2Na + R'SCH{=}CHCO_2C_2H_5$$

Thiols add readily to ethyl propiolate[11] in high yield, and the adducts are oxidized to the corresponding sulfones in yields of 85–90%. The reaction of RSNa with V gives the sodium sulfinate in 85–90% yield. However, the availability of acrylonitrile makes the first route more accessible.

Experimental[12]

Addition of Thiols to Acrylonitrile.—The method used was that described by Hurd and Gershbein.[8] "Triton B" (40% aq., 3 drops) was used as catalyst. The acrylonitrile used was ob-

(7) W. Ziegler and R. Connor, *J. Am. Chem. Soc.*, **62**, 2596 (1940).
(8) C. D. Hurd and L. L. Gershbein, *ibid.*, **69**, 2328 (1947).
(9) S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).
(10) R. Connor, "Organic Chemistry," Vol. 1, H. Gilman, ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 913.
(11) W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **81**, 4931 (1959); F. Montanari and A. Negrini, *Gazz. chim. ital.*, **87**, 1073, 1102 (1957).
(12) All melting points and boiling points are uncorrected.