melted at 166–167°. Infrared absorptions (liquid film) of *trans* and *cis* double bonds were observed at 970 and 705 cm.$^{-1}$, respectively, and the *trans* absorption was stronger than *cis*. Catalytic hydrogenation over palladium–charcoal yielded cyclododecane melting at 58–59°[7] in 91% yield.

Synthesis of Cyclododecatrienes by Method of Wilke.[8]—A mixture of 9 g. of diethylaluminum bromide and 1.7 g. of titanium tetrachloride was treated with butadiene at about 50° for 6 hr. A cyclododecatriene fraction (60 g.) was obtained in 80% yield. The fraction consisted largely of *trans,trans,cis*-1,5,9-cyclododecatriene boiling at 96° (10 mm.) and about 5% of *trans,trans,trans* isomer boiling at 92° (10 mm.), which was separated as a forerun on distillation through a high-efficiency rotating band column. The *trans,trans,trans* isomer fraction crystallized on cooling and the solid melted at 31–32°.[9]

(7) M.p. 60°, L. Ruzicka, M. Stoll, H. W. Huyser, and H. A. Boekenogen, *Helv. Chim. Acta*, **13**, 1152 (1930).

(8) See also ref. 2a.

(9) G. Wilke and M. Kröner, *Angew. Chem.*, **71**, 574 (1959), reported m.p. 33–34°.

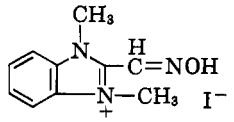
Methylation of Benzimidazole and Benzothiazole Carboxaldoximes[1]

E. J. POZIOMEK,[2] R. H. POIRIER,[3] R. D. MORIN,[3] AND T. F. PAGE, JR.[3]

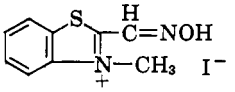
U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, Maryland, and Battelle Memorial Institute, Columbus, Ohio

Received April 30, 1962

In the course of our studies on quaternary heterocyclic aldoxime salts, we had occasion to prepare 1,3-dimethyl-2-formylbenzimidazolium iodide oxime (I) and 2-formyl-3-methylbenzothiazolium iodide oxime (II) through schemes involving methylation of 1-methylbenzimidazole-2-carboxaldoxime and benzothiazole-2-carboxaldoxime, respectively. The usual synthesis of quaternary heterocyclic aldoximes involves alkylation of the appropriate heterocyclic aldoximes in acetone or alcohol.[4] With oximes that



I



II

are difficult to alkylate it has been reported that nitromethane is a better choice of solvent.[5] When the ring nitrogen is hindered sterically, alkylation is very difficult and in the case of quinoline-2-aldoxime it was unsuccessful.[4a] In the case where a methyl group at the 6-position of picolinaldehyde oxime hinders the ring nitrogen sterically, it was shown that alkylation occurs on the nitrogen of the oxime rather than on the ring.[6]

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) U. S. Army Chemical Research and Development Laboratories.

(3) Battelle Memorial Institute.

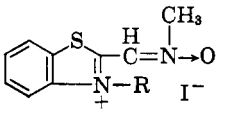
(4) (a) S. Ginsburg and I. B. Wilson, *J. Am. Chem. Soc.*, **79**, 481 (1957); (b) E. J. Poziomek, B. E. Hackley, Jr., and G. M. Steinberg, *J. Org. Chem.*, **23**, 714 (1958).

(5) E. Profft and G. Kruger, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg*, **2**, 281 (1959–1960); *Chem. Abstr.*, **55**, 1607e (1961).

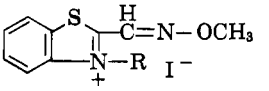
(6) B. E. Hackley, Jr., E. J. Poziomek, G. M. Steinberg, and W. A. Mosher, *J. Org. Chem.* **27**, 4220 (1962).

The studies presented in this paper are somewhat different in that five-membered rings are being methylated and the basicity of the 1-methylbenzimidazole ring is much stronger and that of the benzothiazole ring much weaker than the basicities of the pyridines and quinolines studied previously. No difficulty was found in synthesizing I in ethanol through a room temperature methylation of 1-methylbenzimidazole-2-carboxaldoxime. In contrast, the more vigorous reaction conditions of refluxing nitrobenzene–alcohol were needed in the methylation of the much less basic benzothiazole-2-carboxaldoxime. Besides II, a dimethylation product, N-methyl 2-formyl-3-methylbenzothiazolium iodide oxime (V) was isolated. It appears that the side product was formed through a methylation of II because with lower reflux temperature and longer reaction time only II was isolated.

The more facile synthesis of I than that of II is understandable in view of the stronger basic center in the 1-methylbenzimidazole ring. Failure to find 1-methylbenzimidazolium or benzothiazolium hydroiodides in which monomethylation had occurred on either the oxime nitrogen or oxygen, *e.g.*, III or IV, would indicate that the ring nitrogens were not hindered sterically to any serious extent.



III. R = H
V. R = CH_3



IV. R = H
VI. R = CH_3

The nuclear magnetic resonance spectrum of I in deuterium oxide consists of three resonances: a singlet at 522 c.p.s. (area = 1), =C—CH=N—, a symmetrical multiplet centered at 468 c.p.s. (area = 4), aromatic protons, and a single sharp peak at 249 c.p.s. (area = 6), $=\overset{+}{N}-CH_3$ and $-\overset{+}{N}-CH_3$ protons. The resonance at 249 c.p.s. is undoubtedly a result of the average electronic environment experienced by the two methyl groups because of the resonance of the quaternary center between the two nitrogens. The spectrum of N-methyl-2-pyridone shows a methyl resonance at 215 c.p.s. while that of 1,3,5-trimethylpyridinium iodide of 2-pyridone exhibits 1-methyl resonance at 275 c.p.s.[7] The average of these two values is 245 c.p.s., which is in good agreement with the observed frequency of the methyl groups in I. Traces of water, and possibly some exchange, precluded detection of the =NOH proton in the spectrum obtained in deuterium oxide. By the use of redistilled, dry acetonitrile, the =NOH proton resonance was observed near 740 c.p.s. (area = 1). Oxime protons generally absorb in this region in nonbonding solvents.

A nuclear magnetic resonance spectrum of II could not be obtained, because of the limited solubility of II in solvents commonly used in this work (D_2O and $CDCl_3$). Instead, structure proof was achieved on the basis of elemental analysis, neutralization equivalent, a broad OH stretching band found in the infrared absorption spectrum in potassium bromide, and an observed bathochromic shift of the long wave length

(7) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

band of maximum absorption from dilute acid to dilute base. Alternative structures would be N-(or O-) methyl benzothiazole-2-carboxaldoxime hydroiodides III (or IV), but these choices were eliminated since both N-(and O-) methyl 6-methylpicolinaldehyde oxime hydroiodides exhibit hypsochromic shift of the long wave length absorption band from dilute acid to base.[6]

On the basis of elemental analysis, the side product isolated in the methylation of benzothiazole-2-carboxaldoxime could correspond to either V or VI. Authentic samples were obtained by methylation of N(and O)-methyl benzothiazole-2-carboxaldoximes. A comparison of infrared absorption spectra with those of the side product led to the assignment of the N-methyl oxime structure (V).

It may be of interest to note that I and II are the most acidic of the heterocyclic aldoxime methiodides reported to date (Table I). There is a general trend for oxime acidity to increase as the ring basicity decreases. Major exceptions are I and the 2-formylpyridinium derivative. In order to rationalize these differences it would be necessary to take into account effects on oxime acidity by intramolecular dipole interactions.[8] This would require placing the compounds in categories of *syn* and *anti* configuration and position of substitution on the ring. The configuration of most of the quaternary heterocyclic aldoximes known has not been established. However, an examination of molecular models illustrates clearly that the oxygen of *anti* aldoximes could most readily participate in electrostatic interactions with the positive ring nitrogen. A weakening of the O–H bond with a corresponding increase in acidity would be anticipated and may be reflected in the low pK_a of I relative to the high basicity of its heterocyclic nucleus.

TABLE I

ACID DISSOCIATION CONSTANTS OF QUATERNARY HETEROCYCLIC ALDOXIME IODIDES

Heterocyclic ring	Relative basicity of ring nucleus[a]	pK_a	Ref.
1,3-Dimethyl-2-formylbenzimidazolium (I)	1.00	7.0	..
2-Formyl-1-methylpyridinium	.91	8.0	[b]
4-Formyl-1-methylpyridinium	.88	8.5,[c] 9.0[d]	[e]
4-Formyl-1-methylquinolinium	.80	8.3	[b]
1-Formyl-2-methylisoquinolinium	..	7.7	[f]
2-Formyl-3-methylbenzothiazolium (II)	.39	6.3	..

[a] The relative basicities had been determined by an indirect method involving comparison of the spectrum of a cyanine dye containing the particular heterocyclic ring as a constituent.[9] It involves a measurement of the deviation in λ_{max} which is assumed to be due to the basicity of the heteroaromatic structure. [b] See ref. 4a. [c] *syn* Isomer. [d] *anti* Isomer. [e] See ref. 10. [f] See ref. 11.

Experimental[12]

1-Methylbenzimidazole-2-carboxaldehyde.—M.p. 107–108° (reported[13] 110°). The presence of a strong carbonyl absorption band at 5.9 μ distinguished it from its precursor 1,2-dimethylbenzimidazole, m.p. 109–110°.

1-Methylbenzimidazole-2-carboxaldoxime.—M.p. 224–225° (reported[13] m.p. 204°).

1,3-Dimethyl-2-formylbenzimidazolium Iodide Oxime (I).—1-Methylbenzimidazole-2-carboxaldoxime (0.3 g.) was treated with an excess of methyl iodide in an acetone–ethyl alcohol mixture. After the mixture was allowed to stand at room temperature for 2 days, the 0.1 g. of pale yellow needles, m.p. 204–205° dec., that had crystallized from the reaction mixture was isolated and characterized.

Anal. Calcd. for $C_{10}H_{12}IN_3O$: C, 37.9; H, 3.8. Found: C, 37.9; H, 3.9.

Benzothiazole-2-carboxaldehyde.—M.p. 75–76°, recrystallized from petroleum ether (reported,[14] m.p. 75–77°). Recrystallization from methanol gave the hemiacetal, m.p. 89–91°.

Anal. Calcd. for $C_9H_9NO_2S$: C, 55.4; H, 4.7; S, 16.4. Found: C, 55.5; H, 5.0; S, 16.5.

Benzothiazole-2-carboxaldoxime.—M.p. 168–169° (reported,[15] m.p. 186–187°).

Anal. Calcd. for $C_8H_6N_2OS$: N, 15.7; neut. equiv., 178. Found: N, 15.7; neut. equiv., 172; pK_a, 9.3.

Methylation of Benzothiazole-2-carboxaldoxime. Procedure A.—A solution of benzothiazole-2-carboxaldoxime (11.5 g., 0.065 mole) and methyl iodide (24.6 g., 0.195 mole) in 75 ml. of nitrobenzene–ethanol (4:1) was refluxed for 11 hr. The reaction solution (colored red with a green cast) was cooled to room temperature and allowed to stand for 1 week. Filtration gave 11.0 g. of a red-brown solid. The product was dissolved in 300 ml. of warm methanol; the solution was boiled with activated charcoal and filtered. Fractional crystallization by the addition of ethyl ether and cooling gave three fractions:

Fraction A, **N-methyl 2-formyl-3-methylbenzothiazolium** iodide oxime (V), 0.4 g., m.p. 226–228°.

Anal. Calcd. for $C_{10}H_{11}IN_2OS$: C, 35.9; H, 3.3; O, 4.8. Found: C, 35.7; H, 3.4; O, 4.6.

Fraction B, 7.6 g., m.p. 198–200°; potentiometric titration data indicated that this product was a mixture containing 75% of II.

Fraction C, **2-formyl-3-methylbenzothiazolium iodide oxime** (II), 1.0 g., m.p. 203–204° dec.

Anal. Calcd. for $C_9H_9IN_2OS$: C, 33.8; H, 2.8; O, 5.0; neut. equiv., 320. Found: C, 34.1; H, 2.9; O, 5.2; neut. equiv., 322; pK_a 6.3. The pK_a was determined spectrophotometrically in water.[16] λ_{max} 0.1 *N* HCl, 329 mμ; 0.1 *N* NaOH, 363 mμ.

Procedure B.—A solution of 2.4 g. (0.0135 mole) of benzothiazole-2-carboxaldoxime in 5 ml. of methyl iodide and 15 ml. of methanol was refluxed for 24 hr. The mixture was concentrated, diluted with ethyl ether, and a salt was isolated by filtration; orange solid, 1.3 g., m.p. 189–190° dec. The 1.6 g. of unchanged oxime that was recovered by evaporation of the filtrate was again treated with methyl iodide. After 6 hr. of refluxing, the methiodide was isolated as before; 0.3 g. m.p. 189–190° dec. The products were combined, dissolved in 100 ml. of methanol–ethanol mixture, treated with Norite, concentrated to 50 ml., and allowed to crystallize. Orange crystals were obtained, 1.2 g. (28%), m.p. 190–191°, dec. An infrared absorption spectrum obtained in potassium bromide was identical to that of II isolated in procedure A.

O-Methyl-2-formyl-3-methylbenzothiazolium Iodide Oxime (VI).—To 5.0 g. of benzothiazole-2-carboxaldoxime in 100 ml. of hot methanol was added 8.0 g. of O-methylhydroxylamine hydrochloride. The solution was allowed to warm for 30 min. on a steam bath. Water was added to the point of cloudiness, then

(8) E. J. Poziomek, Ph.D. dissertation, University of Delaware, June, 1961.

(9) L. G. S. Brooker, A. L. Sklar, H. W. J. Cressman, G. H. Keyes, L. A. Smith, R. H. Sprague, E. Van Lare, G. Van Zandt, F. L. White, and W. W. Williams, *J. Am. Chem. Soc.*, **67**, 1875 (1954).

(10) E. J. Poziomek, D. N. Kramer, W. A. Mosher, and H. O. Michel, *ibid.*, **83**, 3916 (1961).

(11) R. H. Poirier, unpublished results.

(12) Melting points are uncorrected. Unless otherwise indicated, pK_a values were obtained at room temperature, from potentiometric data, assuming pK_a to be the pH of half neutralization. In each case approximately 100 mg. of sample dissolved in 25 ml. of methanol–water (1:1) was titrated with 0.1 *N* sodium hydroxide.

(13) Marie-Therese Le Bris and H. Washl, *Bull. soc. chim. France*, 342 (1959).

(14) D. Taber, *J. Am. Chem. Soc.*, **77**, 1010 (1955).

(15) W. Borsche and W. Doeller, *Ann.*, **537**, 53 (1939).

(16) D. H. Rosenblatt, *J. Phys. Chem.*, **58**, 40 (1954).

the mixture was cooled and filtered to give 4.6 g. of O-methyl benzothiazole-2-carboxaldoxime, m.p. 65–68°.

Anal. Found: C, 55.7; H, 4.4.

This product (4.0 g.) and 10 ml. of methyl iodide in 75 ml. of methanol were refluxed for 85 hr. Ether was added to give 0.6 g. of an orange solid, m.p. 201–203° dec.

Anal. Calcd. for $C_{10}N_{11}IN_2OS$: C, 35.9; H, 3.3. Found: C, 35.6; H, 3.3.

N-Methyl-2-formyl-3-methylbenzothiazolium Iodide Oxime (V).—A similar procedure as described for VI (except that N-methylhydroxylamine was used) gave 26% of an orange solid, m.p. 233–235° dec.

Anal. Calcd. for $C_{10}H_{11}IN_2OS$: C, 35.9; H, 3.3. Found: C, 35.7; H, 3.4.

Nuclear Magnetic Resonance Studies.—The spectra were obtained using a Varian Model HR-60 high resolution n.m.r. spectrometer equipped with an electronic integrator. All chemical shifts are reported in cycles per second at 60 Mc./sec. downfield from the reference signals used. Tetramethylsilane was used as a reference for spectra obtained in acetonitrile and the methyl resonance of sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as a reference for the spectra obtained in D_2O.[17] All chemical shifts were determined using the side band technique.[18]

Acknowledgment.—The authors wish to express their gratitude to the Analytical Research Branch of the Research Directorate, U. S. Army Chemical Research and Development Laboratories, for part of the analyses reported here.

(17) G. V. D. Tiers and R. I. Coon, *J. Org. Chem.*, **26**, 2097 (1961).
(18) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

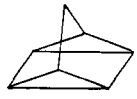
Bridged Polycyclic Compounds. XXII. The Carbenoid Decomposition of Nortricyclenone *p*-Toluenesulfonylhydrazone

STANLEY J. CRISTOL AND J. KENNETH HARRINGTON

Department of Chemistry, University of Colorado, Boulder, Colorado

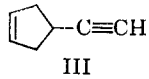
Received November 19, 1962

An attempt to prepare quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]-heptane (I) by treatment of the *p*-toluenesulfonylhydrazone of nortricyclenone (II) using the general procedure described by Friedman and Shechter[2] (heating with sodium methoxide in diglyme at 160°) gave hydrocarbon material (19% yield) which apparently did not contain any I,[3] but instead was a mixture of 69% of 4-ethynylcyclopentene (III), and 29% of 4-vinylidenecyclopentene (IV). The mixture of these two materials was separated by vapor phase chromatography.

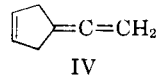


I

II



III



IV

Compounds III and IV were characterized and identified as follows. III gave the correct C,H analysis and decolorized bromine in carbon tetrachloride and 2% aqueous potassium permanganate instantaneously. Catalytic hydrogenation of III with palladium-on-charcoal catalyst in ethanol at room temperature led to rapid absorption of three moles of hydrogen per mole of compound. The boiling point of III was approximately 92° (628 mm.) and indicates a monomer. The infrared spectrum of III clearly showed the presence of an acetylenic function, exhibiting a strong, sharp absorption peak at 3.02 μ and a sharp, but less intense peak at 4.73 μ. Sharp peaks at 3.27 and 6.21 μ are ascribed to the ethylenic hydrogens and carbon–carbon double-bond stretching vibrations. The nuclear magnetic resonance spectrum of III exhibited a singlet at 4.42 τ, a complicated multiplet between 6.8 and 7.8 τ, and a clear doublet at 8.12 τ with relative areas of the peaks being 1.94, 5.09, and 1.00, respectively. The singlet at 4.42 τ is ascribed to the ethylenic hydrogens. Cyclopentene itself has a sharp singlet at 4.40 τ. The doublet at 8.12 τ (J = 2.0 c.p.s.) is assigned to the acetylenic hydrogen which is split by the methinyl hydrogen. Several examples of such 1,3 splittings are known.[4]

It was expected that the spin–spin splitting pattern of the olefinic hydrogens in the nuclear magnetic resonance spectrum of the acetylene would distinguish between the symmetrical compound III and its unsymmetrical isomer, 3-ethynylcyclopentene. However, when the nuclear magnetic resonance spectra of similar isomers, Δ^2 and Δ^3-cyclopentenylacetamide,[5] were obtained, it was found that the splitting pattern of the olefinic hydrogens of the isomers was essentially the same, although the appearance of the over-all spectrum clearly indicated two isomers.

Although IV was unstable, its structure was established unequivocally by spectral means. The infrared spectrum of IV clearly indicated the presence of the allene function by a sharp intense absorption peak at 5.10 μ. The allene function is reported[6] to absorb at 5.08 to 5.12 μ. Sharp peaks of medium intensity at 3.27 and 6.21 μ are again ascribed to the ethylenic hydrogen and carbon–carbon double-bond stretching vibrations. The nuclear magnetic resonance spectrum of IV consists of a sharp singlet at 4.48 τ, a pentuplet centered at 5.40 τ, and a triplet centered at 6.87 τ with relative peak areas of 0.95, 1.00, and 1.97, respectively. The relative intensities of the components of the triplet were 1:2:1 and of the pentuplet 1:4:6:4:1, indicating that the multiplicity is the result of groups of equivalent nuclei splitting with each other.[7] The spectrum is clearly compatible only with the structure IV for the allene. Finally, the fact that the acetylene isolated is isomerized to IV makes it most probable that it is the 4-ethynyl derivative. It is unlikely that the conditions employed are drastic enough to isomerize the carbon–carbon double bond concurrently with the acetylene–allene transformation.

(1) Previous paper in series: S. J. Cristol, Dennis D. Tanner, and Robert P. Arganbright, *J. Org. Chem.*, **28**, 1374 (1963).
(2) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) **82**, 1002 (1960); (c) G. L. Closs, *ibid.*, **84**, 809 (1962).
(3) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).
(4) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.
(5) S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).
(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 61.
(7) The nuclear magnetic resonance spectrum of IV is being considered in detail elsewhere: M. W. Hanna and J. K. Harrington, *J. Phys. Chem.*, in press.