azolium perchlorate[12] (4.35 g) was added. The mixture was stirred and heated to reflux at which time a homogeneous solution resulted. The solution was filtered and cooled; **16** was collected and recrystallized again from HOAc to give 1.01 g, mp 189–190.5° (23%; another modification has mp 176°).

Anal. Calcd for $C_{10}H_{11}ClN_2O_4S_2$: C, 37.21; H, 3.44; N, 8.68; S, 19.87. Found: C, 37.21; H, 3.33; N, 8.85; S, 20.00.

After collection of **16**, the HOAc filtrate was evaporated to dryness, and the residue was extracted with $CHCl_3$. The material thus obtained was recrystallized from hexane–EtOAc to give 0.55 g (20%) of methyl benzoyldithiocarbamate, mp 133–135°, that was identical with the authentic material.[13]

Reaction of 1 (X = Br) with NaN_3.—A mixture of **1** (8.46 g, 0.0314 mol) and NaN_3 (2.2 g, 0.034 mol) in DMF (75 ml) was stirred under nitrogen while the flask was heated in an oil bath. A deep blue color quickly developed. At 80–85° vigorous gas evolution was observed. The solution was kept at 85–90° for 1 hr, and the most of the DMF was removed *in vacuo*. Benzene was added, and the solution was filtered and distilled to give 4.1 g (76%) of 3,5-bis(dimethylamino)-1,2,4-thiadiazole [**6**, bp 120–126° (0.5–0.6 mm)], identical with that synthesized previously).[1b]

Reaction of 3,5-Dipiperidino-1,2,4-dithiazolium Bromide with NaN_3.—The reaction was run as described for the reaction of **1**; a 94% crude yield of 3,5-dipiperidino-1,2,4-thiadiazole was obtained as a light yellow oil. Partial decomposition occurred on attempted distillation [>150° (0.15 mm)] and the distillation was interrupted. Upon cooling, the material remaining in the flask solidified. Two recrystallizations from MeOH–H_2O gave the pure compound, mp 65–66°.

Anal. Calcd for $C_{12}H_{20}N_4S$: C, 57.10; H, 7.99; N, 22.20; S, 12.71. Found: C, 57.24; H, 8.03; N, 22.14; S, 12.51.

Reaction of 9 with NaN_3.—This reaction was run similarly except DMSO was used as the solvent (heated to 100°). The product was obtained by adding H_2O and extracting thoroughly with ether; a 76% yield of crude 3-(dimethylamino)-5-morpholino-1,2,4-thiadiazole (**10**) and 5-(dimethylamino)-3-morpholino-1,2,4-thiadiazole (**11**) was obtained from which samples of the pure compounds were obtained by preparative gas chromatography (5 ft × 0.25 in. 10% Carbowax 20M on 60–80 Chromosorb W, 190°). The collected samples were each recrystallized from hexane:

Isomer **A** (*ca.* 33%), mp 89–90°, had retention time 25 min; δ ($CDCl_3$) 3.04 (Me_2N).

Anal. Calcd for $C_8H_{14}N_4OS$: C, 44.84; H, 6.58; N, 26.15; S, 14.92. Found: C, 44.63; H, 6.61; N, 26.02; S, 15.02.

Isomer **B** (*ca.* 67%), mp 79°, had retention time 32.5 min; δ ($CDCl_3$) 3.08.

Anal. Calcd for $C_8H_{14}N_4OS$: C, 44.84; H, 6.58; N, 26.15; S, 14.92. Found: C, 44.97; H, 6.65; N, 25.94; S, 14.99.

Reaction of 12 with NaN_3.—A mixture of **12** (2.56 g) and NaN_3 (0.75 g) in DMF (20 ml) was heated at *ca.* 130° until no more gas evolution was visible. The deep blue color disappeared; the DMF was stripped; and the residue was partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ was dried and evaporated to give 0.67 g (43%) of crude 5-(dimethylamino)-3-(methylamino)-1,2,4-thiadiazole (**13**) as a light yellow oil that solidified in a distillation apparatus [105–110° (0.15 mm)]. Recrystallization from hexane–EtOAc gave the pure material, mp 77–79°.

Anal. Calcd for $C_5H_{10}N_4S$: C, 37.95; H, 6.37; N, 35.41. Found: C, 37.91; H, 6.16; N, 35.67.

The structural assignment (**13** as opposed to the other possible isomer) is made partly by analogy to the formation of **15** from **14** (*vide infra*) and also by a strong peak in the mass spectrum at *m/e* 88 [$Me_2NC(=S)^+$].

Reaction of 14 with NaN_3.—A mixture of **14** (7.27 g) and NaN_3 (2.09 g) in DMF (40 ml) was heated at reflux 20 min (only a yellow color developed in this case). The solvent was stripped and the residue was extracted with several portions of warm MeOH; these extracts were filtered and evaporated and the remaining solid was washed with water and dried to give 2.44 g (56%) of 3-amino-5-(dimethylamino)-1,2,4-thiadiazole (**15**), mp 225–227.5°. An analytical sample was recrystallized from absolute ethanol, mp 230–232°.

Anal. Calcd for $C_4H_8N_4S$: C, 33.31; H, 5.58; N, 38.86; S, 22.24. Found: C, 33.43; H, 5.63; N, 39.01; S, 21.98.

(12) M. Ahmed and D. M. McKinnon, *Can. J. Chem.*, **48**, 2142 (1970).

(13) J.-L. Derocque and J. Vialle, *Bull. Soc. Chim. Fr.*, 1183 (1966).

The nmr spectrum (DMSO-d_6) was consistent with an amino(dimethylamino)thiadiazole [δ 3.00 (s, 6) and 5.98 (s, 2, exchangeable)] as was the mass spectrum (*m/e* 144). The opposite isomer, 5-amino-3-(dimethylamino)-1,2,4-thiadiazole, has been reported[14] to have mp 161°.

Reaction of 16 with NaN_3.—A mixture of **16** (1.00 g) and NaN_3 (0.269 g) in DMF (28 ml) was refluxed 45 min. The DMF was stripped and the residue was partitioned between benzene and water. The benzene solution was dried and evaporated leaving 0.380 g of an oily tan solid that was extracted with several small portions of MeOH (to remove sulfur). Treatment of the MeOH solution with water precipitated a light tan solid, mp 88–90°, that was again taken up in MeOH to remove a little more sulfur. Evaporation of the MeOH and recrystallization of the residue from hexane gave 0.153 g (24%) of 5-(dimethylamino)-3-phenyl-1,2,4-thiadiazole (**17**), mp 89–90° (reported[7] mp 89°).

Registry No.—**9**, 31354-27-5; **9′**, 31354-28-6; **10**, 31354-29-7; **11**, 31354-30-0; **12**, 31354-31-1; **13**, 31354-32-2; **14**, 31354-33-3; **15**, 31354-34-4; **16**, 31354-35-5; NaN_3, 12136-89-9; 3,5-dipiperidino-1,2,4-dithiazolium bromide, 31354-36-6; 3,5-dipiperidino-1,2,4-thiadiazole, 31354-37-7.

Acknowledgment.—We thank Miss Barbara Bierl for the mass spectra and Mr. R. T. Brown for the preparation of some starting materials.

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Preparation of 2-Alkoxyiminoalkyl Bromides by the Bromination of *O*-Alkyl Oximes with *N*-Bromosuccinimide[1]

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Received April 30, 1971

Several methods are available for the preparation α-halo ketoximes and α-halo aldoximes; these include the reduction of nitro olefins with zinc chloride,[3] the reaction of an olefin with nitrosyl chloride,[4] and the direct oximation of α-halocarbonyls.[5] Reactions of these compounds with certain nucleophiles have also been explored.[3,6] The corresponding *O*-alkyl ethers, however, have not been described.

N-Bromosuccinimide (NBS) can be used to brominate various types of compounds[7] including cyclohexanone and cyclopentanone oximes which yield the

(1) This investigation was supported by U. S. Public Health Service Research Grant RH 00293, National Center for Radiological Health.

(2) Abstracted from the Ph.D. dissertation, University of Illinois at the Medical Center, 1970.

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(4) (a) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 369 (1951); (b) M. Ohno, N. Naruse, S. Torimitsu, and M. Okamoto, *Bull. Chem. Soc. Jap.*, **39**, 1119 (1966).

(5) E. T. Bailey, Ph.D. Thesis, University of Illinois, 1965.

(6) (a) A. Dornow and H. D. Jordan, *Chem. Ber.*, **94**, 76 (1961); (b) A. Dornow, H. H. Marquardt, and H. Paucksch, *ibid.*, **97**, 2165 (1964); (c) M. Ohno and N. Naruse, *Bull. Chem. Soc. Jap.*, **39**, 1125 (1966); (d) M. Ohno, S. Torimitsu, N. Naruse, M. Okamoto, and I. Sakai, *ibid.*, **39**, 1129 (1966); (e) M. Masaki, M. Sugiyama, S. Tayama, and M. Ohta, *ibid.*, **39**, 2745 (1966).

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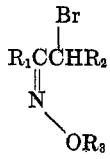
TABLE I

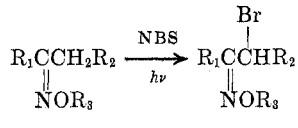
ALKOXYIMINOALKYL BROMIDES PREPARED BY NBS BROMINATION OF O-ALKYL OXIMES



Compd	R_1	R_2	R_3	Yield, %	Bp, °C (mm)	Refractive index	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found	Br, % Calcd	Br, % Found
1	Me	H	Et	32	54–57 (10)	n^{20}D 1.4764	33.35	33.48	5.60	5.55	7.78	7.93	44.38	44.57
2	Me	Me	Et	71	65–68 (12)	n^{25}D 1.4700	37.13	37.35	6.23	6.46	7.22	7.32	41.17	40.97
3	H	Et	Et	71	60–62 (7)	n^{20}D 1.4696	37.13	37.30	6.23	6.41	7.22	7.38	41.17	41.06
4	Me	Et	Et	61	92–94 (42)	n^{23}D 1.4721	40.40	40.49	6.78	6.71	6.73	6.70	38.40	38.36
5	Ph	H	Et	41	76.5–79 (0.02)	n^{15}D 1.5705	49.61	*a*	5.00	*a*	5.70	*a*	33.00	*a*
6	Me	Ph	Et	40	77–79 (0.04)	n^{25}D 1.5455	51.58	51.46	5.51	5.55	5.47	5.45	31.20	31.44
7	Me	H	Me	54	52–53 (31)	n^{21}D 1.4825	28.94	28.93	4.86	5.06	8.44	8.32	48.13	48.40
8	Me	Me	Me	73	64–65 (40)	n^{23}D 1.4726	33.35	33.44	5.60	5.81	7.78	7.81	44.38	44.63
9	H	Et	Me	30	76–78 (40)	$n^{23.5}$D 1.4756	37.13	37.20	6.23	6.19	7.22	7.29	41.17	41.39
10	Me	Et	Me	79	62–64 (0.01)	n^{22}D 1.5813	47.39	47.42	4.42	4.49	6.14	6.14	35.03	35.30
11	Ph	H	Me	70	66–68 (37)	n^{30}D 1.4687	33.35	33.50	5.60	5.62	7.78	7.70	44.38	44.55
12	$-(CH_2)_3-$		Et	47	50–52 (0.01)	n^{20}D 1.5077	40.80	40.71	5.87	5.91	6.80	6.95	38.77	38.56
13	$-(CH_2)_4-$		Et	73	52–56 (0.02–0.03)	n^{20}D 1.5110	43.65	43.64	6.41	6.50	6.36	6.52	36.30	36.44
14	$-(CH_2)_5-$		Me	58	50–52 (0.06)[b]	n^{24}D 1.5162	37.52	37.56	5.25	5.38	7.29	7.26	41.61	41.60

[a] The elemental analysis was not satisfactory. The compound was identified by two solid derivatives, namely sodium S-(2-ethoxyimino-2-phenylethyl) thiosulfate [*Anal.* Calcd. for $C_{10}H_{16}NNaO_5S_2$ (monohydrate): C, 29.89; H, 5.73; N, 4.98; S, 22.79. Found: C, 30.04; H, 5.81; N, 5.11; S, 22.73.] and 2-(2-ethoxyimino-2-phenylethylthio)-2-imidazolinium bromide, mp 133–135° (*Anal.* Calcd for $C_{13}H_{18}BrN_3OS$: C, 45.35; H, 5.27; N, 12.21; S, 9.31. Found: C, 45.41; H, 5.39; N, 12.27; S, 9.30). Attempts were made to purify the compound by chromatography on a silica column (eluting solvent, petroleum ether–$CHCl_3$ 1.3:1) and by preparative thin layer chromatography (silica gel GF-254 plates, mixture of 90 ml of petroleum ether and 70 ml of $CHCl_3$ as developing solvent). The major fraction yielded a light yellow liquid after evaporation of solvent: mass spectrum (70 eV) *m/e* 241, 243 (M^+). The nmr spectrum ($CDCl_3$) showed no bands that did not satisfy the proposed structure nor were the integrals unreasonable. The elemental analysis, however, was not satisfactory. [b] A second product, bp 70–72° (0.06 mm), n^{24}D 1.5575, was analyzed for the dibromo derivative. It has tentatively been assigned the symmetrical structure 2,5-dibromocyclopentanone oxime *O*-methyl ether: nmr spectrum (CCl_4) δ 2.00–2.87 (m, 44), 4.06 (s, 3 H), 4.86–5.17 [two broad bands, 2 H, $(CHBr)_2C{=}N$]. *Anal.* Calcd for $C_6H_9Br_2NO$: C, 26.60; H, 3.35; N, 5.17; Br, 58.98. Found: C, 26.74; H, 3.49; N, 5.34; Br, 58.87.

corresponding α-bromonitrosoalkanes.[8] In this investigation, it was found that *O*-alkyl (methyl or ethyl) ethers of ketoximes or aldoximes react readily with NBS to form the title compounds (Table I) in yields up to 79%.



The reaction was carried out by mixing equimolar quantities of the oxime ethers and pulverized *N*-bromosuccinimide in carbon tetrachloride. The mixture was heated at reflux with the introduction of radiant energy from an ultraviolet sun lamp (GE, 275 W). Preliminary work to determine optimum conditions was carried out utilizing butanone oxime *O*-ethyl ether. It was found that heat alone was unsatisfactory since the reaction time was protracted. Photoactivation by a sunlamp was found superior to dibenzoyl peroxide as an initiator. A combination of both proved to have little advantage over photoactivation alone.

While bromination of methyl and ethyl ethers proceeded without attack on the *O*-alkyl group, butanone oxime *O*-benzyl ether produced an intractable oil which showed that the benzylic carbon had been brominated [nmr δ 9.95 (CCl_4)]. When the mixture was treated with sodium bicarbonate, benzaldehyde was detected by nmr [δ 9.93 (CCl_4)] and its characteristic odor.

Experimental Section

The melting points and boiling points recorded are uncorrected. Melting points were taken on a Thomas-Hoover capillary melting point apparatus. Refractive indices were determined on a Bausch and Lomb Abbe 3L refractometer. Elemental Analyses were performed by Dr. Kurt Eder, Geneva, Switzerland, and by Micro-Tech Laboratories, Inc., Skokie, Ill. The nmr spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as internal reference. The mass spectra were obtained from a Hitachi Perkin-Elmer RMU-60 mass spectrometer.

Materials.—The oximes, ketones, and *N*-bromosuccimide were obtained from commercial sources (Eastman Organic Chemicals, Matheson Coleman and Bell) and were used without further purification. 2-Pentanone oxime, bp 90–93° (33 mm) with n^{20}D 1.4452 (lit.[9] bp 167°, n^{20}D 1.44546), and phenyl-2-propanone oxime, mp 67–69° (petroleum ether) (lit.[10] mp 68–70°), were prepared by a standard method.[11a] Cyclohexanone oxime was prepared according to a known procedure,[11b] mp 88–90° (lit.[11b] mp 89–90°).

The following *O*-alkyl oximes were prepared by alkylating oximes using methyl sulfate or ethyl sulfate according to known procedures:[12] acetone oxime *O*-ethyl ether, bp 92–94°, n^{20}D 1.4040 (lit.[9] bp 93°, n^{20}D 1.4042); butanone oxime *O*-ethyl ether, 113–115°, n^{20}D 1.4128 (lit.[9] bp 113°, n^{20}D 1.4115); 2-pentanone oxime *O*-ethyl ether, bp 132–136°, n^{21}D 1.4181 [lit.[9] bp 134° (754 mm), n^{20}D 1.41836]; cyclohexanone oxime *O*-ethyl ether, bp 72–74° (13–15 mm), n^{19}D 1.4630 [lit.[12a] bp 70° (14 mm), n^{20}D 1.46327]; acetone oxime *O*-methyl ether, bp 68–71°, n^{25}D 1.3971 (lit.[9] bp 73°, n^{20}D 1.40052); butanone oxime *O*-methyl ether, bp 90–94°, $n^{23.5}$D 1.4092 [lit.[12b] bp 66° (301 mm), n^{20}D 1.4099]; acetophenone oxime *O*-methyl ether, bp 89–92° (8 mm), n^{23}D 1.5414 [lit.[12b] bp 73–74° (2.2 mm), n^{20}D 1.5415]; cyclopentanone oxime *O*-methyl ether, bp 50–53° (40 mm), n^{29}D 1.4524 [lit.[12b] bp 36° (10 mm), n^{20}D 1.4560]; acetophenone oxime *O*-ethyl ether,

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(12) (a) M. Hudlicky and J. Hokr, *Collect. Czech. Chem. Commun.*, **14**, 561 (1949); (b) A. Reiser, V. Jehlicka, and K. Dvorak, *ibid.*, **16**, 13 (1951).

bp 50–53° (0.04 mm), n^{20}D 1.5322 [lit.[13] bp 130–135° (20 mm)[14]]; cyclopentanone oxime *O*-ethyl ether reported[15] without physical constants, bp 59–61° (15–16 mm), n^{20}D 1.4540, was analyzed for $C_7H_{13}NO$ (Calcd: C, 66.11; H, 10.30; N, 11.01. Found: C, 66.28; H, 10.14; N, 11.11). Previously unreported oxime ethers included *n*-butyraldoxime *O*-ethyl ether, bp 119–121°, n^{14}D 1.4133 (*Anal.* Calcd for $C_6H_{13}NO$: C, 62.57; H, 11.38; N, 12.16. Found: C, 62.63; H, 11.34; N, 12.19); *n*-butyraldoxime *O*-methyl ether, bp 93–97°, n^{25}D 1.4054 (*Anal.* Calcd for $C_5H_{11}NO$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.52; H, 10.82; N, 13.94); phenyl-2-propanone oxime *O*-ethyl ether, bp 60–66° (0.01–0.1 mm) n^{21}D 1.5070 (*Anal.* Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.53; H, 8.62; N, 8.02); 2-pentanone oxime *O*-methyl ether, bp 118–120°, n^{24}D 1.4152 (*Anal.* Calcd for $C_6H_{13}NO$: C, 62.57; H, 11.38; N, 12.16. Found: C, 62.68; H, 11.30; N, 12.12).

General Procedure for the NBS Bromination of *O*-Alkyl Oximes.—The procedure for the preparation of 3-bromo-2-butanone oxime *O*-methyl ether is representative. A mixture of 20.2 g (0.2 mol) of 2-butanone oxime *O*-methyl ether and 35.6 g (0.2 mol) of *N*-bromosuccinimide in 80 ml of carbon tetrachloride was heated at reflux with occasional shaking and irradiated with a 275-W G.E. sunlamp (about 10 cm away). In about 15 min, vigorous boiling ensued with the development of an intense red-dish-brown color and, after an additional 10 min, the color suddenly disappeared and the boiling subsided. The reaction mixture was cooled and filtered with suction, and the residue was washed with a small amount of carbon tetrachloride. The filtrate was combined with the washings and then shaken with 50 ml of a saturated solution of sodium bicarbonate. The organic layer was dried (Na_2SO_4) and distilled under diminished pressure to remove the solvent. The residual yellow liquid was then distilled twice under reduced pressure giving 26.2 g (72.8%) of **8**. Physical properties, spectral data, and elemental analysis are shown in Tables I and II.

TABLE II

NMR DATA OF 2-ALKOXYIMINOALKYL BROMIDES

Compd	Solvent	Nmr, δ
1	Neat	1.20 (t, 3, J = 7.0 Hz), 1.88 (s, 3), 3.90 (s, 2), 4.04 (q, 2, J = 7.0 Hz)
2	$CDCl_3$	1.23 (t, 3, J = 7.0 Hz), 1.78 (d, 3, J = 7.0 Hz), 1.92 (s, 3), 4.09 (q, 2, J = 7.0 Hz), 4.70 (q, 1, J = 7.0 Hz)
3	Neat	1.00 (t, 3, J = 7.0 Hz), 1.17 (t, 3, J = 7.0 Hz), 1.72–2.27 (m, 2), 4.03 and 4.09 (two q, 2, J = 7.0 Hz), 4.45 and 5.00 (two q, with ratio of 3 to 1, 1, $J \simeq$ 7.5 Hz, CHBr), 6.70 and 7.35 (two d, with ratio of 1 to 3, J = 8.8 Hz)
4	$CDCl_3$	0.98 (t, 3, J = 7.0 Hz), 1.23 (t, 3, J = 7.0 Hz), 1.90 (s, 3) 1.70–2.35 (m, 2), 4.13 (q, 2, J = 7.0 Hz), 4.52 (t, 1, $J \simeq$ 7.5 Hz)
5	$CDCl_3$	1.36 (t, 3, J = 7.0 Hz), 4.37 (q, 2, J = 7.0 Hz, 4.38 (s, 2), 7.30–7.90 (m, 5)
6	CCl_4	1.22 (t, 3, J = 7.0 Hz), 1.87 (s, 3), 4.12 (q, 2, J = 7.0 Hz), 5.80 (s, 1), 7.18–7.61 (m, 5)
7	$CDCl_3$	1.96 (s, 3), 3.90 (s, 3), 3.99 (s, 2)
8	$CDCl_3$	1.81 (d, 3, J = 7.0 Hz), 1.93 (s, 3), 3.89 (s, 3), 4.77 (q, 1, J = 7.0 Hz)
9	CCl_4	1.83–2.67 (m, 6), 3.86 (s, 3), 4.80–5.00 (m, 1)
10	$CDCl_3$	1.01 (t, 3, J = 7.0 Hz), 1.76–2.20 (m, 2), 1.89 (s, 3), 3.85 (s, 3), 4.47 (t, 1, $J \simeq$ 7.5 Hz)
11	$CDCl_3$	4.04 (s, 3), 4.29 (s, 2), 7.22–7.84 (m, 5)
12	Neat	1.29 (t, 3, J = 7.0 Hz), 1.80–3.00 (m, 6), 4.36 (q, 2), 5.18–5.38 (one broad band, 1)
13	Neat	1.29 (t, 3, J = 7.0 Hz), 1.25–3.60 (m, 8), 4.31 (q, 2), 5.17–5.40 and 5.85–6.10 (two broad bands, 1)
14	CCl_4	1.83–2.67 (m, 6), 3.86 (s, 3), 4.80–5.00 (m, 1)

(13) W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **79**, 628 (1901).

(14) The refractive index of this compound was not reported, therefore its structure was confirmed by nmr (neat TMS internal standard): δ 1.27 (t, 3 H), 2.10 (s, 3 H), 4.21 (q, 2 H), 7.50–7.79 (m, 2 H), and 7.08–7.37 (m, 3 H).

(15) L. G. Donaruma, *J. Org. Chem.*, **22**, 1024 (1957).

Registry No.—**1**, 31376-82-6; **2**, 31376-83-7; **3**, 31376-84-8; **4**, 31376-85-9; **5**, 31376-86-0; **6**, 31376-87-1; **7**, 31376-88-2; **8**, 31376-89-3; **9**, 31376-90-6; **10**, 31376-91-7; **11**, 31376-92-8; **12**, 31376-93-9; **13**, 31376-94-0; **14**, 31376-95-1; cyclopentanone oxime *O*-ethyl ether, 31376-96-2; *n*-butyraldoxime *O*-ethyl ether, 20135-03-9; *n*-butyraldoxime *O*-methyl ether, 31376-98-4; phenyl-2-propanone oxime *O*-ethyl ether, 31376-99-5; 2-pentanone oxime *O*-methyl ether, 31377-00-1; sodium *S*-(2-ethoxyimino-2-phenylethyl) thiosulfate, 31377-01-2; 2-(2-ethoxyimino-2-phenylethylthio)-2-imidazolinium bromide, 31377-02-3; 2,5-dibromocyclopentanone oxime *O*-methyl ether, 31377-03-4; NBS, 128-08-5.

Methylation of 2-Aminobenzimidazole

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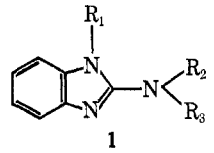
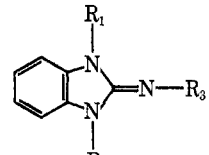
Received March 22, 1971

During an investigation of the preparation and properties of 2-aminobenzimidazoles, we wished to determine the nature of the products formed by direct methylation of these compounds. Methylation of 2-aminobenzimidazole can lead to either of two products, **1** and **2** ($R_1 = R_2 = R_3 = CH_3$). Based upon the observed behavior of the 5-aminotetrazoles,[2a] formation of the imine **2** was anticipated.



1



2

Treatment of 2-aminobenzimidazole with dimethyl sulfate afforded a trimethylated product whose physical properties differed substantially from those of an authentic sample of 1-methyl-2-dimethylaminobenzimidazole[2b] and which was apparently the expected 1,3-dimethyl-2-methyliminobenzimidazole. The ultraviolet spectrum of this compound shows only a single strong absorption at 284 nm rather than the two distinct maxima characteristic of both 2-aminobenzimid-

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