Dimethyl *o*-carboxamidophenoxyfumarate (4) was prepared by stirring together at room temperature for 24 hr a solution of 20 mmol each of salicylamide, 1, and N-methylmorpholine in 27 ml of diethyl ether. Addition of water and agitation precipitated 0.76 g (14%) of the phenol adduct, 4, which was recrystallized from methanol: mp 124.5–126.5°; nmr spectrum ($CDCl_3$) δ 3.75 (s, 3, OCH_3), 3.80 (s, 3, OCH_3), 6.75 (s, 1, vinyl **H**), 7.6 (broad s, 2, NH_2), and 6.6–8.2 ppm (m, 4, Ar **H**); ir (KBr) 3440, 3344, 3300, and 3240 (NH) and 1725 cm^{-1} (C=O).

Anal. Calcd for $C_{13}H_{13}NO_6$: C, 55.91; H, 4.66; N, 5.02. Found: 55.63; H, 4.69; N, 5.07.

Cyclization of 4 in Xylene–Sodium Methoxide.—A solution of 0.40 g (1.4 mmol) of dimethyl *o*-carboxamidophenoxyfumarate, 4, and a catalytic quantity of sodium methoxide (0.4 mmol) in 50 ml of xylene was refluxed for 17 hr, filtered, and concentrated. The crude crystals were washed with cold ether and filtered to yield 0.18 g (45%) of the benzoxazinone, 6, identified by melting point and ir comparison with authentic sample.

Dimethyl *o*-carbomethoxyphenoxy-2-butene-1,4-dioate (12) was synthesized by allowing an ethereal solution of 0.20 mol each of methyl salicylate, triethylamine, and 1 to stand at room temperature for 2 days. The ether was removed, the residue dissolved in benzene, washed well with water, dried ($MgSO_4$), and distilled to yield 37.6 g (64%) of a pale yellow oil: bp 175–180° (1 Torr); nmr spectrum ($CDCl_3$) δ 3.70, 3.78, 3.92, 3.94, 3.98 and 4.03 for the respective methoxy singlets, 5.00 (s, 1, maleate vinyl **H**, 50%), 6.68 (s, 1, fumarate vinyl **H**, 50%) and 6.8–8.2 ppm (m, 4, Ar **H**).

Anal. Calcd for $C_{14}H_{14}O_7$: C, 57.14; H, 4.73. Found: C, 57.20; H, 4.71.

Dimethyl *o*-carbomethoxy-*p*-chlorophenoxy-2-butene-1,4-dioate (13) was prepared from methyl 5-chlorosalicylate as described above: bp 181–184° (1 Torr); 63%; nmr spectrum ($CDCl_3$) δ 3.62, 3.68, 3.71, 3.78, 3.93 and 3.95 for the methoxy singlets, 5.03 (s, 1, maleate vinyl **H**, 42%), 6.68 (s, 1, fumarate vinyl **H**, 58%) and 6.8–8.1 ppm (m, 3, Ar **H**).

Anal. Calcd for $C_{14}H_{13}ClO_7$: C, 51.14; H, 3.96. Found: C, 51.19; H, 4.08.

Registry No.—**1**, 762-42-5; **4** (R = H), 24704-24-3; **6**, 24716-40-3; **7**, 24716-41-4; **8**, 24716-42-5; **9**, 24716-43-6; **10**, 24716-44-7; **11**, 24716-45-8; **12** maleate, 24704-25-4; **13** maleate, 24710-88-1; **12** fumarate, 24710-82-5; **13** fumarate, 24710-83-6.

Fragmentation of a Sydnone *via* Elimination[1a,b]

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Received November 3, 1969

Although a number of characteristic reactions of sydnones have been thoroughly documented,[2] a novel type of fragmentation reaction has now been encountered during the course of an attempted preparation of 3-sydnonealanine (**2a**). It was hoped that **2a** would possess carcinolytic activity because certain sydnones have tumor-inhibiting properties (*cf.* ref 2), the alanine moiety is biologically compatible, and there is a striking structural and electronic (zwitterionic) similarity between **2a** and the isomeric azaserine (**4**), the latter being a well-known antileukemic agent.

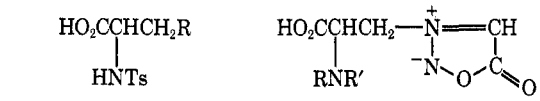
(1) (a) Sydnones. V. Part IV: C. J. Thoman, S. J., D. J. Voaden, and I. M. Hunsberger, *J. Org. Chem.*, **29**, 2044 (1964). (b) This investigation was supported, in part, by a research grant (CA-05478) from the National Cancer Institute of the U. S. Public Health Service. (c) To whom all inquiries should be sent. This paper is taken, in part, from the Ph.D. dissertation of L. J. F., University of Massachusetts, 1965.

(2) F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964).

The projected synthesis of **2a** involved a standard sequence of reactions proceeding from the selectively protected 3-amino-2-(tosylamino)propionic acid (**1b**),[3] which was readily available by Hofmann degradation of N^2-tosylasparagine (**1a**).[3–5] Condensation of **1b** with glycolonitrile[6] followed by acid hydrolysis of the resulting glycinonitrile **1c** and nitrosation of the corresponding glycine **1d** were all carried out in good yield.

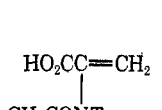
The cyclodehydration of **1e** with acetic anhydride under a variety of conditions gave two products (A and B) or mixtures thereof. Optimum yields (*ca.* 65%) of one of these compounds (A), mp 176–178° dec, were realized after 24 hr at room temperature, whereas heating for 30 min or allowing the reactants to stand at room temperature for 2 weeks produced a second compound (B), mp 143–145° dec, in 30–50% yield along with dark-colored, noncrystalline products.

The presence of both the sydnone ring and the *p*-toluenesulfonamido groups in A was indicated by ultraviolet maxima at 300 and 232 mμ, respectively. Identification of A as the N-acetyl derivative **2c** of the expected sydnone **2b** was supported also by its infrared spectrum, which showed the sydnone ring CH absorption[2] as well as three closely spaced bands in the 1700–1730-cm^{-1} region (C=O). No sulfonamide NH stretching absorption was observed.

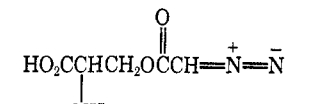


1a, R = $CONH_2$
b, R = NH_2
c, R = $NHCH_2CN$
d, R = $NHCH_2CO_2H$
e, R = $N(NO)CH_2CO_2H$

2a, R = R′ = H
b, R = H; R′ = Ts
c, R = CH_3CO; R′ = Ts



3



4

Ts = *p*-$CH_3C_6H_4SO_2$

N-Acetyl-N-tosylalanine (**5b**) was prepared from N-tosylalanine (**5a**)[4] and acetic anhydride as a model to assist in the assignment of the carbonyl bands of **2c**. Infrared comparison (Nujol) of the two compounds suggests that the high-frequency band (1728 cm^{-1}) of **2c** is the sydnone carbonyl. Differentiation of the carbonyl bands of **2c** was effected further by examining the spectra of **2c** and **5b** in dioxane. Assignments (see Experimental Section) were determined by comparison with N-acetyl-N-tosylglycine in which the positions (in dioxane) of the acetamido (1712 cm^{-1}) and carboxyl (1754 cm^{-1}) functions have been established.[7]

The formation of B from the N-nitrosoglycine **1e** *via* the intermediate sydnone **2c** appeared likely since B

(3) The terms tosylamino and tosyl refer to the *p*-toluenesulfonamido and *p*-tolylsulfonyl functions, respectively.

(4) Since the starting materials for the syntheses described herein were DL-asparagine and DL-alanine, all compounds with an asymmetric center have the DL configuration.

(5) J. Rudinger, K. Poduska, and M. Zaoral, *Collect. Czech. Chem. Commun.*, **25**, 2022 (1960).

(6) J. M. Tien and I. M. Hunsberger, *J. Amer. Chem. Soc.*, **83**, 178 (1961).

(7) M. Zaoral and J. Rudinger, *Collect. Czech. Chem. Commun.*, **26**, 2316 (1961).

also was obtained by heating **2c** with acetic anhydride. The single ultraviolet maximum at 232 mμ precluded the presence of a sydnone ring. Furthermore, the empirical formula indicated that two of the original three nitrogen atoms of **2c** had been lost. The acrylic acid structure **3** is in complete accord with the infrared spectrum of B. Finally, catalytic hydrogenation of **3** provided **5b** which was identical (mixture melting point and infrared spectrum) with the material obtained by treatment of **5a** with acetic anhydride.

This unexpected fragmentation of an otherwise stable sydnone[8] under the usual conditions of its synthesis, *i.e.*, dehydrative cyclization with acetic anhydride, may well prove to be a general reaction for such suitably constructed compounds. While the mechanism of the reaction has not been studied, acetate ion (in equilibrium with the acetic acid formed in the reaction) possibly acts as a mild acceptor for the methine proton activated by the carboxyl and sulfonamido groups. In addition, the cyclic azomethineimine structure[9] for sydnones or structures contributing to the aromatic resonance hybrid have a formal positive charge at ^{3}N.[2] This should lend additional driving force for the E2 elimination. The related problem concerning the fate of the presumed eliminated fragment (*i.e.*, the sydnonyl anion or formally the unknown parent heterocycle, sydnone) must await full elucidation of the reaction stoichiometry.

The sydnone **2c** and the intermediates **1a–e** were submitted to the Cancer Chemotherapy National Service Center for testing in their antitumor screen. All compounds were inactive.

Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were determined with a Beckman IR-5, a Perkin-Elmer Model 21, or a Perkin-Elmer Model 337 spectrophotometer fitted with a grating. Ultraviolet spectra were determined with a Cary Model 14 recording spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

N^2-Tosylasparagine (1a).—This compound was prepared from DL-asparagine monohydrate by the procedure used for the corresponding D isomer.[10] The crude product (85%, a white microcrystalline powder, mp 169–172°) was used for the next step without further purification. Recrystallization from 1:4 ethanol–water gave the analytical sample as colorless plates, mp 171–173° (lit.[11] mp 174.5–175.5°).

Anal. Calcd for $C_{11}H_{14}N_2O_5S$: C, 46.15; H, 4.93; N, 9.79; S, 11.18. Found: C, 46.48; H, 5.04; N, 9.70; S, 11.24.

3-Amino-2-(tosylamino)propionic Acid (1b).—Hofmann degradation of **1a** according to the method for the corresponding L isomer[5] gave crude **1b** (79%), sufficiently pure (mp 223–224° dec) for use in the next step. An analytical sample (colorless lathes) was prepared by recrystallization from 1:3 glacial acetic acid–water and drying for 24 hr at 78° (3 mm) over P_2O_5, mp 225–226° dec.

Anal. Calcd for $C_{10}H_{14}N_2O_4S$: C, 46.51; H, 5.47; N, 10.85; S, 12.39. Found: C, 46.39; H, 5.45; N, 11.02; S, 12.55.

3-[(Cyanomethyl)amino]-2-(tosylamino)propionic Acid (1c).—To a cold solution of 9.60 g (0.240 mol) of NaOH in 162 ml of water, 61.9 g (0.240 mol) of **1b** was added in portions. If all the amino acid did not dissolve, small additional amounts of 5% aqueous NaOH were added until complete solution occurred or until no more solid dissolved. The stirred solution was warmed to room temperature and treated with 23.5 g (0.29 mol) of 70% aqueous glycolonitrile. The white precipitate that formed within 15 min redissolved after *ca.* 30 min. After 12 hr, the orange solution was clarified by filtration and cooled. Slow addition of concentrated HCl to pH 2–3 (pH paper) precipitated a very finely divided solid that was washed with cold water and dried *in vacuo* over P_2O_5: yield 60.4 g (85%) of a peach-colored powder; mp 163–166° dec. This product was suitable for use in the next step.

Crude **1c** crystallized with difficulty from the common organic solvents and partially reverted to the starting material **1b** on attempted recrystallization from water or aqueous ethanol. A sample was purified by dissolving in the minimum amount of 5% aqueous $NaHCO_3$, diluting with a fourfold volume of water, and reprecipitating with 10% aqueous HCl. Thorough washing with water and drying yielded a light pink, microcrystalline solid. This process, repeated three times, gave a sample: mp 172–174° dec, followed by partial resolidification and gradual remelting at 180–193°; ir (Nujol) 3260 (sulfonamide NH), 1630 (ionized carboxyl), 1320 and 1165 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_{15}N_3O_4S$: C, 48.48; H, 5.09; N, 14.14; S, 10.76. Found: C, 48.35; H, 5.13; N, 14.10; S, 10.56.

3-[(Carboxymethyl)amino]-2-(tosylamino)propionic Acid (1d).—A solution of 59.4 g (0.200 mol) of crude **1c** in 630 ml of concentrated HCl was diluted with 315 ml of water and refluxed for 3.5 hr. After evaporating to dryness *in vacuo*, the residue was taken up in ice-cold water, filtered from insolubles, and again evaporated *in vacuo* to dryness. Careful treatment (ice bath) of the red-brown, semisolid residue with 342 ml (*ca.* 10% over theory) of 5% aqueous $NaHCO_3$ gave a suspension (pH 2, pH paper) which was chilled thoroughly and filtered. The solid which was washed with cold water, sucked dry, washed with ether, and dried gave 48.3 g (76%) of a pink, microcrystalline powder, mp 172–174° dec. Recrystallization from 1:1 ethanol–water (charcoal) yielded colorless flat needles (60%): mp 177–179° dec, unchanged by further recrystallization; ir (Nujol) 3260 (sulfonamide NH), 1715 (carboxyl), 1620 (ionized carboxyl), 1330 and 1160 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_{16}N_2O_6S$: C, 45.57; H, 5.10; N, 8.86; S, 10.12. Found: C, 45.46; H, 5.02; N, 8.76; S, 10.11.

3-[(Carboxymethyl)nitrosamino]-2-(tosylamino)propionic Acid (1e).—A stirred suspension of 28.0 g (0.886 mol) of once-recrystallized **1d**, 8 ml of concentrated HCl, and 105 ml of water was treated with small portions of concentrated HCl (*ca.* 11 ml) until complete solution occurred. With cooling (−5°), a solution of 6.73 g of sodium nitrite in 50 ml of water was added during 30 min. Stirring was continued for 1 hr at −5°, 1 hr at 0°, and overnight at room temperature. Sufficient ether was added to dissolve the precipitate and the two clear layers separated. The aqueous layer was saturated with NaCl and extracted with three additional portions of ether, and the combined extracts were dried ($MgSO_4$). Evaporation *in vacuo* gave a frothy oil which was triturated with dry chloroform and air-dried: yield, 29.4 g (96%) of a pale yellow powder (positive Liebermann test); mp 146–149° dec with partial melting from 94°. The melting point of this product, which appeared to be a solvate (probably hydrate), varied widely from run to run. On occasion, melting at 70–77° followed by partial solidification (95–140°) and decomposition (147–149°) was observed. This material could be used for preparation of the sydnone **2c** without further purification; however, superior yields were realized when it was recrystallized from ethyl acetate–hexane, 77–90% recovery of a pale yellow solid (positive Liebermann test), mp 151–153° dec. Additional recrystallization from ethyl acetate–hexane provided an analytical sample: mp 152–153° dec; ir (Nujol) 3145 (sulfonamide NH), 1750 (carboxyl), 1690 (carboxyl), 1335 and 1155 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_{15}N_3O_7S$: C, 41.73; H, 4.38; N, 12.17; S, 9.29. Found: C, 41.82; H, 4.81; N, 11.76; S, 9.06.

N-Acetyl-N-tosyl-3-sydnonealanine (2c).—A stoppered suspension of 6.00 g (0.0174 mol) of once-recrystallized **1e** and 18 ml of acetic anhydride was stirred at room temperature. Within about 12 hr complete solution occurred. After 24 hr, the mixture of crystalline precipitate and yellow supernatant liquid was cooled (ice bath) and 120 ml of ice-cold water added. The ice bath was removed after several hours but stirring continued for several more hours. An additional 90 ml of water was added and the suspension stirred vigorously until all the oily semisolid had solidified. After cooling (ice bath), the product which was washed with cold water and dried gave 4.30 g (67%) of cream-colored powder, mp 172–175° dec. Recrystallization from

(8) Samples of **2c** have been stored for at least a year without appreciable deterioration.

(9) F. H. C. Stewart and N. Danieli, *Chem. Ind.* (London), 1926 (1963).

(10) A. Kjaer and E. Vesterager, *Acta Chem. Scand.*, **14**, 961 (1960).

(11) M. R. Bovarnick, *J. Biol. Chem.*, **148**, 151 (1943).

ethanol–hexane (charcoal) yielded clusters of colorless prisms (negative Liebermann test), mp 175–177° dec. An additional recrystallization yielded pure **2c**: mp 176–178° dec; uv max (dioxane) 232 and 300 mμ (ε 15,000 and 6300); ir (Nujol) 3155 (sydnone CH), 1728 (sydnone C=O), 1714 (carboxyl or acetamido C=O), 1703 (carboxyl or acetamido C=O), 1355 and 1165 cm^{-1} (SO_2); ir (dioxane) 1765 (sydnone C=O), 1750 (carboxyl C=O), and 1715 cm^{-1} (acetamido C=O).

Anal. Calcd for $C_{14}H_{15}N_3O_7S$: C, 45.53; H, 4.09; N, 11.38; S, 8.66. Found: C, 45.06; H, 4.06; N, 11.27; S, 8.65.

2-[N-Acetyl(tosylamino)]acrylic Acid (3). A. From 2c and Acetic Anhydride.—A suspension of 500 mg (1.4 mmol) of **2c** and 2.5 ml of acetic anhydride was heated on the steam bath with protection from moisture. The solid gradually dissolved with moderate evolution of gas; after 30 min the orange solution was cooled (ice bath) and 8.5 ml of ice-cold water was added. Stirring was continued for several hours during which the initially formed oil became a semisolid. On being warmed to room temperature the solid dissolved, and the solution was evaporated to dryness *in vacuo*. Drying *in vacuo* over KOH produced a semisolid which on trituration and washing with several portions of anhydrous ether left 110 mg (29%) of **3** as a light tan powder, mp 140–144° dec. Two recrystallizations from ethyl acetate–hexane (charcoal) yielded clusters of small colorless needles: mp 143–145° dec; ir (Nujol) 1720 (acetamido C=O), 1690 (conjugated carboxyl C=O), 1635 (conjugated olefin C=C), 1350 and 1165 (SO_2), and 915 cm^{-1} (olefin CH deformation).[12]

Anal. Calcd for $C_{12}H_{13}NO_5S$: C, 50.88; H, 4.63; N, 4.95; S, 11.30. Found: C, 50.81, 50.69; H, 4.64, 4.53; N, 4.80; S, 11.34.

B. From 1e and Acetic Anhydride.—A stoppered suspension of 1.00 g (2.9 mmol) of once-recrystallized **1e** and 5 ml of acetic anhydride was allowed to stand in the dark at room temperature with occasional swirling. Within 12 hr complete solution occurred; after 2 weeks the clear, orange solution was added with stirring to 20 ml of cold water (ice bath). The ice bath was removed after several hours, but vigorous stirring was continued overnight until the amorphous semisolid was converted into a uniform suspension of flocculent solid. After cooling, the product which was filtered, washed thoroughly with ice water, and dried gave 0.44 g (54%) of cream-colored powder, mp 141–143° dec. Its ir was identical with that obtained for the product in part A above.

N-Acetyl-N-tosylalanine (5b). A. From 5a and Acetic Anhydride.—A stoppered suspension of 7.29 g (0.0300 mol) of powdered N-tosyl-DL-alanine (**5a**)[13] and 30 ml of acetic anhydride was stirred at room temperature. Within 12 hr solution occurred, and after 26 hr this was cooled (ice bath) and 100 ml of ice-cold water added with stirring. The ice bath was removed after 3 hr but stirring was continued for 1 hr during which the initially formed colorless oil dissolved. A small sample of this solution was removed, diluted with excess water, and scratched to initiate crystallization. The reaction mixture then was seeded, and after standing 2 hr (ice bath) the solid was filtered, washed with cold water, and air-dried: yield, 6.30 g (74%) of a snow-white solid; mp 122–123°. Recrystallization from 2:1 carbon tetrachloride–benzene gave colorless prisms: mp 122.5–123.5°; uv max (dioxane) 232 mμ (ε 14,500); ir (Nujol) 1713 (carboxyl or acetamido C=O), 1700 (carboxyl or acetamido C=O), 1350 and 1170 cm^{-1} (SO_2); ir (dioxane) 1755 (carboxyl C=O) and 1707 cm^{-1} (acetamido C=O).

Anal. Calcd for $C_{12}H_{15}NO_5S$: C, 50.52; H, 5.30; N, 4.91; S, 11.22. Found: C, 50.57; H, 5.19; N, 4.80; S, 11.48.

The acetyl group of **5b** was readily cleaved to regenerate **5a**.[14] Thus, when a solution of 2.00 g (7 mmol) of **5b** and 5 ml concentrated NH_4OH, which had been allowed to stand at room temperature for 1 hr, was diluted with water (5 ml) and acidified (pH 1–2) with concentrated HCl, a colorless oil separated which readily solidified. Filtration, washing, and drying gave a 92% yield of **5a**: mp 140–142°, no melting point depression with authentic[13] **5a** and identical ir.

B. By Catalytic Reduction of 3.—PtO_2 (40 mg), 280 mg (0.99 mmol) of **3**, and 20 ml of glacial HOAc was hydrogenated (Parr apparatus) for 12 hr at 40 psig. The catalyst was washed with a little glacial HOAc the combined filtrates were evaporated *in vacuo* almost to dryness. Addition of 15 ml of water to the residual oil and scratching initiated solidification. After cooling (ice bath), the solid was filtered, washed with cold water, and dried: yield 210 mg (75%) of cream powder; mp 122–124°, mmp 122–124° with sample prepared as in A. The ir was identical with that obtained for the product in A.

Registry No. —**1b**, 24571-53-7; **1c**, 24627-11-0; **1d**, 24599-14-2; **1e**, 24627-12-1; **2c**, 24627-13-2; **3**, 24571-54-8; **5b**, 24627-13-4.

(12) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1960, p 34.

(13) A. F. Beecham, *J. Amer. Chem. Soc.*, **79**, 3257 (1957).

(14) J. M. Swan and V. du Vigneaud, *ibid.*, **76**, 3110 (1954).

Dehydration of Amidoximes with and without Rearrangement[1]

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Received July 24, 1969

Carbodiimides **4** and amidines **5** have been obtained for the first time from the reaction between an N-aryl or N-alkyl amidoxime **1** and benzenesulfonyl chloride in pyridine.[2,3] As expected, a 2-substituted benzimidazole is the major product from an N-aryl amidoxime,[3] but similar dehydration of an N-alkyl amidoxime, previously unexplored, does not give an intramolecular cyclization.

Dehydration of an amidoxime without rearrangement leaves an azomethine nitrene **6**. Presumably as a triplet, the nitrene abstracts hydrogen from solvent to bring about the formation of an amidine **5**. Ring closure by intramolecular insertion into an appropriate aromatic CH bond may proceed from a nitrene such as **6a** and **6d**.[4] However, the formation of benzimidazoles in the dehydration of N-aryl amidoximes **1a** and **1d** does not depend on nitrene intermediacy insofar as ring closure from a corresponding nitrenium cation may occur.[5] The formation of a carbodiimide has been found to be concerted with the elimination of carbon dioxide from an oxadiazolone rather than by rearrangement of an azomethine nitrene which is also produced.[4] We now suggest that carbodiimide formation proceeds from an O-benzenesulfonyl ester **2** of an amidoxime simultaneously with α or 1,3 elimination.

(1) Financial assistance was received from NASA Grant No. NGR 14-012-004.

(2) M. W. Partridge and H. A. Turner, *J. Pharm. Pharmacol.*, **5**, 103 (1959), established the initial product as a carbodiimide (RN=C=NH) which rearranged into a cyanamide (RNHCN) in the similar dehydration of a primary amidoxime.

(3) M. W. Partridge and H. A. Turner, *J. Chem. Soc.*, 2086 (1958), produced 2-substituted benzimidazoles from similar treatment of N-aryl amidoximes. When carried out in aqueous sodium hydroxide, carbodiimides, but not benzimidazoles, were obtained from $C_6H_5NHC(R)$=NOH and benzenesulfonyl chloride.

(4) J. H. Boyer and P. J. A. Frints, in press.

(5) Cyclization into a 2-substituted benzimidazole from azomethine nitrenium cations, produced by dissociation of the ester,[2] has been proposed. A discrepancy between product yields for **3a**,[6] **4a**, and **3d**[7] and the corresponding yields previously obtained[3] (Table I) has not been accounted for.

(6) F. C. Cooper and M. W. Partridge, *J. Chem. Soc.*, 225 (1953). An authentic sample was prepared by mixing equivalent amounts of 2-benzylbenzimidazole and benzenesulfonic acid in chloroform.

(7) K. Hoffmann in "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1953, p 380: **3d** hydrochloride mp 90–92°; **3d** picrate mp 212–213°.