mol) was added dropwise to the stirred suspension maintained at 30–35° by an ice–water bath. The mixture became homogeneous when DCU addition was complete, and it was stirred for an additional 0.5 hr. The reaction solution was poured into water (300 ml), and the precipitate of **5** was filtered and dried (4.32 g, 92% yield): mp 186–190° (lit.[4] mp 188°).

Analytically pure **5**, mp 191–192°, was obtained by recrystallization from benzene: ir ($CHCl_3$) 3480 (NH), 1760 (C=O), 1630 (C=C), 1480, 1190, 1180, 970, 850, 825 cm^{-1}.

Anal. Calcd for $C_8H_4Cl_3NO$: C, 40.63; H, 1.70; Cl, 44.97; N, 5.92. Found: C, 40.49; H, 1.66; Cl, 45.10; N, 5.71.

B.—Indole-3-carboxylic acid (**5c**) (3.22 g, 0.020 mol) was treated with DCU as just described to give **5** (4.20 g, 89% yield), mp 180–185°, identical in every respect (melting point, mixture melting point, ir, nmr) with that obtained from the 2 isomer.

C.—Indole (**5a**) (2.34 g, 0.020 mol) yielded crude **5** (4.20 g), mp 150°, containing considerable colored tarry material. Recrystallization failed to yield the pure product. Chromatography on Florisil (1 g of crude **5**/40 g of adsorbent) and elution with 75% ether–pentane yielded analytically pure **5**, mp 188–191° (0.4 g, 40%), identical in every respect with that obtained from **5b** and **c**.

5-Chlorooxindole (**6**).—To a stirred solution of **5** (2.36 g, 0.01 mol) in hot glacial acetic acid (20 ml), zinc–copper couple[13] (7.0 g in 25 ml of acetic acid) was added, and the mixture was refluxed for 18 hr. After filtration, the filtrate was poured into water (250 ml) and the precipitated solid was filtered and dried: yield of crude **6**, 1.32 g (75%); mp 190–195°. Analytically pure **6**, mp 198–198.5° (lit. mp 192° [4] and 195–196° [10]), was obtained by two recrystallizations from ethanol: ir ($CHCl_3$) 3480 (N–H), 1740 and 1710 (C=O), 1640 (C=C), 1480, 1160, 1100, 870 cm^{-1}.

Anal. Calcd for C_8H_6ClNO: C, 57.33; H, 3.61; Cl, 21.15; N, 8.36. Found: C, 57.23; H, 3.73; Cl, 21.03; N, 8.31.

5-Chloroisatin (**7**).—A solution of **5** (1.18 g, 0.005 mol) in 50% aqueous methanol (50 ml) was refluxed for 6 hr, and the cooled solution was poured into water (250 ml). The precipitated red solid was filtered and dried: yield of crude **7**, 0.80 g (85%); mp 250–252°. Analytically pure **7**, mp 251–252° (lit.[14] mp 246–247°), was obtained by two recrystallizations from ethanol: ir ($CHCl_3$) 3460 (N–H), 1760 (C=O), 1620 (C=C), 1470, 1445, 1290, 1190, 1170, 965, 845 cm^{-1}.

Anal. Calcd for $C_8H_4ClNO_2$: C, 52.92; H, 2.22; Cl, 19.52; N, 7.71. Found: C, 52.46; H, 2.40; Cl, 19.60; N, 7.67.

Reduction of **7** (1.40 g, 0.008 mol) with zinc–copper couple as described for **5** also yielded **6**, mp 194–196° (0.85 g, 65%), identical in every respect (ir, melting point, mixture melting point) with an authentic sample.

Methyl Indole-2-carboxylate (**8a**).—This was prepared in 90% yield from **5b** by conventional esterification with methanol (sulfuric acid catalyst), mp 151–152° (lit.[15] mp 150–151.5°).

Methyl Indole-3-carboxylate (**10a**).—As described for the 2 isomer **5c** was converted into analytially pure **10a** in 60% yield: mp 146–147° (lit.[16] mp 147–148°).

2-Carbomethoxy-2,5,7-trichloroindoxyl (**8**).—**8a** (3.50 g, 0.020 mol) was treated with DCU as previously described for **5a–c** to give crude **8** (4.3 g, 90% yield), mp 191–195° (lit.[4] mp 184°). Analytically pure **8**, mp 203–204°, was obtained after two crystallizations from ethanol: ir ($CHCl_3$) 3450 (N–H), 1750 and 1720 (C=O), 1620 (C=C), 1470, 1220, 1170, 1040, 875 cm^{-1}.

Anal. Calcd for $C_{10}H_6Cl_3NO_3$: C, 40.78; H, 2.05; Cl, 36.11; N, 4.76. Found: C, 40.53; H, 2.35; Cl, 36.03; N, 5.07.

5,7-Dichloroindoxyl (**9**).—A solution of **8** (1.50 g, 0.005 mol) was reduced with zinc–copper couple (3.25 g) in acetic acid (35 ml) as described for the reduction of **5** to give **9** (0.8 g, 80% yield), mp 241–242°. Analytically pure **9**, mp 242–243°, was obtained by recrystallization from ethanol: ir (Nujol) 3300 (N–H), 1725 (C=O), 1610 (C=C), 1450, 1305, 1215, 1170, 945, 875, 860, 715 cm^{-1}.

Anal. Calcd for $C_8H_5Cl_2NO$: C, 47.56; H, 2.50; Cl, 35.09; N, 6.93. Found: C, 47.79; H, 2.54; Cl, 34.81; N, 6.74.

3-Carbomethoxy-3,5-dichlorooxindole (**10**).—**10a** (3.50 g, 0.02 mol) was treated with DCU as previously described for **5a–c** and **8a** to give **10** (3.70 g, 75% yield), mp 192–195°. Recrystallization from ethanol yielded pure **10**: mp 195–196°; ir ($CHCl_3$) 3400 (N–H), 1760 and 1740 (C=O), 1620 (C=C), 1470, 1445, 1290, 1190, 1170, 855 cm^{-1}.

Anal. Calcd for $C_{10}H_7Cl_2NO_3$: C, 46.18; H, 2.71; Cl, 27.26; N, 5.39. Found: C, 46.44; H, 2.78; Cl, 27.02; N, 5.27.

Reduction of **10** (1.30, 0.005 mol) with zinc–copper couple (3.25 g) in hot acetic acid gave 5-chloroxindole (**6** 0.75 g, 89% yield), mp 191–193°, identical with an authentic sample (melting point, mixture melting point, ir).

Registry No.—N,N-Dichlorourethan, 13698-16-3; **5**, 17630-74-9; **5a**, 120-72-9; **6**, 17630-75-0; **7**, 17630-76-1; **8**, 17630-77-2; **9**, 17630-79-4; **10**, 17630-78-3.

---

(13) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(14) N. Buu-Hoi, *Rec. Trav. Chim. Pays Bas*, **73**, 197 (1954).

(15) C. Zatti and J. Ciaician, *Ber.*, **21**, 1929 (1888).

(16) C. Zatti and A. Ferratini, *ibid.*, **23**, 2296 (1890).

Reaction of Tosyl Isocyanate with Carboxylate Salts[1]

ROBERT C. KERBER

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11790

Received January 24, 1968

p-Toluenesulfonyl isocyanate reacts readily with carboxylate salts at room temperature to give N-acyl-*p*-toluenesulfonamides. Benzenediazonium-2-carboxylate, however, gives a more complex reaction leading ultimately to N-(*o*-azidobenzoyl)-*p*-toluenesulfonamide. The mechanism of this reaction is discussed.

The reaction of benzyne with phenyl isocyanate was studied by Sheehan and Daves,[2] who found only products derived from 1,4 addition, phenanthridone and 6-phenoxyphenanthridine. In view of the tendency of isocyanates (and other cumulated double-bond systems) to give 1,2 cycloadditions in some cases[3] we felt that investigation of the reaction of benzyne with isocyanates incapable of reacting by 1,4 addition would be of interest as a route to benzazetinones[4] *via* 1,2 cycloaddition.

This led us to decompose benzenediazonium-2-carboxylate (I) in solutions of aliphatic isocyanates and of tosyl isocyanate (II) in the hope of obtaining benzazetinone products *via* 1,2 cycloaddition. Although no such 1,2 cycloadditions were found, a reaction of tosyl isocyanate with I and with other carboxylate salts was found. This reaction constitutes the major portion of this paper.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord, Model 137-B, calibrated with a polystyrene film. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer and are reported as τ values relative to tetramethylsilane as internal standard (τ 10.00). All melting points are un-

---

(1) Presented in part before the Division of Organic Chemistry, 154th Meeting of the American Chemical Society, Chicago, Ill, Sept 13, 1967.

(2) J. C. Sheehan and G. D. Daves, Jr., *J. Org. Chem.*, **30**, 3247 (1965).

(3) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, pp 135–189.

(4) E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966).

corrected. Magnesium sulfate was used as drying agent throughout.

Benzenediazonium-2-carboxylate (I).[5]—A 250-ml two-necked flask fitted with dropping funnel and drying tube was charged with 6.0 ml of butyl nitrite, 30 ml of tetrahydrofuran (THF) (freshly distilled from $LiAlH_4$), and a few crystals of trichloroacetic acid. The solution was cooled in ice and stirred magnetically while a solution of 6.85 g (0.050 mol) of anthranilic acid in 30 ml of THF was slowly added from the dropping funnel. After the addition was complete (45–60 min), stirring was continued at 0° for 15–30 min. The resulting suspension was filtered rapidly; the precipitate was washed with fresh THF and carbon tetrachloride, and rapidly transferred while wet to a stirred solution of the desired reactant in methylene chloride.

Reaction of I with Butyl Isocyanate.—Benzenediazonium-2-carboxylate, I, prepared by the above procedure, was suspended in a mixture of 9.90 g (0.10 mol) of freshly distilled butyl isocyanate, n^{25}_{D} 1.4048, and 100 ml of methylene chloride. The mixture was refluxed for 1.5 hr, then allowed to stand at room temperature for 6 hr. It was cooled in ice, and 9.30 g (0.10 mol) of aniline was added dropwise to destroy excess isocyanate. After standing overnight the solvent was stripped, and ether was added to the residue, leaving a tan solid (A) and a brown solution (B). The solid A was recrystallized from ethanol, which gave 13.30 g of 1-butyl-3-phenylurea: mp 129–131° (74%) (lit.[6] mp 129–130°); infrared bands at 2.95 (N-H), 6.05 (C=O), 13.3 and 14.1 μ (C_6H_5). The mother liquors and solution B were combined and evaporated, and the residue was chromatographed on silicic acid, which yielded, in addition to small amounts of unidentified materials, some unreacted aniline and an additional 1.99 g (12%) of crude 1-butyl-3-phenylurea, mp 120–125°. A quantity of black material was not eluted from the column, even using more polar solvents.

In another run, I was decomposed in a suspension of 20.0 ml (19.80 g, 0.20 mol) of neat butyl isocyanate by warming gently for 2.5 hr. The excess butyl isocyanate was stripped off at reduced pressure. Chromatography of the residue on silica gel again failed to give usable quantities of recognizable products; the major portion of the material appeared as a brown tar eluted only with methanol. Similar results were obtained with methyl isocyanate, neat or in methylene chloride solution.

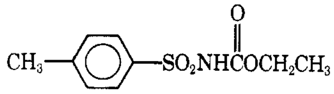
Reaction of I with Phenyl Isocyanate.—I was decomposed by refluxing in a stirred solution of 25 ml of methylene chloride and 10.00 ml (10.95 g, 92.4 mmol) of phenyl isocyanate. After 4 hr, 25 ml of water was added, and the mixture was stirred overnight. The resulting mixture was filtered, and the precipitate was washed with 50 ml of water and four 25-ml portions of ether. Drying left 7.16 g of 1,3-diphenylurea, mp 238–240° (lit.[7] mp 238–240°). The infrared spectrum was identical with an authentic spectrum.[8] The two-layer filtrate was separated, and the aqueous layer was washed with two 50-ml portions of ether. The combined ether layers were dried and evaporated, leaving a brown oily residue, which was chromatographed on Florisil. Elution with 50% benzene–hexane yielded 0.76 g of crude 6-phenoxyphenanthridine (2.8 mmol, 11%), mp 116–118° after recrystallization from ethanol (lit.[2] mp 118–119°); the ir spectrum showed bands at 6.3 (C=N), 6.85, 7.38, 13.2, 13.8, and 14.5 μ. Benzene–ether mixtures of increasing polarity yielded in turn 0.71 g of ethyl carbanilate (4.3 mmol, 4%, identified by infrared comparison with an authentic spectrum[9]) 0.25 g of 1,3,5-triphenylbiuret [mp 148–150° (lit.[2] mp 150–151°), ir bands at 3.01 (N-H), 5.85, 6.25, 8.45, 13.2, and 14.4 μ], and an additional 1.57 g of 1,3-diphenylurea (mp 230–235°, ir identical with authentic[8]), making a total yield of 8.73 g (41.2 mmol, 89%) of the urea. Elution with methanol left a black tar, sublimation of which at 160° (0.2 mm) gave 0.045 g of phenanthridone: mp 287–289° (lit.[2] 285–290°); ir identical with authentic.[10]

Reaction of I with *p*-Toluenesulfonyl Isocyanate (II).—I was added to a solution of 10.0 ml (11.9 g, 0.060 mol) of II in 25 ml of methylene chloride. Reaction began immediately, with vigorous gas evolution, which was complete within 15 min, leaving a homogeneous solution. The solvent was stripped; water was cautiously added to destroy any excess II; and more gas was evolved. Chloroform was added, and the layers were separated. The water layer was washed with chloroform and the combined chloroform layers were extracted with 10% aqueous sodium bicarbonate solution until no more material was extracted (about 200 ml). The bicarbonate layers were acidified with concentrated hydrochloric acid and extracted with four 40-ml portions of ether. Evaporation of these ether layers left material A. Extraction of the chloroform layers with 1% sodium hydroxide followed by acidification left 5.13 g of a red solid, B. The chloroform solution remaining was dried and evaporated, leaving material C. Recrystallization of B from cyclohexane, ethanol–water, and carbon tetrachloride yielded a material of mp 153.5–154.5° with gas evolution. The infrared spectrum of this material in Nujol showed bands at 3.02, 4.65, 5.92, 6.23, 7.40, 8.53, 11.15, 11.8, 12.3 and 13.3 μ. The nmr spectrum in $CDCl_3$ showed resonances at τ −0.2 (s, 1), 1.7–2.0, (m, 3), 2.4–2.9 (m, 5), and 7.58 (s, 3). Titration of the material in 50% aqueous ethanol with 0.02 *N* sodium hydroxide gave a neutralization equivalent of 306 ± 12. These data suggested that the material was N-(*o*-azidobenzoyl)-*p*-toluenesulfonamide, III.

Anal. Calcd for $C_{14}H_{12}N_4SO_3$: C, 53.2; H, 3.79; N, 17.7; S, 10.1; mol wt, 314. Found: C, 53.0; H, 3.74; N, 17.6; S, 9.8.

Hydrolysis of a 0.093-g sample by refluxing for 24 hr in 5% aqueous hydrochloric acid, followed by extraction of the solution with ether, and drying and evaporating the ether left 0.053 g of *p*-toluenesulfonamide, mp 126–131°, (100%); mixture melting point with authentic material, mp 136–138°, was 128–132°.

Chromatography of the material A on silicic acid yielded (1) 0.082 g (1%) of *p*-tolyl *p*-toluenethiolsulfonate, mp 70–72° (lit.[11] mp 75°), infrared and nmr spectra identical with authentic;[11,12] (2) an additional 0.083 g of III, mp 145–147°; (3) 0.47 g of light yellow oil whose spectra were uniquely consistent with the structure[13]



and which was hydrolyzed to *p*-toluenesulfonamide, mp 133–135° (mmp 134–136° with authentic sample), on 3 hr boiling with 5% aqueous hydrochloric acid; and (4) 2.43 g of crude *p*-toluenesulfonamide, mp 136–138° after recrystallization from benzene–heptane, mmp 135–137° with authentic material. Similar chromatography of the residue from the mother liquors from recrystallization of B yielded 0.037 g of *p*-tolyl *p*-toluenethiosulfonate, 0.167 g of III, 0.467 g of N-carbethoxy-*p*-toluenesulfonamide, and 1.85 g of *p*-toluenesulfonamide. Chromatography of the neutral material C gave no identifiable products.

The total crude yields of products are III (5.30 g, 16.8 mmol, 56%); *p*-tolyl *p*-toluenethiolsulfonate (0.94 g, 3.9 mmol, 6%); and *p*-toluenesulfonamide (4.28 g, 25.0 mmol, 41%).

Synthesis of Authentic III.—*o*-Azidobenzoic acid was prepared by the method of Bamberger.[14] The acid (0.56 g, 3.4 mmol) was dissolved in 20 ml of THF and treated with 0.0256 g (3.2 mmol) of lithium hydride. After a few minutes gas evolution ceased, and then 1.00 ml (1.19 g, 6.00 mmol) of II was added. The mixture was stirred at room temperature for 18 hr, then poured into 75 ml of 3% sodium bicarbonate. The resulting solution was extracted with ether to remove *p*-toluenesulfonamide, then acidified and reextracted with ether. Drying and evaporation of the latter ether extracts left 0.68 g of product, which was recrystallized from ethanol–water to yield 0.43 g of III, mp 146–149°, mmp 149–151° with III obtained as described above. The ir and nmr spectra were the same for both samples.

Reaction of Benzenediazonium-4-carboxylate with II.-A 250-ml three-necked flask fitted with stopper, dropping funnel, and drying tube was charged with 6.00 ml of butyl nitrite, 30 ml of THF, and a few crystals of trichloroacetic acid. The solution was ice cooled, and a solution of 6.85 g of *p*-aminobenzoic acid (0.050 mol) in 50 ml of THF was slowly added while the mixture was stirred magnetically. After addition was complete, stirring

---

(5) L. Friedman, *J. Amer. Chem. Soc.*, **89**, 3071 (1967). We are grateful to Professor Friedman for describing this very convenient method of preparing I to us before publication.

(6) T. L. Davis and N. D. Constan, *J. Amer. Chem. Soc.*, **58**, 1800 (1936).

(7) G. Young and E. Clark, *J. Chem. Soc.*, **73**, 361 (1898).

(8) Sadtler Standard Spectrum No. 3899, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1967.

(9) Sadtler Standard Spectrum No. 23619; *cf.* ref 8.

(10) Sadtler Standard Spectrum No. 21101; *cf.* ref 8.

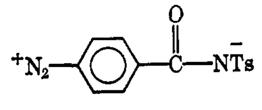
(11) H. Rottendorf and S. Sternhell, *Aust. J. Chem.*, **16**, 647 (1963).

(12) Sadtler Standard Spectrum No. 15579; *cf.* ref 8.

(13) K. Lanyi and Z. Szabo, *Acta. Chim. Acad. Sci. Hung.*, **29**, 85 (1961); *Chem. Abstr.*, **56**, 7194*f* (1963).

(14) E. Bamberger and E. Demuth, *Ber.*, **37**, 1337 (1901).

was continued an additional 75 min, then the mixture was filtered, and the yellow precipitate was washed with fresh THF and added to a solution of 10.00 ml (11.9 g, 0.060 mol) of II in 25 ml of methylene chloride. After 19 hr, the reaction mixture was filtered, and the precipitate was washed with methylene chloride, and dried under vacuum. This yielded 1.02 g of white solid, mp 148–160° with gas evolution. The infrared spectrum showed bands at 4.35, 6.25, 6.4, 7.5, 7.95, 8.5, 8.75, 12.05, 12.35, and 13.1 μ. The nmr spectrum in 5% aqueous NaOH solution showed only aromatic protons at τ 1.7–3.0 and methyl protons at 7.5 (relative areas about 3:1). Addition of a small quantity of this material to an alkaline solution of β-naphthol gave an instantaneous wine-red color. These data suggested that the material was



A sample of this solid (0.914 g, 3.04 mmol) was added in small portions to a solution of 100 ml of 50% hypophosphorous acid at 0°, containing a few crystals of cupric sulfate. Gas was evolved slowly as the solution was stirred for 4.5 hr at 0°, then allowed to warm to room temperature. The solution was diluted with 100 ml of water and extracted with four 40-ml portions of ether. The combined ether layers were extracted with four 25-ml portions of 10% aqueous sodium bicarbonate solution; the resulting solution was acidified with hydrochloric acid and reextracted with three portions of ether. Drying and evaporating the final ether extracts left 0.716 g of red solid, mp 124–135° (85% crude yield of N-benzoyl-p-toluenesulfonamide). Recrystallization from ethanol–water gave pink needles, mp 144–147°, mmp 144–147° with authentic material (*vide infra*).

The filtrate from which the above solid was obtained showed no evidence of azide groups in the infrared, either before or after extraction with base, nor did any of the base-soluble products. Consequently further work with these materials was abandoned.

Reaction of II with Sodium Benzoate.—Solid sodium benzoate (1.74 g, 12.1 mmol) was slowly added to a solution of 2.00 ml (2.38 g, 12.1 mmol) of II in 10 ml of methylene chloride. The mixture was magnetically stirred for 15 hr, then water was added. No gas was evolved. The material was dissolved in ether and 10% aqueous sodium bicarbonate solution, and the layers were separated. The ether layer was extracted with another portion of sodium bicarbonate, and the combined aqueous layers were acidified with hydrochloric acid. The resulting white precipitate was collected by filtration and recrystallized from ethanol–water to yield 3.02 g of white needles, mp 145–148° (91%), of N-benzoyl-p-toluenesulfonamide. An additional recrystallization brought the melting point to 147–148° (lit.[15] mp 147°). The infrared spectrum was identical with an authentic one.[16]

Potassium acetate reacted similarly, giving a 99% yield of N-acetyl-p-toluenesulfonamide, mp 136–138° (lit.[17] mp 139°).

Results

No evidence of direct reaction between phenyl isocyanate or the aliphatic isocyanates and benzenediazonium-2-carboxylate (I) was obtained. The phenyl isocyanate reacted with benzyne from decomposition of I to give 6-phenoxyphenanthridine and phenanthridone, in yields of 11 and <1%, respectively, based on I.[2] The aliphatic isocyanates did not yield characterizable products under these conditions.

In contrast, the more electrophilic p-toluenesulfonyl isocyanate (II) reacted immediately and vigorously with I. Addition of I to a methylene chloride solution of II resulted in immediate reaction, with evolution of gas; the reaction was complete in 15 min. Work-up yielded as the principal product a white solid, mp 153.5–154.5° with decomposition. Its spectra, its analysis, and its neutralization equivalent suggested that this material was N-(o-azidobenzoyl)-p-toluenesulfonamide (III). This was confirmed by its hydrolysis to p-toluenesulfonamide on boiling in 5% aqueous hydrochloric acid, and synthesis of an authentic sample by treating lithium o-azidobenzoate with II.

A small quantity of p-tolyl p-toluenethiolsulfonate was also obtained, presumably from disproportionation of p-toluenesulfinic acid.

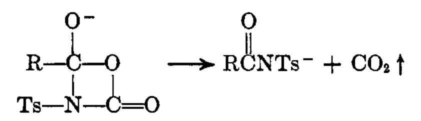
In order to ascertain whether conversion of the diazonium group into the azide group is a result of the proximity of the diazonium and carboxylate groups in I or is a general reaction of II with diazonium salts, the reaction of II with the isomeric benzenediazonium-4-carboxylate was run. This reaction produced in low yield the inner salt, benzenediazonium-4-(N-p-toluenesulfonyl)carboxamidate. The structure of this material was shown by its spectra, its coupling reaction with sodium β-naphthoxide, and its reduction by hypophosphorous acid[18] to N-benzoyl p-toluenesulfonamide. Neither the crude reaction mixture nor any fractions showed any evidence of azide groups in the infrared spectrum, before or after treatment with base.

Lastly, the reaction of II with some simple carboxylate salts was shown to produce excellent yields of N-acyl-p-toluenesulfonamides.[19]

Discussion

The tendency of the isocyanate group to react with nucleophiles at the central carbon atom is greatly enhanced in the sulfonyl isocyanates.[20] This is clearly illustrated by the facile reaction of tosyl isocyanate with the weakly nucleophilic carboxylate salts, even under heterogeneous conditions. The products, N-acyl-p-toluenesulfonamides, have frequently been prepared heretofore by reaction of II with the carboxylic acid at high temperatures.[20] The procedure presented herein of converting the acid into the salt and adding excess tosyl isocyanate at room temperature is rapid and proceeds in high yield. This therefore represents an improved method for the synthesis of N-acylsulfonamides, which can readily be isolated by extraction from the reaction mixture with aqueous sodium bicarbonate. Acidification cleanly regenerates the product.

The reaction of II with a carboxylate salt presumably proceeds by attack of the nucleophile at the central carbon of the isocyanate group, followed by loss of CO_2 (eq 1).



$$RCO_2^- + TsNCO \longrightarrow \underset{-TsN-C=O}{\overset{O}{\overset{\|}{R C}}-O} \longrightarrow \underset{Ts-N-C=O}{R-\overset{O^-}{C}-O} \longrightarrow R\overset{O}{\overset{\|}{C}}NTs^- + CO_2\uparrow \qquad (1)$$

---

[15] A. D. Kemp and H. Steven, *J. Chem. Soc.*, 110 (1948).

[16] Sadtler Standard Spectrum No. 3643; *cf.* ref 8.

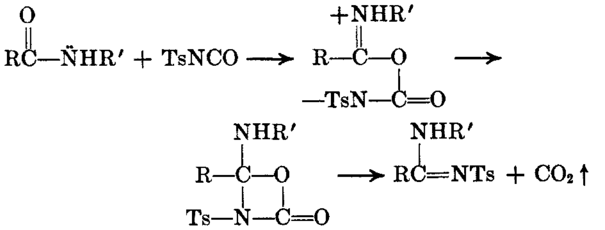
[17] E. Mundlos and R. Graf, *Ann.*, **677**, 108 (1964).

[18] N. Kornblum, *Org. Reactions*, **2**, 294 (1944).

[19] This reaction has also been observed by Dr. Henri Ulrich of the Upjohn Co., North Haven, Conn. We are grateful to Dr. Ulrich for communicating this information to us.

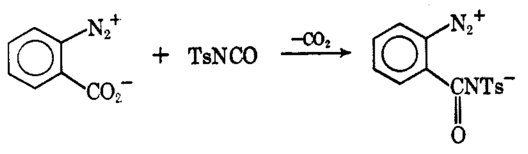
[20] H. Ulrich, *Chem. Rev.*, **65**, 369 (1965).

A similar process has been found to occur with some amides[20] (eq 2).



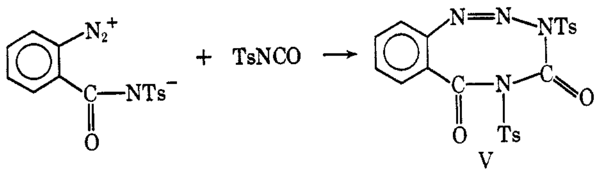
(2)

The reaction of II with benzenediazonium-2-carboxylate apparently is initiated in the same manner as the reaction with other carboxylate salts to produce the inner salt, IV (eq 3). This species may react with another molecule of II to produce a relatively stable intermediate V,[21] hydrolysis of which on work-up produces the observed product, III (eq 4–6). The last step (eq 6), loss of *p*-toluenesulfinate ion from the sulfonyltriazene anion, is also a key step in the conversion of diazonium salts into azides by use of sulfonamides,[22] and reaction of sulfonyl azides with aryl Grignard reagents to give aryl azides.[23]



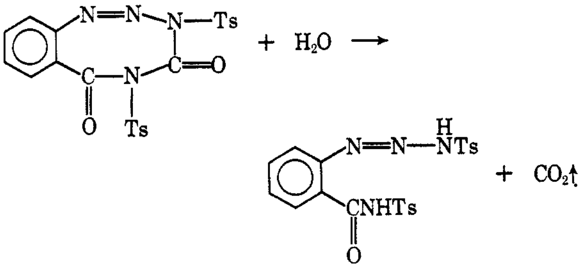
(3)

IV

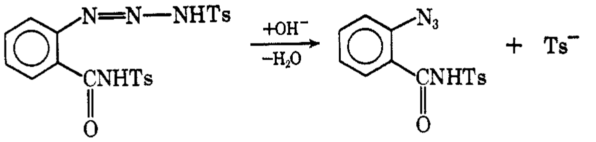


(4)

V



(5)



(6)

III

$$ArN_2^+ + Ar'SO_2NH_2 \xrightarrow{\text{base}} Ar{-}N{=}N{-}NHSO_2Ar' \xrightarrow{-Ar'SO_2H} ArN_3$$

$$ArMgBr + Ar'SO_2N_3 \longrightarrow \underset{MgBr^+}{Ar{-}N{=}N{-}\overset{-}{N}SO_2Ar'} \xrightarrow{-Ar'SO_2MgBr} ArN_3$$

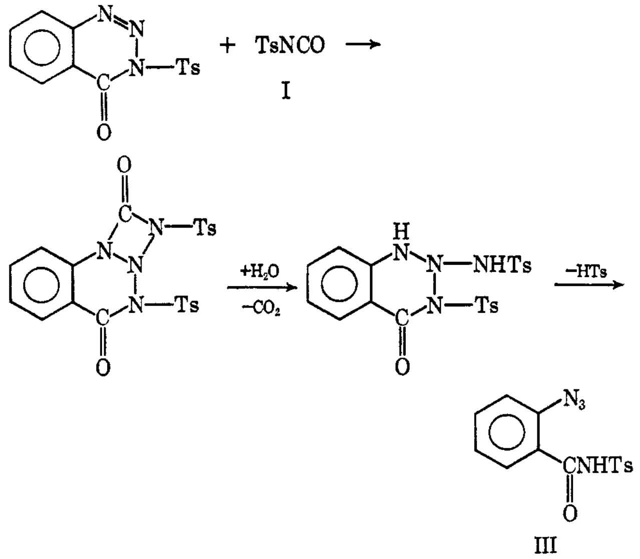
The cyclic nature of the reaction proposed herein is further supported by the fact that benzenediazonium-4-carboxylate fails to yield any products containing azide groups on reaction with II, although reaction at the carboxylate group is rapid, as evidenced by evolution of CO_2.

Registry No.—I, 1608-42-0; II, 4083-64-1; III, 17953-93-4; PhNCO, 103-71-9; benzenediazonium-4-carboxylate, 1837-05-4; BuNCO, 111-36-4; sodium benzoate, 532-32-1.

Acknowledgment.—This work was supported by grants from the Petroleum Research Fund, administered by the American Chemical Socity, and the Research Foundation of the State University of New York. We gratefully acknowledge this support.

---

[21] An alternative scheme for the formation of III may be formulated, involving cycloaddition of tosyl isocyanate to the ring-closed tautomer of IV. However, work being conducted in these laboratories by Mr. Thomas Ryan has shown no evidence of cycloaddition reactions between azo compounds or triazenes and II.



I

III

[22] H. Bretschneider and H. Rager, *Monatsh.*, **81**, 970 (1950).

[23] P. A. S. Smith, L. B. Bruner, and L. O. Krbecheck, unpublished results, quoted in P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, p 248.