Experimental Section[13]

The following general procedure is representative for this reaction. To a stirred solution of 1,3-di-*tert*-butylaziridinone (3a),[14] 553.5 mg (3.35 mmol), in methylene chloride was added a molar solution of triethyloxonium fluoroborate[15] in methylene chloride (3.5 ml) in a drybox. After 4 hr of stirring at room temperature, the solvent was removed by evaporation at low pressure to give a hygroscopic solid, infrared (Nujol) 1670, 1250, and 1150–1020 cm⁻¹. The residue was treated with a 5% aqueous sodium bicarbonate solution and extracted with a diethyl ether, 4 × 15 ml. The combined ether extract was dried over anhydrous magnesium sulfate and the ether was evaporated to give 540 mg of ethyl 2-*N-tert*-butylamino-3,3-dimethylbutyrate (5a): infrared (film) 3425, 1735, and 1225 cm⁻¹; nmr (CDCl₃) δ 4.05 (quartet, 2 H), 3.1 (quartet, 1 H), 1.7 (broad, 1 H), 1.2 (singlet, 9 H), 1.08 (triplet, 3 H), and 0.98 ppm (singlet, 9 H). *Anal.* Calcd for $C_{12}H_{25}NO_2$: C, 66.93; H, 11.70; N, 6.50. Found: C, 66.74; H, 11.63; N, 6.38.

Registry No.—5a, 26153-99-1; **5b**, 26154-00-7; **5c**, 26154-01-8; **5d**, 26154-02-9; **5e**, 26154-03-0.

(13) The infrared spectra were obtained on a Perkin-Elmer 237 spectrophotometer, and nmr spectra were recorded on a Varian A-60 and/or T-60 spectrometer. The mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Microanalyses were performed at the Microanalytical Laboratory of the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., and/or by Galbraith Laboratories, Inc., Knoxville, Tenn.

(14) J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, **89**, 292 (1967).

(15) H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

Reactions of
1,3,3-Trimethyl-2-methyleneindoline
# (Fischer's Base) with Sulfonyl Chlorides[1]

K. Nagarajan* and S. R. Mehta

CIBA Research Centre, Bombay 63, India

Among the reported enamine reactions of Fischer's Base [2–4] (1), there is no mention of its behavior toward organic sulfonyl chlorides.[5] We find that the reaction of methane sulfonyl chloride with Fischer's Base affords in about 50% yield, a mixture of two isomeric products in the ratio of approximately 2:1. The major part, mp 139–141°, was recognized as the cycloaddition product of methylene sulfene[6] to 1. The ir spectrum of 2 had bands at 1145 and 1320 cm⁻¹ for the SO_2 group.[7] The uv spectrum had maxima at 257 nm (log ε 3.97) and 297 (3.46) and was characteristic of an indoline.[8] The 60-Mc nmr spectrum of 2 in CDCl₃ showed signals at 1.33 [singlet, 6 H, C(CH₃)₂], 2.95 (singlet, 3 H, NCH₃), and

* To whom correspondence should be addressed.

(1) Contribution No. 180 from CIBA Research Centre, Bombay 63, India.

(2) M. Coenen, *Angew. Chem.*, **61**, 11 (1949).

(3) K. Blaha and O. Cervinka, *Advan. Heterocycl. Chem.*, **6**, 147 (1966).

(4) A. G. Cook, "Enamines: Synthesis, Structure and Reactions," Marcel Dekker, New York, N. Y., 1969.

(5) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(6) J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 69 (1963).

(7) I. J. Borowitz, *J. Amer. Chem. Soc.*, **86**, 1146 (1964).

(8) T. R. Govindachari, K. Nagarajan, and H. Schmid, *Helv. Chim. Acta*, **46**, 433 (1963).

4.28 ppm (center of a complex A_2B_2 multiplet for 4 H from two CH₂ groups) and the four aromatic protons as multiplets from 6.5 to 7.3 ppm.
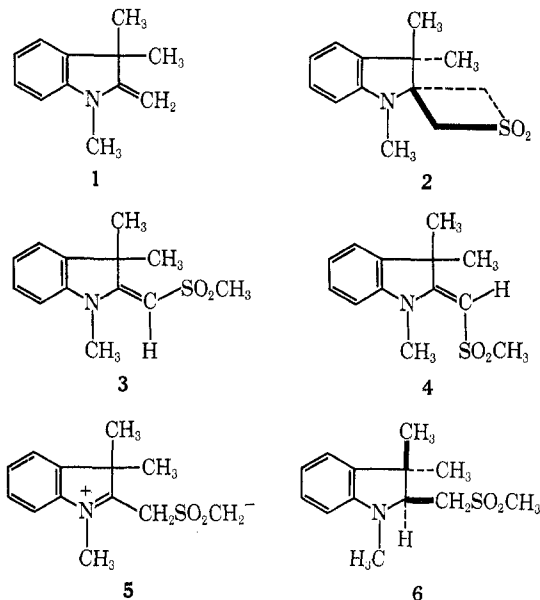
The minor product, mp 120–121°, was identified as the methanesulfonyl derivative **3**. Its ir spectrum showed, in addition to the bands due to the SO_2 group at 1130 and 1300 cm⁻¹, strong absorption for C=C at 1550 cm⁻¹.[9] Its uv spectrum, with maxima at 220 nm (log ε 4.33) and 292 (4.43), indicated that the indoline chromophore was distorted. The nmr spectrum of a fresh solution of **3** in DMSO-d_6 showed signals at 1.67 [singlet, 6 H, C(CH₃)₂], 3.07 (singlet, 3 H, –SO₂CH₃), 3.15 (singlet, 3 H, –NCH₃), and 5.33 ppm (singlet, 1 H, =CH), besides 4 aromatic proton signals spread between 6.7 and 7.4 ppm. The C–CH₃ signals were shifted significantly downfield from their respective positions in **1** (1.27 ppm), **2** (1.33 ppm), and *N*-benzoyl-3,3-dimethyl indoline[10] (1.30 ppm), indicating that this product had the *gem*-dimethyl and –SO₂CH₃ groups cis as in **3** and not trans as in **4**. The smaller shift to downfield of the *N*-methyl group in **3** in comparison with its position in **1** (2.87 ppm) and **2** (2.95 ppm) is to be attributed to its conjugation with the –SO₂CH₃ group. Interestingly, a 24-hr old DMSO-d_6 solution showed new signals (whose intensities did not change further on keeping) at 1.33 ppm [singlet, C(CH₃)₂, ~20% of 6 H], 3.13 ppm (singlet, –SO₂CH₃, ~20% of 3H), and 3.63 ppm (singlet, –NCH₃, ~20% of 3 H). This is best interpreted by assuming that **3** had set up an equilibrium with the cis isomer **4**, using the partial single bond character of the enamine double bond. Compound **4** had the –NCH₃ and –SO₂CH₃ groups cis, accounting for the marked downfield shift of the former, while the *gem*-dimethyl group has the "normal" chemical shift of about 1.3 ppm. Similar equilibria were set up rapidly in pyridine and old samples of CDCl₃ but at measurable rates in fresh CDCl₃. However the ratios of **3** and **4** at equilibrium in the three different solvents were approximately the same (4:1).

It was established that the cycloaddition product **2** was not the precursor of the methanesulfonyl derivative

(9) J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9**, 489 (1966).

(10) K. Nagarajan and P. M. Pillai, *Indian J. Chem.*, **7**, 848 (1969).

3 in its formation from 1 and *vice versa.* Thus 2 was recovered unchanged after being left for 4 days in ether containing excess triethylamine and 1 molar equiv of triethylamine hydrochloride. Its nmr spectrum in pyridine remained unchanged during 48 hr. Compound 3 appeared to decompose to a small extent under the experimental conditions, but 2 was not generated. Moreover the nmr spectrum of 3 in pyridine did not suffer any alteration in 24 hr. Thus 2 and 3 were formed independently in the reaction of 1 with methanesulfonyl chloride, probably from a common zwitterionic intermediate, presumably 5.[4,5]

In vacuo, above its melting point, thietane dioxide (2) partially decomposed to an array of products, among which only traces of 1 and 3 were detectable (tlc), thus differing in this respect from the thermal behavior of thietane dioxide derived from 1-morpholinocyclohexene.[7] The mass spectrum of 2 and 3 also indicated that 2 was not isomerizing to 3 significantly in the probe. Thus the spectrum of 3 showed, in addition to the mass peak at m/e 251, equally intense peaks at 236 (M − CH₃), 172 (M − ·SO₂CH₃), and 157 (M − ·SO₂CH₃ − CH₃). The spectrum of 2 had the mass peak at *m/e* 251 and peaks of greater intensity at *m/e* 173 (M − CH₂SO₂) and 158 (M − CH₂SO₂ − ·CH₃). There was a peak at *m/e* 236 but it was of insignificant intensity.

Thietane dioxide (2) was stable to platinum-catalyzed hydrogenation, while 3 was readily reduced to 6. Spectral data [uv λ_max 249 nm (log ε 3.91), 295 (3.40); nmr (in CDCl₃) signals at 1.13 (singlet, −CCH₃), 1.42 (singlet, −CCH₃), 2.82 (singlet, SO₂CH₃), 2.98 (singlet −NCH₃), 3.42 (multiplet, 3 H, −CHCH₂−), 6.4–7.3 (multiplet, aromatic H)] were in agreement with the structure.

Hot alcoholic alkali treatment of 2 resulted in 50% recovery, 22% isomerization to 3, and about 5% conversion to 1. Under identical conditions, 3 was unaffected.

The reaction of Fischer's Base with *p*-toluenesulfonyl chloride was extremely sluggish as well as complex and afforded two products in minute yields. One, mp 215° dec was recognized as bis-*p*-tolyl sulfone (7) and the other (2% yield), mp 187–188°, as the bis-*p*-toluenesulfenyl derivative (8), from analysis and nmr spectrum.

$$CH_3-\langle\ \rangle-SO_2-SO_2-\langle\ \rangle-CH_3$$

7

8
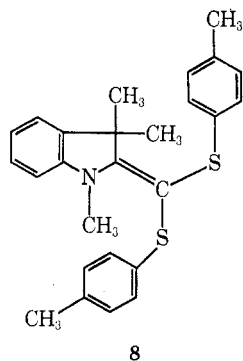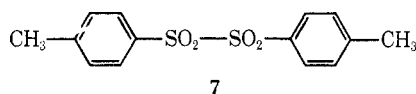
The latter showed singlets at 1.72 [6 H, C(CH₃)₂], 2.28 (6 H, aromatic CH₃), and 3.57 ppm (3 H, −NCH₃). The lower chemical shifts of both the geminal methyl and *N*-methyl groups are to be attributed to deshielding by the benzene rings. The identity of 8 was further

confirmed by comparison with a sample synthesized in 33% yield from Fischer's Base and *p*-toluenesulfenyl chloride.[11]

Compound 8 may be considered to have been formed by initial reduction of *p*-toluenesulfonyl to *p*-toluenesulfenyl chloride by the enamine, followed by addition of the sulfenyl chloride to unchanged enamine. The disulfone (7) is known to be formed from *p*-toluenesulfonyl chloride under reducing conditions.[12] The minute yields of 8 in this reaction do not warrant detailed mechanistic speculation.

Experimental Section

Melting points are uncorrected. Ir spectra were taken in CHCl₃ on a Perkin-Elmer Model 421 spectrophotometer and uv spectra in 95% EtOH on Beckman DK-2A spectrophotometer. Nmr spectra were run on a Varian A-60 spectrometer. Chemical shifts are in ppm downfield from TMS internal standard.

Reaction of Fischer's Base with Methanesulfonyl Chloride.— To a stirred solution of 1 (10.4 g) and triethylamine (6.04 g) in 100 ml of dry ether cooled in an ice bath was added during 0.5 hr, methanesulfonyl chloride (6.86 g) in 10 ml of ether. The mixture was allowed to warm to room temperature, set aside overnight, and filtered. The residue was washed with water. The ether filtrate was concentrated to a small volume and the crystalline precipitate collected. The combined solids were chromatographed over a column of silica gel (0.05–0.2 mm, E. Merck), the column being developed with 1:1 benzene–chloroform mixture. Fifty-ml fractions were collected. Fractions 3–6 on evaporation gave 2 (5.6 g), which was crystallized from ether: mp 139–141° (*Anal.* Calcd for C₁₃H₁₇NO₂S: C, 62.14; H, 6.82; N, 5.57; S, 12.74. Found: C, 62.38; H, 7.00; N, 5.79; S, 13.08%); mass spectrum peaks at *m/e* 251 (17), 236 (<0.5), 173 (100), 158 (100%). Fractions 12–16 were evaporated to give 3 (2.8 g) which was crystallized from alcohol: mp 120–121° (*Anal.* Calcd for C₁₃H₁₇NO₂S: C, 62.14; H, 6.82; N, 5.57; S, 12.74. Found: C, 62.11; H, 6.82; N, 5.67; S, 12.77); mass spectrum peaks at *m/e* 251 (100), 236 (85), 172 (100), 157 (100%). Compound 3 was recovered unchanged after being left in chloroform solution for 48 hr.

Action of Alkali on Thietane Dioxide (2).—A solution of 2 (2 g) in alcohol (50 ml) containing potassium hydroxide (0.6 g) in water (2 ml) was heated under reflux for 6 hr. Most of the solvent was then evaporated off and the residue diluted with water and extracted with ether (50 ml). The ether layer was extracted with three 15-ml portions of 2 *N* hydrochloric acid, washed with water, and dried. Evaporation and trituration of the residue with a little alcohol gave recovered 2 (1 g), mp and mmp 139–141°. The acid extracts were made basic with aqueous sodium hydroxide and extracted with ether. The dried ether layer on evaporation gave soggy crystals (0.7 g), which were washed with a little ether and crystallized from the same solvent to give sulfone 3 (0.44 g), mp and mmp 120–121°. The mother liquor was concentrated and the residual base (0.1 g) converted to the picrate, which on crystallization from aqueous alcohol, had mp 143–145° (*Anal.* Calcd for C₁₈H₁₈N₄O₇: C, 53.73; H, 4.51; N, 13.93. Found: C, 53.50; H, 4.67; N, 13.57), mixture melting point with picrate of 1 was undepressed.

Catalytic Hydrogenation of Sulfone 3.—A solution of 3 (0.2 g) in methanol (10 ml) was shaken with hydrogen at 1 atm pressure in the presence of 10% palladium on charcoal (0.1 g); hydrogen uptake ceased after 1 mol of absorption. Filtration and evaporation gave an oil which formed a hydrochloride, mp 185° dec, after crystallization from methanol–ethanol mixture. The free base 6 was regenerated and crystallized from ether–hexane, mp 99–100° (*Anal.* Calcd for C₁₃H₁₉NO₂S: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.96; H, 7.33; N, 5.82).

Reaction of Fischer's Base with *p*-Toluenesulfonyl Chloride.— An ice-cooled, stirred solution of 1 (15.4 g) and triethylamine (9.1 g) in 100 ml of dry ether was treated with *p*-toluenesulfonyl chloride (17.2 g) in 50 ml of dry ether. The mixture was left

(11) For bis addition of sulfenyl chlorides to enamines, see M. E. Kuehne, *J. Org. Chem.,* **28**, 2124 (1963).

(12) I. A. Pearl, T. W. Evans, and W. M. Dehn, *J. Amer. Chem. Soc.,* **60**, 2478 (1938).

at 30° for 3 days. The ether layer was decanted off from a dark colored sludge which was washed with ether and water and then triturated with alcohol to give a solid. The ether decantate was washed successively with 2 N HCl, water, aqueous $NaHCO_3$ and water, and dried and evaporated. The residue became crystalline with alcohol. The combined solids (1.5 g) were shaken with cold chloroform to give an insoluble part, which was crystallized from hot chloroform to give the disulfone 7 (0.5 g), mp 215° dec (lit.[13] mp 212°) (*Anal.* Calcd for $C_{14}H_{14}O_4S_2$: C, 54.19; H, 4.55. Found: C, 54.43; H, 4.55; N, 0). The chloroform soluble fraction was concentrated and an intermediate fraction separated. The mother liquor was evaporated and the residue crystallized from acetone to give 8 (0.6 g), mp 187–188° (*Anal.* Calcd for $C_{26}H_{27}NS_2$: C, 74.80; H, 6.52; N, 3.36; S, 15.33. Found: C, 75.09; H, 6.73; N, 3.37; S, 14.67).

Reaction of Fischer's Base with p-Toluenesulfenyl Chloride.— A solution of 1 (3.4 g) and triethylamine (4.5 g) in 50 ml of dry ether was mixed at 0° with a solution of p-toluenesulfenyl chloride in carbon tetrachloride (prepared from 5 g of p-toluenethiol and chlorine in nitrogen atmosphere). After being left overnight, the mixture was filtered and washed with ether and water. The crystalline precipitate was recrystallized from acetone to give 8 (2.8 g): mp 185–186° identical with the previous preparation (*Anal.* Calcd for $C_{26}H_{27}NS_2$: C, 74.80; H, 6.52; N, 3.36. Found: C, 75.08; H, 6.62; N, 3.57).

Registry No.—1, 118-12-7; **2**, 26212-68-0; **3**, 26212-69-1; **3** picrate, 26212-70-4; **6**, 26212-71-5; **6** hydrochloride, 26212-55-5; **8**, 26212-56-6.

(13) T. P. Hilditch, *J. Chem. Soc., London, Trans.*, **97**, 2586 (1910).

Synthesis and Properties of *N*-Ethynylcarbazole and Poly-*N*-ethynylcarbazole[1]

YOSHIYUKI OKAMOTO* AND SAMAR K. KUNDU

Research Division, Department of Chemical Engineering, School of Engineering and Science, New York University, University Heights, New York, New York 10453

Recently much attention has been focused on the electronic properties of organic solids and in particular on those exhibiting photoconductive behavior.[2–4] Although numerous organic compounds have been shown to have photoconductive properties, one of the most significant is poly-*N*-vinylcarbazole.[5] In this polymer, carbazole moieties are pendent to a polymer chain containing carbon–carbon single bonds. No conjugation exists in this main chain.

Currently available experimental data show that, in conjugated chain structures, large numbers of electrons cause a decrease of the excitation energy of the π electrons resulting in a compound that shows electrical

conductive properties. It was therefore thought that the conjugate form $(_R>C=C<_H)_n$, where R is carbazole, might possess enhanced electrical conduction. Thus, a study of the polymer might shed additional light on the relationship between chemical structure and electronic properties. Such conjugated polymers appeared to be most easily prepared by polymerization of acetylenic compounds.[6,7] Therefore, we wish to report the preparation and properties of *N*-ethynylcarbazole[8] and its polymers.

The most attractive method for the synthesis of **3** appeared to be by conversion of the commercially available *N*-vinylcarbazole to the α,β-dihalo derivative followed by dehydrohalogenation. Although the preparation of *N*-(α,β-dibromoethyl)carbazole was reported,[9] we were unable to repeat the synthesis even at low temperature and under basic conditions, *e.g.*, by pyridinium hydrobromide perbromide.[10]

An alternate route for the preparation of **3** is from *N*-acetylcarbazole by successive treatment with phosphorus pentachloride and then with potassium hydroxide or sodium amide in liquid ammonia.[7] Accordingly, when *N*-acetylcarbazole (**1**) was reacted with phosphorus pentachloride in refluxing benzene or toluene, *N*-(α,β-dichloroethenyl)carbazole (**2**) was obtained. Dechlorination of **2** with zinc dust,[11] *e.g.*, moist zinc dust in tetrahydrofuran or isopropyl ether, failed. In each case, starting material was recovered. When **2** was refluxed with moist zinc dust in *n*-butyl ether, *N*-(β-chloroethenyl)carbazole was obtained. If **2** was treated with ethanolic potassium hydroxide, nucleophilic substitution by ethoxide occurred instead of dehydrochlorination.

The synthesis of **3** was finally achieved by treatment of **2** with sodium amide in liquid ammonia and then decomposition with ammonium chloride. The structure of **3** was established by elemental analysis and ir, pmr, and mass spectra. The ir spectrum of **3** showed a typical triple bond absorption at 2145 cm^{-1} and acetylenic hydrogen absorption at 3330 cm^{-1}. Its pmr spectrum showed the characteristic singlet due to acetylenic proton at τ 6.82.[12] The presence of a terminal acetylenic group was also confirmed by the formation of silver, copper, and mercury acetylides.[13]

When **3** was allowed to stand at room temperature, it became dark. It was thermally polymerized in toluene, cyclohexane, or without solvent at 100–120° in the absence of a catalyst in sealed tubes under vacuum. These polymers (**4**) were dark brown, soluble in solvents such as benzene, chloroform, and tetrahydrofuran, and insoluble in methanol and ethanol. The ir spectra showed the absence of acetylenic absorption and the presence of intense carbon–carbon double bond absorp-

* To whom correspondence should be addressed.

(1) This work was supported in part by the Air Force Cambridge Research Laboratory, Contract F 19-(628)-69-C-0154.

(2) Y. Okamoto and W. Brenner, "Organic Semiconductors," Reinhold, New York, N. Y., 1964.

(3) F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967.

(4) J. E. Katon, Ed., "Organic Semiconducting Polymers," Marcel Dekker, New York, N. Y., 1968.

(5) H. Hoegl, O. Süs, and W. Neugebauer, German Patent 1,068,115 (1957); 1,111,935 (1958). H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).

(6) Y. Okamoto, A. Gordon, F. Movsovicius, H. Hellman, and W. Brenner, *Chem. Ind. (London)*, 2004 (1961).

(7) Y. Okamoto and D. Alia, *ibid.*, 1311 (1964).

(8) *N*-Ethynylcarbazole has an ynamine structure. For an extensive review on ynamines, see H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **7**, 767 (1967).

(9) T. Talik and J. Pielichowski, *Rocz. Chem.*, **41**, 849 (1967); *Chem. Abstr.*, **67**, 116783v (1967).

(10) L. F. Fieser and M. Fieser, "Reagents for Organic Chemistry," Wiley, New York, N. Y., 1967, p 967.

(11) F. Kunckell and K. Eras, *Chem. Ber.*, **33**, 3264 (1900); **36**, 915 (1903).

(12) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Elmsford, N. Y., 1964, p 61.

(13) The detailed description of the preparations and properties of these acetylides will be reported elsewhere.