of this bond might be considered to provide further evidence that the hybridization of the carbons in an episulfide ring is closer to $sp^2$ than $sp^3$.[10,11]

The naphthalene ring and urethane group, normally expected to be planar to attain full p-orbital overlap, form a dihedral angle of 55.1°; C-11 is 1.05 Å out of the plane of the naphthalene ring. The disruption in p-orbital overlap is reflected in the relatively long bond [1.428(9) Å] between C-1 and N-1 as compared to the 1.325(9) Å bond between N-1 and C-11. The noncoplanarity may be partially caused by nonbonded steric interaction between H-2 and O-1; the energy lost by the disruption of p-orbital overlap is at least partially offset by that gained in the formation of an intermolecular hydrogen bond [2.24(9) Å] between H-1 and O-1 (perpendicular to the viewing axis in Figure 1 and in the packing diagram, Figure 3). This is the shortest intermolecular distance; the N-1–H-1 bond length is 0.74 Å, and the shortest intermolecular distance between nonhydrogen atoms (O-1 and N-1) is 2.89(8) Å.

(11) D. R. Lide, Jr., *Tetrahedron*, **17**, 129 (1961). This sort of shortening has also been observed in substituted cyclopropanes: I. L. Karle, R. D. Gilardi, A. V. Fratini, and J. Karle, *Acta Crystallogr., Sect. B*, **25**, 1469 (1969).

**Registry No.**—(2*S*,3*S*)-1-Cyano-2-hydroxy-3,4-epithiobutane-α-naphthylurethane, 34456-50-3.

**Acknowledgments.**—We thank M. E. Daxenbichler, W. H. Tallent, C. H. VanEtten, and I. A. Wolff of the USDA, Peoria, Ill., for providing crystals, L. L. Reed and P. L. Johnson for valuable advice, the University of Arizona Computer Center for computer time, and the Public Health Service (CA-10944) and Sloan Foundation (Fellowship to R. B. B.) for financial aid.

# Studies on a β-Keto Sulfone. Halogenation and Cyclization of γ-Methylsulfonyl-γ-benzoylbutyronitrile

DOV DILLER AND FELIX BERGMANN*

*Department of Pharmacology, Hebrew University-Hadassah Medical School, Jerusalem, Israel*

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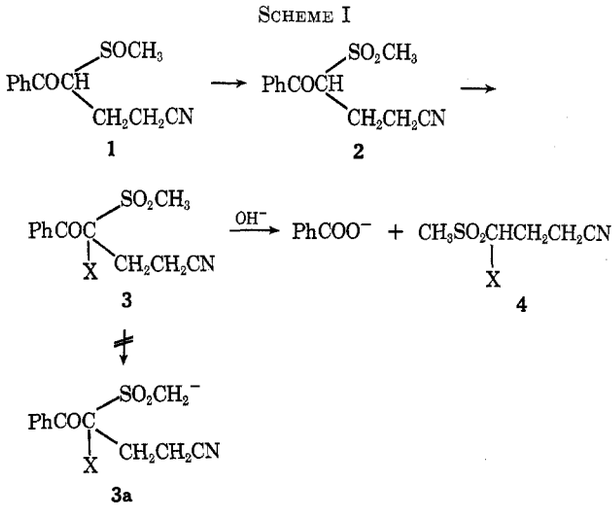
γ-Methylsulfonyl-γ-benzoylbutyronitrile (**2**) can be halogenated at the α position to the carbonyl group in weakly alkaline media. The halogen derivatives **3** are, however, unstable under alkaline conditions and split off the benzoyl group; therefore they are unable to undergo the Ramberg–Bäcklund rearrangement. Anhydrous acids cyclize compound **2** to 3,4-dihydro-5-methylsulfonyl-6-phenyl-2-pyridone (**7**), while with bromine **2** is converted into the 3-bromo derivative of **7**. Photolysis of **2** proceeds either by a Norrish type II cleavage to ω-methylsulfonylacetophenone (**12**) or by rupture of the C–S bond to γ-benzoylbutyronitrile (**13**).

Addition of acrylonitrile to ω-methylsulfinylacetophenone yields the β-keto sulfoxide **1**, which is oxidized by hydrogen peroxide to the corresponding β-keto sulfone, γ-methylsulfonyl-γ-benzoylbutyronitrile (**2**)[1] (see Scheme I). The reactions and properties of the latter form the subject of the present investigation.

SCHEME I




Halogenation of **2** with bromine in aqueous methanolic bicarbonate gave **3** (X = Br). Another successful procedure was treatment of a chloroform solution of **2** with *N*-bromo- or *N*-chlorosuccinimide.

The halogen derivatives **3** proved unstable under a variety of conditions. (1) They easily underwent reduction to **2** when heated in THF or when treated with sodium azide or potassium cyanide in acetonitrile.[2] (2) Dilute (0.5 *N*) NaOH in 50% dioxane or $NaHCO_3$ in dilute methanol splits compounds **3** into benzoate and γ-halogeno-γ-methylsulfonylbutyronitrile (**4**) (see Scheme I), the bromo derivative reacting about twice as fast as the chloro compound. Similarly, the chloro derivative **3** (X = Cl) was decomposed by sodium methoxide in absolute methanol to **4** (X = Cl) and methyl benzoate.

Attempts to iodinate **2** at room temperature in methanolic solution, in the presence of $NaHCO_3$, directly led to the formation of **4** (X = I). Apparently, the sensitivity of **3** to alkaline fission increases in the order X = Cl < Br < I.

Compound **2** itself proved much more stable to alkali. Only contact with 1 *N* NaOH (2 equiv) at room temperature for 24 hr split this compound into benzoic acid and the known γ-methylsulfonylbutyronitrile.[3]

It should be noted that, in contrast to the behavior of 3-substituted pentane-2,4-diones,[4] enolization of

(1) F. Bergmann and D. Diller, *Israel J. Chem.*, **7**, 57 (1969).

(2) Similar reductions of α-halogenosulfones have been described by F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).

(3) W. E. Truce, W. W. Bannister, and R. H. Knospe, *ibid.*, **27**, 2821 (1962).

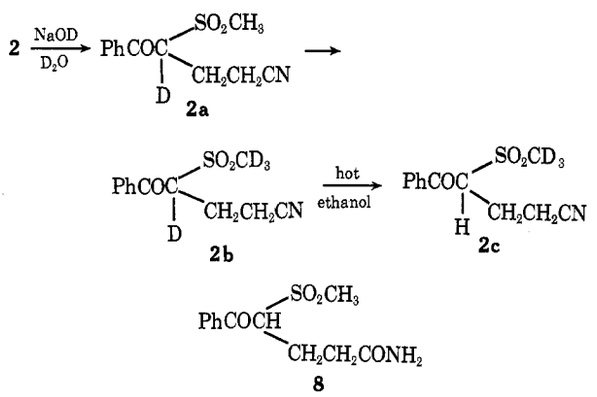
(4) J. B. Conant and A. F. Thompson, *J. Amer. Chem. Soc.*, **54**, 4036 (1932).

the tertiary hydrogen in **2** is lacking, as shown by ir and nmr spectra.[5]

The sensitivity of compounds **3** to alkaline cleavage may be responsible for the failure of the Ramberg–Bäcklund rearrangement,[6] which would require formation of an anion like **3a**. As far as we are aware, only one similar case of a β-keto sulfone with a quaternary carbon has been studied: α-bromo-α-benzylsulfonylcyclohexanone did undergo the expected rearrangement.[7] However, in this derivative, the aromatic substituent facilitates anion formation in the $CH_2$ group, α to the phenyl and the sulfonyl group. It is well known that introduction of phenyl groups into dimethyl sulfone lowers the p$K$ considerably (p$K$ of dimethyl sulfone, 28; of dibenzyl sulfone, 22).[8]

**Deuteration of 2.**—In the presence of 1 equiv of 0.5 $N$ NaOD in $D_2O$ at room temperature, **2** was converted into the tetradeuterio derivative **2b**. Upon heating in ethanol, **2b** lost one deuterium atom to give the trideuterio derivative **2c**. Thus exchange takes place first at the tertiary carbon (**2a**) and subsequently in the methylsulfonyl group (**2b**) (see Scheme II). In fact, the tertiary CH group exchanges even

SCHEME II

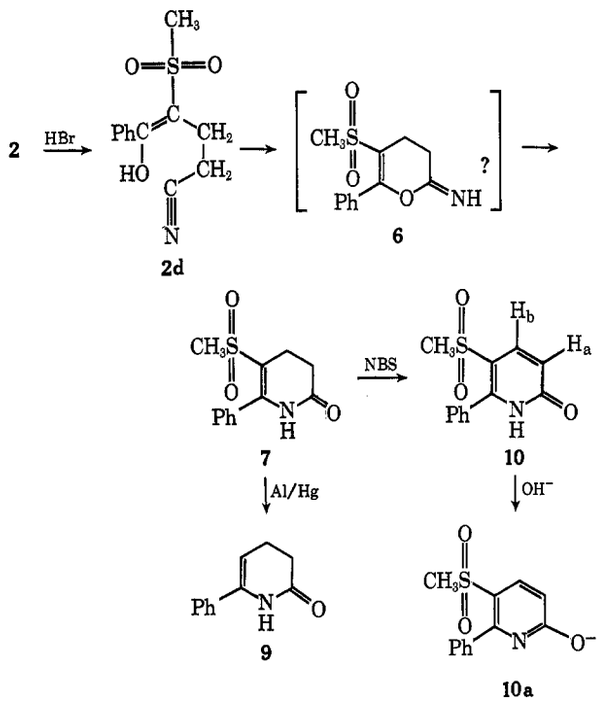


in acetonitrile–$D_2O$ at neutral pH and room temperature to give **2a**, while the methyl group is not attacked under these conditions. The methylene groups, α and β to the nitrile, do not participate in the exchange reactions. Localization of the deuterium atoms in **2a–c** was achieved by means of nmr spectra.

**Cyclization Reactions.**—Treatment of the keto sulfone **2** with HBr in methylene chloride yielded 3,4-dihydro-5-methylsulfonyl-6-phenyl-2-pyridone (**7**). Cyclization of γ-keto nitriles has been studied previously by Kohler, *et al.*,[9] and by Allen and Ball,[10] who assumed the intermediate formation of the amide. We have, however, found that the amide **8**, obtained from **2** by treatment with hydrochloric acid, is resistant to hydrogen bromide. Moreover, treatment of **7** with HBr in dilute acetic acid caused ring opening and gave a quantitative yield of amide **8**. We suggest enolization of **2** and cyclization to the dihydropyran **6**, which rearranges to **7** (see Scheme III). In samples withdrawn during the reaction of **2** with HBr in methylene chloride, tlc showed the presence of a transient intermediate which may be **6**, but this compound could not be isolated.

SCHEME III

CYCLIZATION OF γ-METHYLSULFONYL-γ-BENZOYLBUTYRONITRILE (**2**)



The methylsulfonyl group of **7** was removed by Al/Hg to give 3,4-dihydro-6-phenyl-2-pyridone (**9**), identical with the cylization product of γ-benzoylbutyronitrile.[11] NBS dehydrogenated **7** to the 2-pyridone **10** (see Scheme III).

The structure of **7** is supported by the following observations. (1) In the ir spectrum of **7**, the nitrile band of **2** (at 2250 $cm^{-1}$) has been replaced by two new bands at 3100 and 3200 $cm^{-1}$, characteristic for the NH stretching frequency of lactams.[12] (2) In the nmr spectrum of **7**, bands of vinyl hydrogens are absent; *i.e.*, the double bond must be located at 5,6.

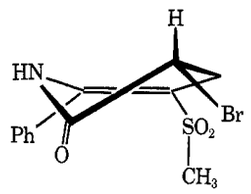
Structure **10** is based on the following data. Two doublets, $H_a$, δ 6.66, and $H_b$, δ 8.08, in $CD_3CN$–$D_2O$, characterize the two vinyl protons.[13] Assignment was possible by the nuclear Overhauser effect (15% increase in the intensity of $H_b$ upon irradiation with the frequency of the methyl signal). A molecular model shows the close proximity of the hydrogen at C-4 to the methyl group of the 5-sulfonyl substituent.

In the anion of **10**, the signal of $H_a$ shifts upfield by 0.34 ppm, the one of $H_b$ only by 0.15 ppm.[14]

**The 3-Bromo Derivative of the Dihydropyridone 7.**—When bromination of **2** was carried out in an aprotic solvent (methylene chloride) in the absence of base, again cyclization took place, but the reaction yielded a

(5) G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1701 (1944).
(6) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968).
(7) I. Shahak and E. D. Bergmann, *Israel J. Chem.*, **8**, 589 (1970).
(8) F. G. Bordwell, R. N. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967).
(9) E. P. Kohler, A. Graustein, and D. R. Merrill, *ibid.*, **44**, 2536 (1922).
(10) C. F. H. Allen and M. L. Ball, *ibid.*, **59**, 686 (1937).
(11) H. Krimm, DBP 1,092,919 (1961).
(12) K. Blaha, J. Smolikova, and K. Vitek, *Collect. Czech. Chem. Commun.*, **31**, 4296 (1966).
(13) Similarly, 6-phenyl-2-pyridone shows $H_a$, 6.51; $H_b$, 7.56; $H_c$, 6.69 (in DMSO–$D_2O$, 2:1). For related observations on 6,*N*-dimethyl-2-pyridone see J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).
(14) Likewise, in the anion of 6-phenyl-2-pyridone the upfield shift for $H_a$ is 0.30.

bromo derivative **11** of the dihydropyridone **7**. The $\lambda_{max}$ of **11** is 265 nm ($\lambda_{max}$ of **7**, 267 nm); its ir spectrum resembles closely that of **7**, but the carbonyl stretching frequency is at 1700 $cm^{-1}$, while that of **7** is at 1680 $cm^{-1}$. α-Halogenation of ketones, by reducing the polarity of the C=O group, raises the carbonyl stretching frequency by 15–20 $cm^{-1}$,[15] but such an effect is missing in α-halo amides. This difference has been explained by Bellamy and Williams[16] in the following way. The amide nitrogen, by virtue of its partial positive charge, attracts the halogen atom and thus brings it into a gauche position relative to the carbonyl oxygen. Furthermore, the partial negative charge at the oxygen atom repels the halogen atom and thus supports the gauche form in which the α halogen has no effect on the polarity of the carbonyl group, in contrast to α-halo ketones. The shift of the carbonyl band in the ir spectrum of **11**, relative to that of **7**, leads us therefore to ascribe to the cyclic amide **11** the following structure, where the bromine atom assumes preferen-



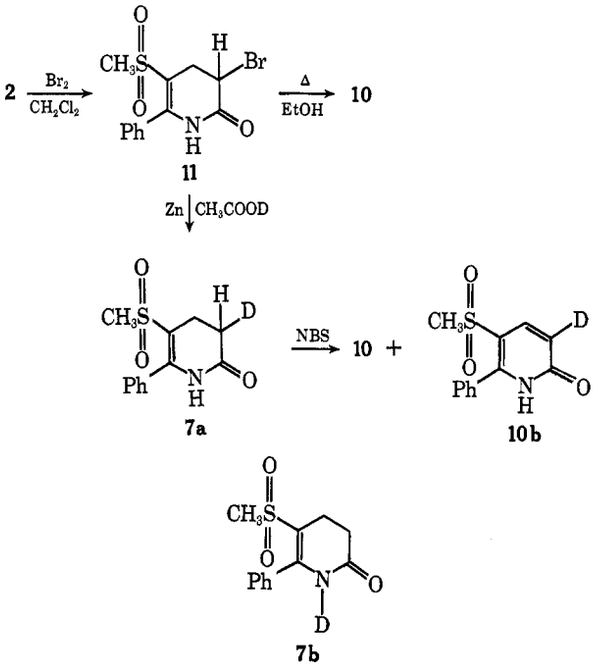
tially the equatorial conformation, thus coming into the plane of the carbonyl group. This may explain the elevation of the carbonyl stretching frequency in **11**. In any case, this elevation is evidence for location of the bromine atom at position 3, *i.e.*, α to the carbonyl; a β halogen would not influence the position of the carbonyl stretching band at all.

When **7** was exposed to bromine under the conditions used for **2**, with or without hydrogen bromide, some degradation products were found, but **11** was not obtained. Therefore the latter is probably formed by bromination of an intermediate state, *e.g.*, **6**.

When **11** was heated in ethanol, it lost HBr to form **10** (see Scheme IV). Therefore, if isolation of **11** was not carried out under special precautions the compound was usually contaminated with the pyridone **10**.

Treatment of **11** with hydrogen–Pd/C or with Zn–acetic acid gave the dihydropyridone **7**. Under the same conditions, or by hydrogen–Raney nickel, **10** was not attacked. These observations made it possible to connect the structure of **11** and **10** in such a way as to confirm the point of attachment of the bromine atom in the former (see Scheme IV). Treatment of **11** with $Zn/CH_3COOD$ gave the monodeuterio derivative **7a**. In the nmr spectrum of the latter, the signal at δ 2.60–2.95 integrates for six instead of seven protons (three of the methyl group, two of the 4-methylene group, and one of the α hydrogen). Dehydrogenations of **7a** with NBS in chloroform yielded a 1:1 mixture of **10** and its monodeuterio derivative **10b**. In the nmr spectrum of this mixture, the doublet at δ 6.66 ($J$ = 10 cps) has remained unchanged, but its area has been halved. Furthermore, instead of the doublet at δ 8.08, three lines are present. In addition to the two

SCHEME IV



components of the doublet at δ 8.16 and 7.99, a signal appears in the middle, *i.e.*, at δ 8.08. It is thus clear that only 50% of the 4-H signal, characterized by δ 8.08, is split by the neighboring vinyl proton, *i.e.*, the latter has been partly replaced by deuterium.[17]

We may thus safely conclude that in **11** the bromine is attached to position 3. It should be recalled that in alkaline media, bromination of **2** takes place exclusively at the tertiary carbon, *i.e.*, at that CH group which dissociates in alkali to form the anion. In contrast, in compound **11** the carbon atom, originally α to the nitrile group, has been halogenated.

**Photochemical Fission of Compound 2.**—Ultraviolet irradiation of **2** in benzene solution furnished two main fission products (see Scheme V): (a) ω-methylsulfonylacetophenone (**12**) (path 1) (Norrish type II cleavage[18]); and (b) γ-benzoylbutyronitrile (**13**) (path 2).

A third product was identified as acetophenone, which could be formed in two ways: (1) by Norrish type II reaction of γ-benzoylbutyronitrile; or (2) from **12**, either by a process analogous to the splitting of γ-benzoylbutyronitrile, or by rupture of the C–S bond to form the radical $C_6H_5COCH_2\cdot$. The latter would then stabilize itself by scavenging a hydrogen atom. In order to decide between these possibilities, both **12** and **13** were irradiated. Only the latter furnished acetophenone (yield practically quantitative), while this product was missing from the photolysis mixture of the β-keto sulfone.

γ-Benzoylbutyronitrile itself could also be formed from **2** in two ways: (1) by intramolecular hydrogen transfer from the methylsulfonyl group, followed by β fission; or (2) by rupture of the C–S bond and formation of radical **13b**, which is then stabilized by abstraction of hydrogen from an external source. These

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958.

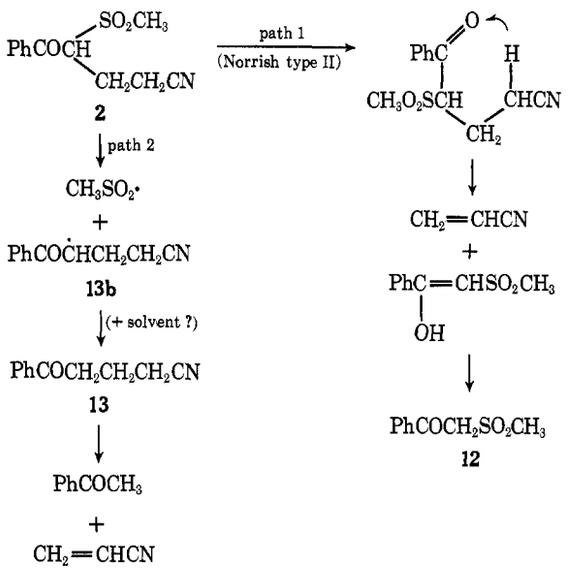
(16) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957).

(17) In accordance with these observations, in the anion of **10b** the halved signal at δ 6.66 undergoes a large upfield shift of 0.34 ppm.

(18) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).

SCHEME V

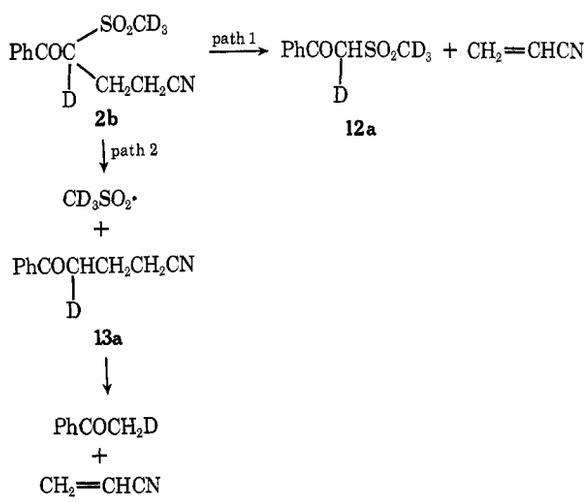
PHOTOLYTIC REACTIONS OF γ-METHYLSULFONYL-γ-BENZOYLBUTYRONITRILE (2)




alternatives can be tested by the use of deuterated derivatives (see Scheme VI).

SCHEME VI

PHOTOLYSIS OF THE TETRADEUTERIO DERIVATIVE 2b




Photolysis of the tetradeuterio derivative **2b** yielded γ-benzoylbutyronitrile with a single deuterium atom at the γ position (**13a**). Likewise the acetophenone, resulting from further splitting, had the structure $C_6H_6COCH_2D$. These results exclude a Norrish type II reaction for the formation of **13** and show that the alternative pathway (2) is correct (see Scheme V). The radical **13b** is stabilized by abstraction of a hydrogen from an external source, *e.g.*, from the solvent (benzene), but not from the methylsulfonyl radical. Abstraction of hydrogen from benzene during photochemical processes has been proposed by various authors.[19,20] Irradiation of **2** in $CCl_4$ yielded only **12**, while **13** and acetophenone were missing.

The photochemical reactions described provide two examples in which a γ-CH group, connected to the carbonyl *via* a chain bearing a sulfonyl, *e.g.*, $\overset{\gamma}{C}HSO_2$-CHCO, is unable to transfer its hydrogen to the CO group by a Norrish type II mechanism. This accords with the observations of McIntosh, *et al.*[21]

(19) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).
(20) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2039 (1963).
(21) C. L. McIntosh, P. de Mayo, and R. W. Yip, *Tetrahedron Lett.*, 37 (1967).

## Experimental Section

All melting points are uncorrected. Microanalyses are by F. Strauss, Oxford. Uv spectra were measured in absolute ethanol on a Beckman DU spectrophotometer ($\epsilon_{max}$ values are given after the wavelength of the absorption maximum), and ir spectra were measured in KBr on a Perkin-Elmer Model 337 infrared spectrophotometer. Nmr spectra (TMS internal standard) were run on a Varian T-60 and a Jeol C-60-H instrument. *pK* values were determined in water from a plot of $\lambda_{max}$ as a function of pH.

For tlc, fluorescent silica gel GF 254 was used. Three solvents served for separation: A, chloroform–methanol, 9:1 v/v; B, chloroform–tetrahydrofuran, 2:1 v/v; C, chloroform–ethyl acetate, 7:1 v/v. Spots were detected with the aid of a Mineralight short-wave lamp ($\lambda \sim 255$ nm) or by exposure to iodine vapor.

**Bromination of γ-Benzoyl-γ-methylsulfonylbutyronitrile to 3 (X = Br).**—To a mixture of γ-benzoyl-γ-methylsulfonylbutyronitrile (**2**)[1] (7.5 g, 0.03 mol) in methanol (180 ml) and sodium bicarbonate (5.8 g, 0.07 mol) in water (135 ml) was added a solution of bromine (5.5 g, 0.034 mol) in methanol (18 ml). The clear solution was stirred at room temperature for 15 min, when the color had disappeared and a colorless precipitate had formed. The solid was recrystallized from aqueous methanol as colorless rhombohedra: mp 91°; yield 6.3 g (64%); $uv_{max}$ 263–264 nm (ε 9870); $R_f$ (A) 0.68; ir 1675 (C=O), 1150, 1320 ($SO_2$), 2250 $cm^{-1}$ (CN); nmr ($CDCl_3$) δ 2.50–3.20 (m, 4, $CH_2$ β and γ to $SO_2$), 3.26 (s, 3, methyl), 7.55 (m, 3, meta and para hydrogens of phenyl), 8.16 (m, 2, ortho hydrogens).

*Anal.* Calcd for $C_{12}H_{12}BrNO_3S$: C, 43.6; H, 3.6; N, 4.2; Br, 24.2. Found: C, 43.9; H, 3.8; N, 4.2; Nr. 24.3.

**Preparation of γ-Benzoyl-γ-chloro-γ-methylsulfonylbutyronitrile (3, X = Cl).**—A solution of **2** (1.75 g) and *N*-chlorosuccinimide (1 g) in chloroform (14 ml) was refluxed for 45 min. The solution was chromatographed on 20 silica gel plates (0.75 mm thickness) in solvent A. The bands of **3** (X = Cl) were extracted with chloroform, the solvent was evaporated, and the residue was recrystallized from isopropyl alcohol as colorless prisms: mp 80–81°; yield 1.6 g (80%); $uv_{max}$ 261 nm (ε 9960); $R_f$ (A) 0.72; ir 1675 (C=O), 1147, 1318 ($SO_2$), 2250 $cm^{-1}$ (CN); nmr ($CDCl_3$) δ 2.50–3.05 (m, 4, $CH_2$ β and γ to $SO_2$), 3.20 (s, 3, $CH_3$), 7.83 (m, 3, meta and para protons of phenyl), 8.13 (m, 2, ortho hydrogens).

*Anal.* Calcd for $C_{12}H_{12}ClNO_3S$: C, 50.4; H, 4.2; N, 4.9; Cl, 12.4. Found: C, 50.2; H, 4.5; N, 4.9; Cl, 12.5.

**γ-Halogeno-γ-methylsulfonylbutyronitriles (4). A. 4, X = Cl.**—A solution of **3** (X = Cl) (0.6 g) in methanol (12 ml) was mixed with a solution of potassium carbonate (0.3 g) in water (6 ml). After standing at room temperature for 45 min, the solution was concentrated *in vacuo* and the residue was recrystallized from benzene–cyclohexane as colorless rods: mp 74°; yield 0.2 g (84%); no uv absorption above 220 nm; $R_f$ (A) 0.50; ir 1140, 1315 ($SO_2$), 2250 $cm^{-1}$ (CN); nmr ($CDCl_3$) δ 4.83 (m, 1, CH), 2.20–3.00 (m, 4, $CH_2$ β and γ to $SO_2$), 3.10 (s, 3, $CH_3$).

*Anal.* Calcd for $C_5H_8ClNO_2S$: C, 33.1; H, 4.4; Cl, 19.6. Found: C, 33.4; H, 4.3; Cl, 19.7.

The same compound was obtained in 50% yield by treatment of **3** (X = Cl) with 1 *N* $NaOCH_3$ in methanol.

**B. 4, X = Br.**—To a mixture of **2** (1 g) in methanol (24 ml) and of potassium carbonate (0.6 g) in water (12 ml) was added a solution of bromine (0.7 g) in methanol (3 ml). After standing for 30 min at room temperature, the solution was concentrated *in vacuo*. The residue was treated as described for the chloro derivative, and obtained as colorless rods: yield 0.8 g (89%); mp 89°; $R_f$ 0.54; ir 1132, 1305 ($SO_2$), 2240 $cm^{-1}$ (CN); nmr ($CDCl_3$) δ 4.85 (m, 1, CH), 2.25–3.00 (m, 4, $CH_2$ β and γ to $SO_2$), 3.15 (s, 3, $CH_3$).

*Anal.* Calcd for $C_5H_8BrNO_2S$: C, 26.6; H, 3.5; N, 6.2; S, 14.2. Found: C, 26.9; H, 3.9; N, 6.2; S, 14.1.

**C. 4, X = I.**—To a mixture of **2** (0.5 g) in methanol (15 ml) and sodium bicarbonate (0.4 g) in water (10 ml) was added a solution of iodine (0.6 g) in methanol (6 ml). After standing at room temperature for 24 hr, the methanol was removed *in vacuo* and the aqueous layer was extracted with chloroform. The organic layer was dried over sodium sulfate and brought to dryness *in vacuo*. The residue crystallized upon treatment with toluene. From benzene–cyclohexane colorless needles were obtained: mp 77°; yield 0.25 g (46%); $uv_{max}$ 256 nm (ε 725); $R_f$ 0.54; ir 1137, 1307 ($SO_2$), 2240 $cm^{-1}$ (CN); nmr ($CDCl_3$) δ 4.95 (m, 1, CH), 2.20–2.95 (m, 4, $CH_2$ β and γ to $SO_2$), 3.20 (s, 3, $CH_3$).

*Anal.* Calcd for $C_5H_8INO_2S$: C, 22.0; H, 2.9; N, 5.1; I, 46.5. Found: C, 22.1; H, 3.0; N, 4.8; I, 46.6.

**γ-Methylsulfonylbutyronitrile (4, X = H).**—A suspension of **2** (5 g) in 1 *N* NaOH was stirred at room temperature for 24 hr, when a clear solution was obtained. Acidification with concentrated HCl precipitated a solid, mp 122°, identified as benzoic acid. The filtrate was extracted with chloroform and the solvent was evaporated *in vacuo*. The sirupy residue (0.45 g) was chromatographed on ten silica plates with the aid of solvent A. **4** (X = H) was localized by means of iodine vapor and extracted with chloroform. The chloroform residue crystallized spontaneously, mp 44°. It proved identical with the compound described by Truce, *et al.*[3]: $R_f$ 0.38; ir 1130 ,1305 ($SO_2$), 2250 $cm^{-1}$ (CN); nmr ($CDCl_3$) δ 3.19 (t, 2, $CH_2$ α to $SO_2$), 2.26 (m, 2, $CH_2$ β to $SO_2$), 2.65 (t, 2, $CH_2$ γ to $SO_2$), 2.97 (s, 3, $CH_3$).

*Anal.* Calcd for $C_5H_9NO_2S$: C, 40.8; H, 6.1; S, 21.8. Found: C, 40.8; H, 6.1; S, 22.0.

**γ-Benzoyl-γ-methylsulfonylbutyramide (8).**—A suspension of **2** (5 g) in concentrated HCl (50 ml) was stirred at room temperature for 4–5 hr, until a clear solution was obtained. The precipitate, resulting from neutralization with sodium bicarbonate, crystallized from methanol or THF–cyclohexane in rhomboids: mp 154°; yield 3.6 g (67%); $uv_{max}$ 254 nm (ε 26,000); $R_f$ (A) 0.26; ir (Nujol) 1675 (C=O), 1122, 1310 ($SO_2$), 1650, 3175, 3300, 3410 $cm^{-1}$ ($CONH_2$); nmr ($CD_3CN$) δ 5.37 (t, 1, CH), 2.15–2.85 (m, 4, $CH_2$ β and γ to $SO_2$), 2.97 (s, 3, $CH_3$), 7.70 (m, 3, meta and para hydrogens of phenyl), 8.17 (m, 2, ortho hydrogens).

*Anal.* Calcd for $C_{12}H_{15}NO_4S$: C, 53.5; H, 5.6; N, 5.2; S, 11.9. Found: C, 53.3; H, 5.6; N, 5.5; S, 12.2.

**Deuteration of 2.**—**2** (10 g) was stirred with 1 equiv of 0.5 *N* NaOD in $D_2O$ at room temperature for 24 hr. By addition of 1 equiv of $CH_3COOD$, a white precipitate (5.5 g) was formed; it was filtered off and washed with $D_2O$. It was identified as the tetradeuterio derivative **2b** by the nmr and mass spectra. A sample of **2b** was dissolved in hot absolute ethanol. From the cooled solution the trideuterio derivative **2c** was isolated.

**Cyclization of 2 to 3,4-Dihydro-5-methylsulfonyl-6-phenyl-2-pyridone (7).**—Through a solution of **2** (4 g) in methylene chloride (30 ml), cooled to 0°, was passed dry HBr gas until saturation. The solution was then kept at room temperature for 22 hr. The precipitate was removed and treated in warm methanol with solid sodium bicarbonate. From the filtrate, we obtained 1.8 g (45%) of solid **7** and from methanol long, colorless needles: mp 255°; $uv_{max}$ 227 nm (ε 8700), 267 (10,700); $R_f$ (A) 0.49, (B) 0.40; $pK_a$ 11.3; ir 1680 (C=O), 1140, 1302 ($SO_2$), 3100, 3200 $cm^{-1}$ (NH); nmr ($CD_3COOD$) δ 2.60–2.95 (m, 4, 3- and 4-$CH_2$), 2.95 (s, 3, $CH_3$), 7.55 (s, 5, aromatic).

*Anal.* Calcd for $C_{12}H_{13}NO_3S$: C, 57.4; H, 5.2; N, 5.6. Found: C, 57.4; H, 5.2; N, 5.7.

**5-Methylsulfonyl-6-phenyl-2-pyridone (10).**—A solution of the dihydropyridone **7** (2.5 g) and *N*-bromosuccinimide (3.6 g) in chloroform (150 ml) was refluxed for 3 hr. The solvent was removed *in vacuo* and the sirupy residue was dissolved in 15 ml of 60% ethanol. From the mixture, kept in the refrigerator for 24 hr, colorless crystals separated. From ethanol 1.5 g (60%) of colorless needles were obtained: mp 260–265°; $uv_{max}$ 207 nm (ε 16,600), 248 (14,500), 303 (6920); $R_f$ (A) 0.43, (B) 0.26; p*K* 8.6; ir 1660 (C=O), 1128, 1303 ($SO_2$), 3040, 3110 $cm^{-1}$ (NH);[22] nmr ($CD_3CN$–$D_2O$, 2:1) 6.66 (d, 1, 3-H, $J_{3,4}$ = 10 Hz), 8.08 (d, 1, 4-H), 2.87 (s, 3, $CH_3$), 7.57 (s, 5, aromatic); nmr (DMSO-$d_6$) δ 6.46 (d, 1, 3-H, $J_{3,4}$ = 10 Hz), 7.86 (d, 1, 4-H), 2.85 (s, 3, $CH_3$), 7.48 (s, 5, aromatic).

*Anal.* Calcd for $C_{12}H_{11}NO_3S$: C, 57.8; H, 4.4; N, 5.6; S, 12.9. Found: C, 58.0; H, 4.4; N, 5.7; S, 12.9.

**Conversion of Pyridone 10 into 3,4-Dihydro-6-phenyl-2-pyridone (9).**—A solution of the pyridone **10** (4 g) in 240 ml of THF, containing 10% water and cooled to 4°, was stirred with aluminum amalgam (prepared from 12 g of aluminum foil according to Corey and Chaykovsky[23]). A sample, removed after 2 hr, showed on tlc the formation of the dihydro derivative **7**. The latter was identified by uv, ir, and nmr spectra. After 16 hr, a mixture of **7** and **9** was present, while after 24 hr only the latter derivative had been left. The conversion of **10** → **9** thus takes place in the following two steps: **10** → **7** → **9**. The reaction mixture was filtered and the filtrate was brought to dryness *in vacuo*. The mixture was chromatographed on 20 silica gel plates using solvent C. The product **9** was extracted with benzene and recrystallized first from benzene–cyclohexane, then from methanol as colorless plates (0.6 g), mp 155°. The substance proved identical with a sample of 3,4-dihydro-6-phenyl-2-pyridone prepared according to Krimm:[11] $uv_{max}$ 223 nm (ε 17,000), 270 (6300); $R_f$ (A) 0.70, (B) 0.51; p*K* > 13.5; ir 1680 (C=O), 3100, 3200 $cm^{-1}$ (NH); nmr ($CDCl_3$) δ 2.45–2.75 (m, 4, 3- and 4-$CH_2$), 5.45 (t, 1, 5-CH), 7.38 (s, 5, aromatic).

**3-Bromo-3,4-dihydro-5-methylsulfonyl-6-phenyl-2-pyridone (11).**—A mixture of **2** (4 g) and bromine (2.8 g) in methylene chloride (40 ml) was kept at room temperature for 4 days, when the color of the halogen had disappeared. The precipitate was filtered off and dissolved at room temperature in tetrahydrofuran. Cautious addition of two volumes of cyclohexane caused crystallization of colorless needles: mp 259°; yield 3.3 g (62%); $uv_{max}$ (acetonitrile) 234 nm (ε 8900), 265 (7950); $R_f$ (A) 0.59, (B), 0.56; ir 1700 (C=O), 1140, 1305 ($SO_2$), 3105, 3205 $cm^{-1}$ (NH); nmr (DMSO-$d_6$) δ 4.81 (t, 1, 3-H), 3.22 (d, 1) and 3.30 (d, 1, both for 4-$CH_2$), 2.86 (s, 3, $CH_3$), 7.40 (s, 5, aromatic).

*Anal.* Calcd for $C_{12}H_{12}BrNO_3S$: C, 43.6; H, 3.6; N, 4.2; Br, 24.2. Found: C, 43.8; H, 3.7; N, 3.8; Br, 24.5.

**Reduction of 11 to 7.**—A solution of **11** (0.8 g) in THF (50 ml) was shaken with 10% Pd/C (0.4 g) and MgO (0.4 g) under a hydrogen pressure of 2 atm at room temperature for 2 hr. The filtrate was brought to dryness and the solid residue was recrystallized from ethanol as long, colorless rods, yield 0.5 g (83%), mp 255°, identical with product **7** described above.

**Reduction of 11 to 7a.**—A solution of the bromo derivative **11** (165 mg) in $CH_3COOD$ (12 ml) was mixed with zinc powder (100 mg) and refluxed for 2 hr. The residue, obtained after filtration and evaporation of the solvent, was recrystallized from absolute ethanol as colorless rods, mp 255°, yield 108 mg (86%), identical with **7**, but containing a single deuterium atom, as determined by nmr and mass spectra.

The 3-deuterio derivative **7a** was dehydrogenated with *N*-bromosuccinimide, as described before for the conversion of **7** → **10**. The product was a 1:1 mixture of **10** and **10b** (see Scheme IV).

**Dehydrobromination of 11 to 10.**—A suspension of the bromo derivative **11** (5 g) in ethanol (150 ml) was refluxed for 20 hr. When cooled, the solution deposited colorless crystals, yield 3 g (79%). From ethanol, colorless needles were obtained, mp 260–265°, identical with the pyridone **10** described before.

The same reaction could be effected by dissolving the bromo derivative **11** in 1 *N* NaOH.

**Photochemical Reactions. A. Photolysis of 2.**—A solution of **2** (1 g) in absolute benzene (225 ml) was stirred at room temperature and irradiated for 140 min under nitrogen. A brown turbidity was removed by filtration and the solvent was evaporated. The residue was dissolved in THF and chromatographed on 15 plates with solvent C. Five components were separated (Table I).

**B. Photolysis of γ-Benzoylbutyronitrile (13).**—γ-Benzoylbutyronitrile (0.5 g) in benzene (250 ml) was irradiated as above for 30 min. On tlc, only one product (acetophenone) was separated, in nearly quantitative yield.

**C. Photolysis of ω-Methylsulfonylacetophenone (12).**—This

(22) Since the NH band is found in the region where also the absorption due to stretching of aromatic CH bonds appears, the assignment was verified with the corresponding ND derivatives. In the latter, the bands at 3050, 3040, and 3110 $cm^{-1}$, respectively, are missing and a new band near 2250 $cm^{-1}$ has appeared; the ratio $\nu_{NH}/\nu_{ND}$ is 1.37, as expected. See C. N. R. Rao in "Chemical Application of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 15.

(23) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

TABLE I

| $R_f$ | Amount, mg | Identified as[a] |
|---|---|---|
| 0.60 | 110 | Acetophenone |
| 0.52 | 350 | γ-Benzoylbutyronitrile (**13**) |
| 0.29 | 80 | ω-Methylsulfonylacetophenone (**12**) |
| 0.22 | 80 | **2** |
| 0.08 | 115 | *b* |

[a] Identification is based on ir and nmr spectra and on $R_f$ values. [b] Not identified.

compound was irradiated for 60 min under the same conditions as described above. A multitude of products was obtained on tlc, but acetophenone was not detected.

**Registry No.**—**3** (X = Br), 34502-55-1; **3** (X = Cl), 34502-56-2; **4** (X = Cl), 34502-57-3; **4** (X = Br), 34502-58-4; **4** (X = I), 34502-59-5; **4** (X = H), 34502-60-8; **7**, 34502-61-9; **8**, 34502-62-0; **9**, 34502-63-1; **10**, 34502-64-2; **11**, 34502-16-4.

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# The Pyrolysis of 2*H*-Naphth[1,8-*cd*]isothiazole 1,1-Dioxide and Its 2-Phenyl Analog

D. C. DE JONGH*[1] AND G. N. EVENSON

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202*

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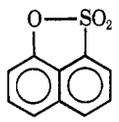
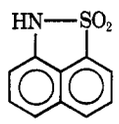
The pyrolytic reactions of 2*H*-naphth[1,8-*cd*]isothiazole 1,1-dioxide (**2**) and 2-phenylnaphth[1,8-*cd*]isothiazole 1,1-dioxide (**3**) are described. The major products from the pyrolysis of **2** were 2-cyanoindene (**5**) and 3-cyanoindene (**6**) (1.2/1, 68%). The major product from the pyrolysis of **3** was 7*H*-benz[*k*,*l*]acridine, in 43% yield. The mass spectra of **2** and **3** are discussed. Synthetic routes to **5** and **6** were developed in order to aid in their identification in the mixture obtained from the pyrolysis of **2**.

We have reported the mass spectra and pyrolyses of *o*-phenylene sulfite,[2,3] *o*-phenylene carbonate,[4,5] 2-pyrone, and 2-pyridone.[6] This procedure has recently been used by Chapman to obtain cyclopentadienone on a low-temperature ir cell from *o*-benzoquinone, *o*-phenylene sulfite, and *o*-phenylene carbonate.[7]

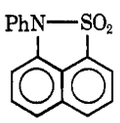
As part of this project, we have pyrolyzed naphth[1,8-*cd*]-1,2-oxathiole 2,2-dioxide (**1**).[8] The formation



**1**



**2**

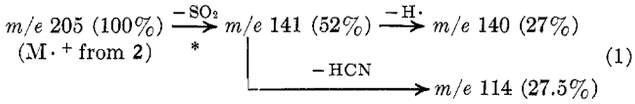


**3**

of the products which are isolated can be rationalized in terms of loss of $SO_2$ from **1**, followed by the trapping of the intermediate which results. We have also studied 2*H*-naphth[1,8-*cd*]isothiazole 1,1-dioxide (**2**) and 2-phenylnaphth[1,8-*cd*]isothiazole 1,1-dioxide (**3**) and describe our procedures and results in this article.

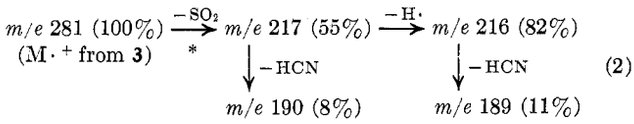
## Results and Discussion

The major peaks in the mass spectrum of **2** arise from loss of $SO_2$ from the molecular ions, followed by H· or HCN (eq 1). The most intense fragment ion



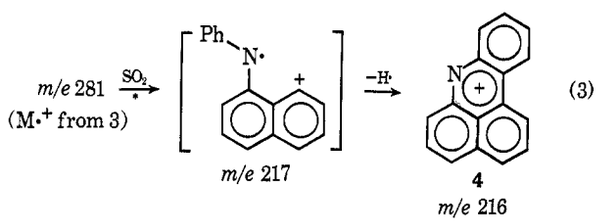

(1)

is *m/e* 141, and a metastable peak is present for the loss of $SO_2$ from *m/e* 205. Similar behavior is observed from **3** (eq 2). However, in this case the most




(2)

intense fragment ion results from the elimination of $SO_2$ followed by H·. It is possible to postulate a stable structure (**4**) for *m/e* 216, which may explain its high relative intensity (eq 3). However, no evidence is




(3)

available to support these postulations.

On the basis of these facile losses of $SO_2$ from **2** and **3** in the mass spectrometer, we were encouraged to try to find products from similar losses of $SO_2$ pyrolytically.

Compound **2** was pyrolyzed in a stream of $N_2$ by sublimation into a pyrolysis zone containing a heated coil constructed from chromel wire. A series of cold traps condensed the products as they emerged from the pyrolysis zone. The highest yields were obtained when the temperature was 720–740° and when the pressure of $N_2$ was 3.0–3.5 mm. The ir spectrum of

(1) Departement de Chimie, Université de Montréal.

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