superimposed signals, one triplet and another quartet, which proved to be coupled with the counterparts of methyl or methylenic signals in the higher field, by double-resonance methods. Namely, when the triplet of methyl at δ 1.18 was irradiated ($\Delta\omega$ = 134.3 cps), the quartet at δ 3.47 coalesced, and, when the triplet of methylene at δ 1.79 was resonated, the triplet at δ 3.37 again changed into a singlet. *Anal.* Calcd for $Cl_3SiC_4H_9$: Cl, 51.3; Si, 13.5. Found: Cl, 51.0; Si, 14.0. This compound was again identified after being converted to 2-triethoxysilylethyl ethyl ether.

A fraction boiling at 65.5° (6 mm) was identified as 2-trichlorosilyl ethyl acetate (1:1 adduct): bp 65.5° (6 mm) [lit.[2] 64.5–66.5° (6 mm)]; $n^{20}D$ 1.4454; ir 1745 (C=O), 1230 cm^{-1} (C–O). *Anal.* Calcd for $Cl_3SiC_4H_7O_2$: Cl, 48.01; Si, 12.68. Found: Cl, 48.31; Si, 12.56.

Distillation residues (>70° (6 mm)) of several runs were collected. Distillation (3 mm) of the collected residues (100 g) indicated decomposition slowly occurring, but gave 21 g of a fraction (110–130°) and 17 g of lower boiling fraction which could not be identified. Two distillations of the higher boiling fraction at 2 mm gave 15 g of a fraction boiling at 113–115° (2 mm) which was identified as 4-trichlorosilyl-3-acetoxybutyl acetate (1:2 adduct): ir 1745 (C=O), 1230 cm^{-1} (C–O). *Anal.* Calcd for $Cl_3SiC_8H_{13}O_4$: Cl, 34.62; Si, 9.13. Found: Cl, 33.74; Si, 9.03.

γ-Induced Reduction of 2-Trichlorosilylethyl Acetate.—A mixture of 2-trichlorosilylethyl acetate (11.1 g, 0.05 mol) and trichlorosilane (40.6 g, 0.3 mol) was irradiated under total dose of 9.6 MR at a dose rate of 0.6 MR/hr. Distillation of the irradiated products, after the removal of the unchanged trichlorosilane, gave 6.9 g (0.033 mol, 67%) of 2-trichlorosilylethyl ethyl ether. The boiling point and ir and nmr spectra coincided completely with those cited above.

Triethoxylation of the Trichlorosilyl Group.—The ethanolysis was carried out by the modified procedure of Nagel, *et al.*,[7] and Langer.[12] A mixture of ethanol (25 g, 0.54 mol) and pyridine (90 g, 1.17 mol) added to 2-trichlorosilylethyl acetate (33.7 g, 0.152 mol) gave 2-triethoxysilylethyl acetate (26.9 g, 71%): bp 90.6° (3.5 mm); $n^{20}D$ 1.4109; ir 1745 (C=O), 1230 (C–O). *Anal.* Calcd for $SiC_{10}H_{22}O_5$: Si, 11.22; C, 47.97; H, 8.86; mol wt, 250.4. Found: Si, 11.45; C, 48.03; H, 9.36; mol wt, 243.5.

A mixture of ethanol (16.0 g, 0.348 mol) and pyridine (60 g, 0.758 mol) with 2-trichlorosilylethyl ethyl ether (21.0 g, 0.101 mol) yielded 2-triethoxysilylethyl ethyl ether (19.8 g, 83%): bp 75.5° (6 mm); $n^{20}D$ 1.4067. *Anal.* Calcd for $SiC_{10}H_{24}O_4$: Si, 11.88; C, 50.81; H, 10.23; mol wt, 236.4. Found: Si, 11.88; C, 51.63; H, 10.04; mol wt, 236.

Attempted Addition of Triethoxysilane to Vinyl Acetate.—A mixture of triethoxysilane (26.3 g, 0.16 mol) and vinyl acetate (3.45 g, 0.04 mol) was γ irradiated under a total dose of 0.6 MR, at a dose rate of 0.2 MR/hr. 2-Triethoxysilylethyl acetate could not be found by distillation.

Pyrolysis.—2-Triethoxysilylethyl acetate (9.9 g, 0.0395 mol) was vaporized and made to flow under 1 mm of pressure through a Pyrex reactor (*ca.* 20-cm path) packed with Pyrex helices and externally heated at 550°, in a stream of nitrogen.[14] The pyrolysates were collected in two traps cooled in an ice and a liquid nitrogen bath. The content of the latter trap was dissolved in ether and washed with water, aqueous sodium bicarbonate, and then water. The ether solution gave 6.2 g (0.326 mol, 82.5%) of vinyltriethoxysilane, the boiling point and $n^{20}D$ coincided with those[17] reported, and the ir and nmr spectra matched those of a commercial sample. *Anal.* Calcd for $SiC_8H_{18}O_3$: C, 50.49; H, 9.53; mol wt, 190. Found: C, 49.62; H, 10.26; mol wt, 186.

2-Trichlorosilylethyl acetate (10.4 g) was pyrolyzed by the same procedure. An aliquot of a fraction trapped with liquid nitrogen, after distillation, gave vinyltrichlorosilane; the physical properties (boiling point, $n^{20}D$, and nmr spectrum) coincided with those reported.[3,18] The remaining part of the fraction was analyzed by glpc using vinyltrichlorosilane obtained above as a standard. Considering the unchanged amount (2.5 g) of the starting acetate, pyrolysis yielded 71.7% vinylsilane.

2-Triethoxysilylethyl ethyl ether (6.0 g, 0.0254 mol) was pyrolyzed. A fraction trapped with liquid nitrogen was identified to be ethylene by glpc. The other fraction was distilled, giving tetraethoxysilane (3.4 g, 0.0167 mol, 64.5%): bp 82–83° (30 mm) and 161.3° (760 mm) [lit.[19] 165.5° (760 mm)]; nmr (CCl_4) δ 1.21 (t, 3, J = 12 Hz, CH_3), 3.72 (q, 2, J = 12 Hz, CH_2). *Anal.* Calcd for $SiC_8H_{20}O_4$: C, 46.12; H, 9.68; Si, 13.45. Found: C, 46.39; H, 10.32; Si, 13.85.

(17) R. Y. Mixer and D. L. Bailey, *J. Polym. Sci.*, **18**, 573 (1955).

(18) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 3.

Registry No.—Trichlorosilane, 10025-78-2; vinyl acetate, 108-05-4; 4-trichlorosilyl-3-acetoxybutyl acetate, 22538-44-9; 2-triethoxysilylethyl acetate, 22538-45-0; 2-triethoxysilylethyl ethyl ether, 17980-59-5.

Acknowledgments.—Partial support of this work by the Science and Techniques Agency of the Government is gratefully acknowledged. We thank Dr. S. Kawamura and Mr. R. Akagi for the nmr spectral and elemental analyses, respectively.

(19) "Beilstein, Handbuch der Organischen Chemie," Vol. 1, 1918, p 334.

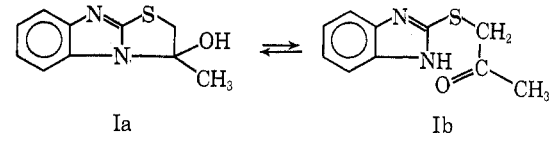
Potentially Tautomeric α-(2-Benzimidazolylthio)acetophenones

HOWARD ALPER AND ANNE E. ALPER

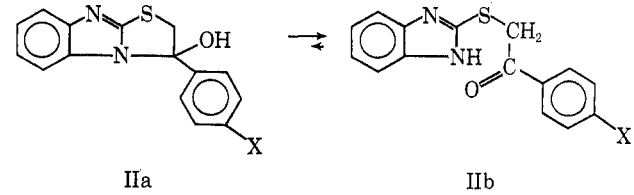
Department of Chemistry
State University of New York at Binghamton,
Binghamton, New York 13901

Received July 24, 1969

Ring–chain tautomeric investigations have shown 3-hydroxy-2,3-dihydrothiazolo[3,2-*a*]benzimidazoles unsubstituted on the thiazolidine ring (as well as the 2-methyl compound) to exist only as the cyclic carbinolamines, both in the solid state and in solution.[1] 3-Hydroxy-3-methyl-2,3-dihydrothiazolo[3,2-*a*]benzimidazole also exists as the ring tautomer (Ia) in the solid state (infrared studies using potassium bromide disks), but nmr spectra of dimethyl sulfoxide-d_6 (DMSO-d_6) solutions have clearly indicated the presence of a 1:2 mixture of Ia and the open-chain amino ketone tautomer Ib, respectively. α-(2-Benzimidazolylthio)acetophenone (II, X = H), on the other hand, exists solely



Ia Ib



IIa IIb

in the chain form IIb, both in the solid state and in solution. As the 3-methyl compound Ia is in tautomeric equilibrium with Ib in solution, it seemed conceivable that IIb, appropriately substituted, would be capable of interconverting with the cyclic tautomer IIa. This communication reports an investigation of the influence of a *para* substituent on the position of the ring–chain tautomeric equilibrium IIa ⇄ IIb.

(1) A. E. Alper and A. Taurins, *Can. J. Chem.*, **45**, 2903 (1967).

A series of α-(2-benzimidazolylthio) 4′-substituted acetophenones (II, X = OCH_3, C_6H_5, Cl, Br, NO_2) was prepared by condensation of 2-benzimidazolinethione with the suitably substituted 2-bromoacetophenone. The infrared spectra of the products in KBr disks, or in chloroform or methylene chloride solution, showed no absorption bands due to OH but did exhibit carbonyl stretching for an aryl ketone in the region of 1680–1695 cm^{-1}. As expected for structure IIb, the methylene protons appeared as a singlet in the nmr spectra (DMSO-d_6) at 5.06–5.28 ppm. In all cases, no quartet was observed for the methylene protons, as was reported for Ia and expected for IIa.

These results clearly show that a *para* substituent, whether strongly electron donating (II, X = OCH_3) or electron withdrawing (II, X = NO_2), has no effect on the position of the tautomeric equilibrium. The lack of substituent effects on the ring–chain tautomerism IIa ⇄ IIb contrasts with the report by Lutz and Moncure[2] that *para* substitution in the aroyl group of *cis*-β-aroylacrylic acids significantly affects the position of equilibrium with its lactone ring tautomer, electron-attracting groups assisting cyclization and electron-donating substituents favoring the open-chain form. In addition, Beke and coworkers[3] found that ring–chain tautomerism in cotarnine is appreciably influenced by substitution of the NCH_3 group by N-2,4-dinitrophenyl. Finally, Beke[4] has noted that the electron density on the carbinolamine carbon atom can be affected by the nature of the substituent on carbon.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were carried out by F. B. Strauss, Oxford, England. Infrared spectra were recorded on Perkin-Elmer 137 and 337 spectrophotometers. Nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer. Tetramethylsilane was used as internal standard.

α-(2-Benzimidazolylthio)-4′-methoxyacetophenone (II, X = OCH_3).—2-Benzimidazolinethione (2.10 g, 0.014 mol) and 2-bromo-4′-methoxyacetophenone (3.21 g, 0.014 mol) were suspended in 235 ml of 2-butanone and the mixture was refluxed for 6 hours. The reaction mixture was cooled and filtered to yield 4.65 g of α-(2-benzimidazolylthio)-4′-methoxyacetophenone hydrobromide, mp 248°. The hydrobromide was suspended in 50 ml of ethanol and the mixture was heated to reflux. Freshly distilled triethylamine was added dropwise until the salt had dissolved and the reaction mixture was then refluxed for 15 min and poured into 400 ml of water. The resulting white precipitate was filtered and dried, giving 3.48 g (84%) of II, X = OCH_3, mp 162.0–163.0°. Fluffy white needles, mp 163.0–163.5°, were obtained upon recrystallization from benzene.

Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73; N, 9.39. Found: C, 64.49; H, 4.73; N, 9.09.

α-(2-Benzimidazolylthio)-4′-phenylacetophenone (II, X = C_6H_5).—2-Benzimidazolinethione and 2-bromo-4′-phenylacetophenone were allowed to react as above, giving α-(2-benzimidazolylthio)-4′-phenylacetophenone hydrobromide, mp 242.0–245.0°. Work-up as for II, X = OCH_3, gave II, X = C_6H_5, mp 201.0–203.0°, in 65% yield. Recrystallization from benzene–chloroform (3:1) gave an analytical sample, mp 200.5–202.0°.

Anal. Calcd for $C_{21}H_{16}N_2OS$: C, 73.23; H, 4.68; N, 8.13. Found: C, 72.91; H, 5.00; N, 8.36.

α-(2-Benzimidazolylthio)-4′-chloroacetophenone (II, X = Cl).—2-Benzimidazolinethione and 2-bromo-4′-chloroacetophenone were refluxed in 2-butanone for 1.5 hr, giving α-(2-benzimidazolylthio)-4′-chloroacetophenone hydrobromide, mp 247.0–248.0°. Work-up as above gave II, X = Cl, mp 181.0–183.0°, in 87% yield. Recrystallization from benzene–chloroform (7:3) gave II, X = Cl, as a very fine, white powder, mp 184.–185.0°.

Anal. Calcd for $C_{15}H_{11}ClN_2OS$: C, 59.50; H, 3.66; N, 9.29. Found: C, 59.75; H, 3.92; N, 9.52.

α-(2-Benzimidazolylthio)-4′-bromoacetophenone (II, X = Br).—2-Benzimidazolinethione and 2,4′-dibromoacetophenone were refluxed in 2-butanone for 3.5 hr, giving α-(2-benzimidazolylthio)-4′-bromoacetophenone hydrobromide, mp 240.0–243.0°. Work-up as above gave II, X = Br, mp 208.0–210.0°, in 40% yield. Recrystallization from chloroform–benzene (2:1) gave II, X = Br, as a white powder, mp 208.5–210.0°.

Anal. Calcd for $C_{15}H_{11}BrN_2OS$: C, 51.89; H, 3.19; N, 8.07. Found: C, 52.10; H, 3.02; N, 7.97.

α-(2-Benzimidazolylthio)-4′-nitroacetophenone (II, X = NO_2).—2-Benzimidazolinethione and 2-bromo-4′-nitroacetophenone were refluxed in 2-butanone for 4 hr, giving α-(2-benzimidazolylthio)-4′-nitroacetophenone hydrobromide, mp 245.0–248.0°. Work-up as above gave crude II, X = NO_2, mp 180.0–182.0°, in 68% yield. Recrystallization from chloroform–benzene (7:3) gave II, X = NO_2, as pale yellow needles, mp 195.0–197.0°, in 42% yield.

Anal. Calcd for $C_{15}H_{11}N_3O_3S$: C, 57.50; H, 3.54; N, 13.14. Found: C, 57.68; H, 3.48; N, 13.42.

Registry No.—IIb, X = OCH_3, 22794-86-1; IIb, X = OCH_3, hydrobromide, 22794-87-2; IIb, X = C_6H_5, 22794-88-3; IIb, X = C_6H_5, hydrobromide, 22866-47-3; IIb, X = Cl, 22794-89-4; IIb, X = Cl, hydrobromide, 22794-90-7; IIb, X = Br, 21547-82-0; IIb, X = Br, hydrobromide, 22866-48-4; IIb, X = NO_2, 22794-92-9; IIb, X = NO_2, hydrobromide, 22794-93-0.

(2) R. E. Lutz and H. Moncure, Jr., *J. Org. Chem.*, **26**, 746 (1961).

(3) D. Beke, C. Szantay, and M. Barczai-Beke, *Acta Chim. Acad., Sci. Hung.*, **21**, 153 (1959).

(4) D. Beke, *Advan. Heterocycl. Chem.*, **1**, 172 1963.

A Simple Synthesis of the Naphth[2,1-*b*]oxepin and Naphth[2,1-*b*]oxocin Systems[1]

JAROSLAV JONAS[2] AND T. P. FORREST

Chemistry Department, Dalhousie University, Halifax, N. S., Canada

Received July 15, 1969

Acetals are known to readily form the stabilized α-alkoxy carbonium ion which, being an electrophilic species, reacts with a variety of nucleophilic reagents.[3] Protonation of vinyl ethers, too, gives rise to the α-alkoxy carbonium ion.[3] Semicyclic diacetals, *e.g.*, 2,5-dimethoxytetrahydrofuran (**1**), and cyclic vinyl ether acetals, *e.g.*, 2-ethoxy-2,3-dihydro-4H-pyran (**2**), can react with a nucleophilic reagent *via* the above-mentioned intermediate at both of the positions α to the ring oxygen. This has led us to an idea of forming new heterocyclic systems with suitable reagents, containing two nucleophilic sites.

We now wish to report a reaction of **1** and **2** with β-naphthol (**3**) and some transformations of the products obtained.

A solution of **3** in aqueous acetic acid with a small amount of hydrochloric acid reacted with **1** and **2** at

(1) Presented at the 3rd Symposium on the Chemistry of Heterocyclic Compounds, Brno, Czechoslovakia, Sept 1969.

(2) (a) Dalhousie University Postdoctoral Research Fellow, 1967–1969. (b) Presently at the Department of Organic Chemistry, Purkyné University, Brno, Czechoslovakia. (c) To whom all inquiries should be directed.

(3) E. Schmitz and I. Eichhorn in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, pp 310–351, and literature cited therein.