

**1,1-Bis(trifluoromethyl)nonen-1-ols:** 1,1-bis(trifluoromethyl)-4-pentyltetrahydrofuran, 72%, bp, 184°. The infrared and nmr spectra are consistent with the latter described as follows: HCO, 4.2 (complex);  $-(CH_2)_2-$ , 1.2-2.4 (complex);  $CH_3-$  0.89 ppm (triplet,  $J = 7$  Hz). Anal. Calcd for  $C_{11}H_{16}F_6O$ : C, 47.48; H, 5.79. Found: C, 47.83; H, 5.56.

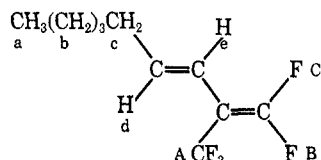
**V. 1,1-Bis(trifluoromethyl)-3-alken-1-ols from the Thermal Reaction of 1-Alkenes and Hexafluoroacetone.**—Reactions were carried out in a manner identical with those above. The 1,1-bis(trifluoromethyl)-3-buten-1-ols gave a 61% yield of 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene while the 1,1-bis(trifluoromethyl)-3-penten-1-ols yielded 71% 1,1-bis(trifluoromethyl)-4-methyltetrahydrofuran.

**VI. Reactions of 1,1,1-Trifluoro-2-trifluoromethyl-2,4-pentadiene (1). Polymerization.** In Bulk.—A mixture of 1.90 g (0.10 mol) of 1 and 0.010 g of benzoyl peroxide was placed in a vial, flushed with nitrogen, and heated at 60° for 66 hr. After distilling excess monomer *in vacuo* the residue (0.5 g, 25%) had a molecular weight of 4500. The infrared spectrum shows aliphatic CH (2800-3000), vinyl CH (3000-3100), and  $C=C(CF_3)_2$  (1680  $cm^{-1}$ ). These characteristics and the absence of other  $C=C$  absorption indicate that polymerization occurs to a large extent across the less substituted double bond by 1,2 addition.

**In Emulsion.**—A mixture of 11.8 g (0.06 mol) of 1, 34 ml of water, 0.060 g of potassium persulfate, and 0.36 g of Duponol (surfactant) was placed in a vial, flushed with nitrogen, and heated at 50-60° with vigorous stirring for 20 hr. Evaporation of the water yielded 7.9 g (87%) of a clear, tough polymer having a molecular weight of 83,000. The infrared spectrum is similar to that of the polymer from the bulk reaction.

**VII. Hydrogenation.**—Diene 1 (48 g), 50 ml of acetic acid, and 0.5 g of 5% Pd-C were placed in a Parr apparatus and hydrogenated at 50 psig. The theoretical amount of hydrogen was quickly absorbed. Filtration and distillation of the product solution yielded 37 g (77%) of 1,1-bis(trifluoromethyl)butane (bp 66-67°). The  $^1H$  nmr spectrum shows three complex envelopes at 0.7-1.4 ppm (area = 3), 1.4-2.2 (4), and 2.6-3.2 (1). The  $^{19}F$  spectrum shows a doublet at -9.88 ppm ( $J = 7$  Hz). Anal. Calcd for  $C_6H_8F_6$ : C, 37.12; H, 4.15. Found: C, 37.47; H, 3.90.

**VIII. Reaction with *n*-Butyllithium.**—A solution (1.6 M, 19 ml) of *n*-butyllithium in hexane (0.030 mol) was added slowly to a cold (0°) solution of 5.7 g (0.030 mol) of 1 in hexane. After stirring for 1 hr, the reaction was hydrolyzed with 5% hydrochloric acid, and after drying over sodium sulfate the organic layer was distilled (8-in. Vigreux) to yield 3.10 g (45%) of *trans*-1,1-difluoro-2-trifluoromethyl-1,3-nonadiene, bp 148-150°. The infrared spectrum is consistent, showing bands at 1630 ( $-CH=CH-$ ) and 1710  $cm^{-1}$  ( $C=CF_2$ ). The nmr spectra are described below.

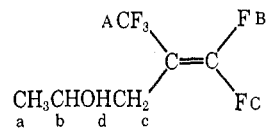


$^1H$  ( $\delta$ , ppm): a, 0.90; b, 1.3 (complex); c, 2.0-2.3 (complex); d, 5.8-6.2 (complex); e, 5.70 (doublet,  $J_{de} = 16$  Hz).  $^{19}F$  ( $\phi$ , ppm): A, -17.88 (two doublets,  $J_{CA} = 28$  Hz,  $J_{BA} = 10$  Hz); B, +1.1 (two quartets,  $J_{AB} = 10$  Hz,  $J_{CB} = 10$  Hz); C, -0.3 (two quartets,  $J_{AC} = 28$  Hz,  $J_{BC} = 10$  Hz). Anal. Calcd for  $C_{10}H_{13}F_6$ : C, 52.67; H, 5.81. Found: C, 52.70; H, 5.91.

**4,4-Bis(trifluoromethyl)-3-buten-2-one.**—Triphenylphosphineacetylmethylene, mp 201-203° (lit.<sup>4</sup> 205-206°), was prepared according to the method of Ramirez and Dershowitz<sup>4</sup> and allowed to react with a slight excess of hexafluoroacetone as outlined by Plakhova and Gambaryan.<sup>2</sup> The yield of 4,4-bis(trifluoromethyl)-3-buten-2-one was 90%, bp 109-111° [lit.<sup>2</sup> bp 68° (135 mm)]. The infrared spectrum shows  $C=O$  (1720) and  $C=C$  (1670  $cm^{-1}$ ). The  $^1H$  nmr spectrum shows sharp singlets for the vinyl proton (6.97 ppm) and the three methyl protons (2.38 ppm).

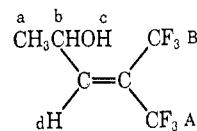
**IX. Lithium Aluminum Hydride Reduction of 4,4-Bis(trifluoromethyl)-3-buten-2-one.** Using 0.50 Mol of  $LiAlH_4$ .—A solution of 10.3 g (0.050 mol) of 4,4-bis(trifluoromethyl)-3-buten-2-one in 50 ml of ether was cooled to 0° and 0.95 g (0.025 mol) of finely crushed  $LiAlH_4$  was added over a period of 1 hr. The reaction mixture was stirred at 0° for 1 hr and after hydrolysis

with 5% hydrochloric acid and drying over sodium sulfate, the solvent was removed from the product by careful distillation. The residue was distilled to yield 6.3 g (67%) of 5,5-difluoro-4-trifluoromethyl-4-penten-2-ol. The infrared spectrum shows OH absorption (3500  $cm^{-1}$ ) and also  $C=CF_2$  (1740  $cm^{-1}$ ). The nmr spectra are described below.



$^1H$  ( $\delta$ , ppm): a, 1.25 (doublet,  $J_{ba} = 6$  Hz); b, 3.95 (complex); c, 2.3 (complex); d, 2.30.  $^{19}F$  ( $\phi$ , ppm): A, -17.84 (two doublets,  $J_{BA} = 10$  Hz,  $J_{CA} = 20$  Hz); B, -2.28 (broad multiplet); C, +0.18 (broad multiplet). Anal. Calcd for  $C_6H_7F_5O$ : C, 37.91; H, 3.60. Found: C, 37.77; H, 3.69.

**Using 0.25 Mol of  $LiAlH_4$ .**—The reduction was carried out as above using 0.475 g (0.0125 mol) of lithium aluminum hydride. Distillation gave 6.5 g of product, bp 118-134°. Glpc analysis (8-ft silicone grease column) showed the product yield to be starting material, 33%; 5,5-difluoro-4-trifluoromethyl-4-penten-2-ol, 21%; 4,4-bis(trifluoromethyl)-3-buten-2-ol, 12%. The first two materials were identified by comparison of the glpc retention times and infrared spectra with those of the respective authentic compounds. A sample of the third was obtained by preparative scale glpc techniques. The infrared spectrum is consistent, showing OH (3500  $cm^{-1}$ ) and  $C=C(CF_3)_2$  (1680  $cm^{-1}$ ) absorptions. The nmr spectra are described below.



$^1H$  ( $\delta$ , ppm): a, 1.38 (doublet,  $J_{ba} = 7$  Hz); b, 4.9 (complex); c, 2.02 (singlet); d, 6.70 (doublet,  $J_{bd} = 9$  Hz).  $^{19}F$  ( $\phi$ , ppm): A, -13.2 (quartet,  $J_{BA} = 7$  Hz); B, -20.0 (quartet,  $J_{AB} = 7$  Hz). Anal. Calcd for  $C_6H_8F_6O$ : C, 34.62; H, 2.90. Found: C, 34.81; H, 2.85.

**Registry No.**—1, 1422-33-9; *cis*-2, 24010-42-2; *trans*-2, 24010-43-3; 1,1-bis(trifluoromethyl)tetrahydrofuran, 24010-61-5; 1,1-bis(trifluoromethyl)-4-propyltetrahydrofuran, 24010-62-6; 1,1-bis(trifluoromethyl)-4-pentyltetrahydrofuran, 24010-63-7; 1,1-bis(trifluoromethyl)butane, 24010-64-8; *trans*,1,1-difluoro-2-trifluoromethyl-1,3-monadiene, 24010-44-4; 4,5-difluoro-4-trifluoromethyl-4-penten-2-ol, 24010-65-9; 4,4-bis(trifluoromethyl)-3-buten-2-ol, 656-80-4.

### $\alpha,\alpha'$ -Dianilinosilbenes. The Cyanide Ion Catalyzed Dimerization of Aromatic Schiff Bases

HANS-DIETER BECKER

General Electric Research and Development Center, Schenectady, New York 12301

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The alkali cyanide catalyzed dimerization of benzaldehyde anil (1a) in liquid ammonia has been described to give a fluorescent, yellow dimer to which the anilinoanil structure 2a was assigned because of the analogous formation of benzoin from benzaldehyde.<sup>1</sup> Since the dimerization product was found to be readily oxidized upon exposure to air to give benzil dianil (4a), structure 2a was suggested to be in equilibrium

(1) H. H. Strain, *J. Amer. Chem. Soc.*, **50**, 2218 (1928).

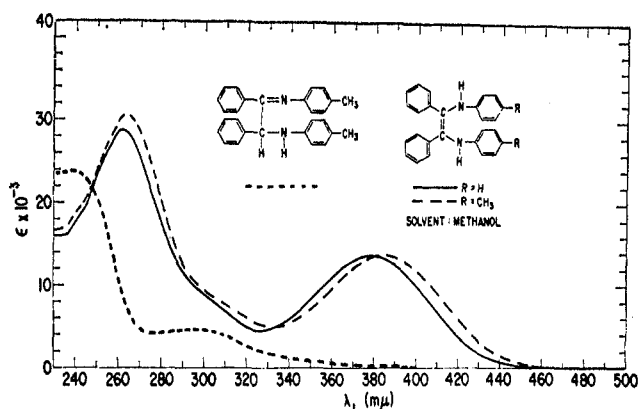
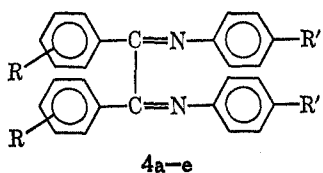
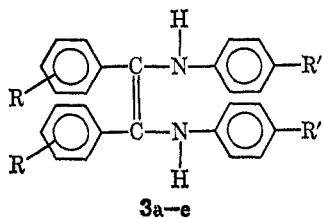
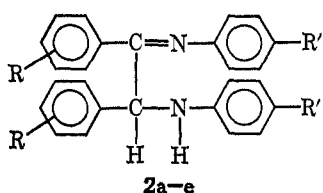
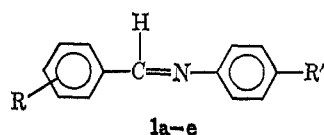
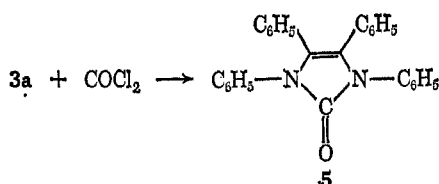


Figure 1.

with the enediamine structure **3a**.<sup>2,3</sup> According to a recent communication, however, the reaction of **1a** with an equimolar amount of sodium cyanide in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) leads directly to benzil dianil.<sup>4</sup>



- a, R = H; R' = H  
 b, R = 4-CH<sub>3</sub>; R' = H  
 c, R = 4-OCH<sub>3</sub>; R' = H  
 d, R = 3,4-OCH<sub>2</sub>O-; R' = H  
 e, R = H; R' = CH<sub>3</sub>



We were prompted to investigate the cyanide ion catalyzed dimerization of **1a** when we needed spectroscopic data of the anilinoanil **2a** for comparison with those of an anilinoanil obtained in the base catalyzed reaction of **1a** with DMSO.<sup>5</sup> This report deals with our findings which differ from those published previously by other authors.

Following the literature procedure for the cyanide ion catalyzed dimerization of **1a** in liquid ammonia,<sup>6</sup> the previously described yellow crystalline dimer with green fluorescence was obtained in 30% yield. We found in the course of this study that the same compound is obtained more conveniently and in higher yield (80%) by treatment of **1a** with a catalytic amount of sodium cyanide in DMF at room temperature, under nitrogen. Likewise, treatment of **1a** with an equimolar quantity of sodium cyanide in DMSO leads to this dimerization product, provided the reaction is carried out in the absence of oxygen. In accordance with earlier<sup>2,3</sup> observations, the dimerization product in solution upon exposure to air is readily oxidized to give benzil dianil (**4a**) in high yield. Thus, the recently observed formation of **4a** in the cyanide ion catalyzed reaction of **1a** does not proceed according to the proposed<sup>4</sup> mechanism but is the result of an inadvertent autoxidation of the previously<sup>1,2</sup> described compound whose mass spectrum we found to be in agreement with the molecular composition C<sub>26</sub>H<sub>22</sub>N<sub>2</sub>.

Spectroscopic data do not, however, support the structure of the dimer, (anilinoanil **2a**). The uv spectrum (Figure 1) shows a longest wavelength absorption maximum at 378 mμ (ε 13,600), quite different from that of benzaldehyde anil.<sup>8</sup> The ir spectrum shows absorption bands in the NH region (see Experimental Section) but no absorption in the region typical of a C=N bond. The nmr spectrum (see Experimental Section) reveals the presence of two magnetically equivalent protons which can be exchanged for deuterium by treatment with D<sub>2</sub>O. These data are in excellent agreement with α,α'-dianilinoanil (**3a**). Whether or not the cyanide ion catalyzed dimerization of **1a** leads to a pure geometrical isomer (either *cis* or *trans*) or to a mixture of isomers has not been investigated. The reaction of the dimerization product with phosgene gives in good yield 1,3,4,5-tetraphenylimidazolone-2 (**5**); however, it is conceivable that a *cis-trans* isomerization occurs under the conditions of phosgenation of **3a**.

Using DMF as a solvent, the cyanide ion catalyzed reaction of anils **1b-1d** was found to give the correspondingly substituted fluorescent α,α'-dianilinoanils **3b-3d** in good to excellent yields (see Table I, Experimental Section). Their structure is supported by ir, nmr, and uv spectroscopic data. As observed for the parent compound **3a**, α,α'-dianilinoanils **3b-3d** in solution upon exposure to air are readily oxidized to give the corresponding dianils **4b-4d** in excellent yield.

The cyanide ion catalyzed dimerization of benzylidene-*p*-toluidine (**1e**) in DMF leads to a fluorescent yellow crystalline dimer for which spectroscopic data [ir, nmr, uv (see Figure 1)] are in agreement with α,α'-

(2) H. H. Strain, *J. Amer. Chem. Soc.*, **51**, 269 (1929).

(3) P. L. Julian, E. W. Meyer, A. Magnani, and W. Cole, *ibid.*, **67**, 1203 (1945).

(4) J. S. Walia, J. Singh, M. S. Chattha, and M. Satyanarayana, *Tetrahedron Lett.*, 195 (1969).

(5) H.-D. Becker, *J. Org. Chem.*, **34**, 4162 (1969).

(6) An earlier<sup>7</sup> attempt to repeat this dimerization had failed because we did not realize that the reaction should be carried out in a sealed tube.

(7) H.-D. Becker, *ibid.*, **29**, 2891 (1964); cf. ref 5.

(8) H. B. Bürgi and J. D. Dunitz, *Chem. Commun.*, 472 (1969).

TABLE I  
 ALKALI CYANIDE CATALYZED DIMERIZATION OF AROMATIC ANILS

Run	R	R'	1, mmol	Catalyst, mmol	Solvent, ml	Reaction time, hr	Yield of 3, %
1	H	H	60	NaCN, 2	DMF, 50	2	54
2	H	H	200	NaCN, 2	DMF, 75	17	66
3	H	H	200	NaCN, 5	DMF, 100	24	80
4	H	H	20	NaCN, 20	DMSO, 50	15	69
5	H	H	27	KCN, 20	NH <sub>3</sub> , 50	24	30
6	4-CH <sub>3</sub>	H	110	NaCN, 4	DMF, 50	14	90
7	4-CH <sub>3</sub>	H	27	NaCN, 20	NH <sub>3</sub> , 50	24	3
8	3,4-O-CH <sub>2</sub> -O	H	33	NaCN, 10	DMF, 50	28	69
9	4-OCH <sub>3</sub>	H	20	NaCN, 1	DMF, 15	48	35
10	H	CH <sub>3</sub>	10	NaCN, 4	DMF, 50	20	51
11	H	CH <sub>3</sub>	14	NaCN, 6	DMF, 100	40	58

di-*p*-toluidinostilbene **3e**. Autoxidation of **3e** leads to the expected substituted dianil **4e** in high yield. By contrast, the cyanide ion catalyzed dimerization of benzylidene *p*-toluidine in liquid ammonia gives a (nonfluorescent) colorless crystalline dimer which had been reported<sup>1</sup> previously. The uv spectrum of this dimer whose molecular composition is confirmed by its mass spectrum, is completely different from that of its fluorescent isomer, but is in agreement with that of the originally<sup>1</sup> proposed anilinoanil structure **2e** (see Figure 1). Nmr spectroscopic evidence for structure **2e** is even more revealing. Using deuteriobenzene as solvent, the nmr spectrum of **2e** exhibits two different methyl groups, whereas that of its isomer **3e** shows two magnetically equivalent methyl groups. Furthermore, the CH group and the NH group in **2e** appear as doublets, due to magnetic coupling (see Experimental Section).

In neutral methanol solution, compound **2e** was found to be stable toward autoxidation. In methanol containing a small amount of hydrochloric acid, however, **2e** does oxidize readily upon exposure to air to give the dianil **4e**. The autoxidation is probably preceded by an acid-catalyzed isomerization of **2e** to give **3e**. When dissolved in DMF containing sodium cyanide, the colorless dimer **2e** smoothly isomerizes to give the yellow fluorescent di-*p*-toluidinostilbene **3e**. Apparently, the cyanide ion catalyzed dimerization of anils proceeds according to a mechanism analogous to that of the benzoin condensation,<sup>9</sup> and the formation of  $\alpha, \alpha'$ -dianilinostilbenes is due to a subsequent double-bond isomerization of anilinoanils of structure **2**. There is, however, no nmr spectroscopic indication for the previously assumed equilibrium between anilinoanils and their isomeric dianilinostilbenes.

#### Experimental Section

Dimethylformamide was distilled *in vacuo* and stored over molecular sieves. The melting points of the  $\alpha, \alpha'$ -dianilinostilbenes were determined in sealed capillaries, while those of the dianils were taken on a hot-stage microscope. Ir spectra were taken in KBr. Uv spectra were measured in methanol. The nmr spectra were recorded on a 100-Mc Varian spectrometer, using deuteriochloroform as solvent and tetramethylsilane as internal standard.

$\alpha, \alpha'$ -Dianilinostilbene (**3a**).—A solution of benzaldehyde anil (36.2 g, 0.2 mol) in dry DMF (100 ml) containing pulverized sodium cyanide (250 mg, 5 mmol) was agitated with a stream of nitrogen. After 24 hr the yellow reaction mixture containing a crystalline yellow precipitate was diluted with 150 ml of methanol and kept under nitrogen for 4 hr in the refrigerator. Filtra-

tion gave 29 g (80%) of yellow crystalline product showing strong green fluorescence, mp 205–210°. Recrystallization by dissolving the product under N<sub>2</sub> in a small amount of warm chloroform and addition of methanol did not raise the melting point. Spectra follow: uv  $\lambda_{\max}$  378 m $\mu$  ( $\epsilon$  13,600); ir 3365, 3400 cm<sup>-1</sup> (NH); nmr  $\delta$  5.50 (2 NH), 6.40–7.60 (20 aromatic H).

Anal. Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>2</sub> (362.45): C, 86.16; H, 6.12; N, 7.73. Found: C, 86.31; H, 6.24; N, 7.60.

Dianilinostilbenes **3b–3e** were prepared in the same fashion as described for **3a**. Experimental details are summarized in Table I.

$\alpha, \alpha'$ -Dianilino-4,4'-dimethylstilbene (**3b**).—Yellow crystals with blue fluorescence were recrystallized by dissolving in chloroform and addition of methanol, mp 165–172°. The nmr spectrum of this product indicates a mixture of isomers. Spectra follow: uv  $\lambda_{\max}$  362 m $\mu$  ( $\epsilon$  14,400); ir 3355, 3380, 3410 cm<sup>-1</sup> (NH); nmr  $\delta$  2.22 (CH<sub>3</sub>), 2.26 (CH<sub>3</sub>), 5.46 (NH), 5.50 (NH), 6.40–7.50 (18 aromatic H).

Anal. Calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub> (390.50): C, 86.11; H, 6.71; N, 7.17. Found: C, 86.12; H, 6.92; N, 7.09.

$\alpha, \alpha'$ -Dianilino-4,4'-dimethoxystilbene (**3c**).—Yellow crystals with blue fluorescence were recrystallized by dissolving in chloroform and addition of methanol, mp 160–165°. Spectra follow: uv  $\lambda_{\max}$  368 m $\mu$  ( $\epsilon$  18,000); ir 3365, 3400 cm<sup>-1</sup> (NH); nmr  $\delta$  3.53 (2 OCH<sub>3</sub>), 5.30 (2 NH), 6.30–7.30 (18 aromatic H).

Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub> (422.55): C, 79.59; H, 6.20; N, 6.63. Found: C, 79.62; H, 6.05; N, 6.73.

$\alpha, \alpha'$ -Dianilino-3,4-methylenedioxy-3',4'-methylenedioxystilbene (**3d**).—Pale green crystals with blue-green fluorescence were recrystallized by dissolving in chloroform and addition of methanol, mp 180–186°. Spectra follow: uv  $\lambda_{\max}$  375 m $\mu$  ( $\epsilon$  16,800); ir 3400 cm<sup>-1</sup> (NH); nmr  $\delta$  5.50 (2 NH), 5.90 (2 OCH<sub>2</sub>O), 6.50–7.30 (16 aromatic H).

Anal. Calcd for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> (450.47): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.47; H, 4.76; N, 6.04.

$\alpha, \alpha'$ -Di-*p*-toluidinostilbene (**3e**).—The yellow crystals with blue green fluorescence were recrystallized by dissolving in acetone and addition of ethanol, mp 172–182°. Spectra follow: uv  $\lambda_{\max}$  385 m $\mu$  ( $\epsilon$  13,600); ir 3405 cm<sup>-1</sup> (NH); nmr  $\delta$  2.10 (2 CH<sub>3</sub>), 5.50 (2 NH), 6.30–7.60 (18 aromatic H).

Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub> (390.50): C, 86.11; H, 6.71; N, 7.17. Found: C, 85.87; H, 6.75; N, 7.15.

Sodium Cyanide Catalyzed Dimerization of Benzylidene-*p*-toluidine in Liquid Ammonia (**2e**).—A mixture of benzylidene-*p*-toluidine (5 g) and sodium cyanide (1 g) in liquid ammonia (50 ml) was placed in a sealed tube and was kept at room temperature for 24 hr. Evaporation of ammonia from the reaction mixture left a light yellow oil which was triturated under nitrogen with methanol (50 ml). After 10 min, colorless needle-shaped crystals separated from the solution. They were recrystallized by dissolving in little acetone and precipitation with methanol: yield 1.5 g (30%); mp 126–128° (lit.<sup>1</sup> 122°); ir 3355 (NH), 1642 cm<sup>-1</sup> (C=N). The nmr spectrum of **2e** in benzene-*d*<sub>6</sub> was recorded on a Varian T-60 spectrometer:  $\delta$  1.93 (s, 1 CH<sub>3</sub>), 2.13 (s, 1 CH<sub>3</sub>), 5.52 (d,  $J_{AB}$  = 5 cps, 1 CH), 6.4 (d,  $J_{AB}$  = 5 cps, 1 NH), 6.5–7.5 (18 aromatic H). Upon deuteration, the doublet at 6.4 disappears, and the doublet at 5.52 collapses to give a singlet.

Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub> (390.50): C, 86.11; H, 6.71; N, 7.17. Found: C, 85.94; H, 6.65; N, 7.22.

Isomerization of **2e** to give **3e**.—A solution of **2e** (100 mg) and sodium cyanide (20 mg) in DMF (10 ml) was kept under nitrogen

(9) A. Lapworth, *J. Chem. Soc.*, **83**, 995 (1903); **85**, 1206 (1904).

for 4 hr. Dilution of the yellow solution with aqueous methanol gave a pale yellow crystalline precipitate (80 mg) with blue fluorescence. Its ir spectrum was superimposable with that of **3e** prepared by cyanide ion catalyzed dimerization of **1e** in DMF.

**Benzildianil (4a)**.—A solution of  $\alpha,\alpha'$ -dianilinosilbene (**1** g) in a mixture of chloroform (120 ml) and methanol (25 ml) was kept standing in an open beaker at room temperature under the hood. After 12 hr, when all solvent had evaporated the brownish crystalline residue was washed with little methanol and recrystallized from boiling methanol, yield 800 mg (80%), mp 146–148° (lit. 145–147°).

*Anal.* Calcd for  $C_{26}H_{20}N_2$  (360.44): C, 86.63; H, 5.59; N, 7.77. Found: C, 86.49; H, 5.60; N, 7.70.

The oxidation of  $\alpha,\alpha'$ -dianilinosilbenes **3b–3e** was carried out in the same manner as described for **3a**.

**4,4'-Dimethylbenzildianil (4b)**.—Yellow crystals, mp 149–150°, yield 90%.

*Anal.* Calcd for  $C_{28}H_{24}N_2$  (388.49): C, 86.56; H, 6.23; N, 7.21. Found: C, 86.61; H, 6.32; N, 7.20.

**4,4'-Dimethoxybenzil Dianil (4c)**.—Yellow crystals, mp 153–154°, yield 75%.

*Anal.* Calcd for  $C_{28}H_{24}N_2O_2$  (420.49): C, 79.97; H, 5.75; N, 6.66. Found: C, 79.90; H, 5.82; N, 6.66.

**3,4-Methylenedioxy-3',4'-methylenedioxybenzil Dianil (4d)**.—Yellow crystals, mp 127–128°, yield 95%.

*Anal.* Calcd for  $C_{28}H_{20}N_2O_4$  (448.46): C, 74.99; H, 4.50; N, 6.25. Found: C, 74.74; H, 4.65; N, 6.21.

**Benzil-4,4'-dimethyl Dianil (4e)**.—Yellow crystals, mp 163–164°, yield 96%.

*Anal.* Calcd for  $C_{28}H_{24}N_2$  (388.49): C, 86.56; H, 6.23; N, 7.21. Found: C, 86.46; H, 6.15; N, 7.26.

**1,3,4,5-Tetraphenylimidazolone-2 (5)**.—Phosgene was introduced into a solution of  $\alpha,\alpha'$ -dianilinosilbene (3.62 g, 10 mmol) in methylene chloride (250 ml) and pyridine (2 ml) which was agitated with a stream of nitrogen. By varying the rate of nitrogen introduction, the reaction temperature was kept between 20 and 26°. The solution first turned dark brown and then light yellow. After 1 hr the reaction mixture was diluted with 20 ml of methanol and 0.5 ml of concentrated hydrochloric acid. Vacuum evaporation of the methylene chloride and dilution of the residual methanol solution with 10 ml of water gave 3 g (77%) of colorless crystalline precipitate, mp 208–209° (lit.<sup>10</sup> 207°).

*Anal.* Calcd for  $C_{27}H_{20}N_2O$  (388.45): C, 83.48; H, 5.19; N, 7.21. Found: C, 83.7; H, 5.26; N, 7.24.

**Registry No.**—**2e**, 24099-47-6; **3a**, 24099-48-7; **3b**, 24099-49-8; **3c**, 24099-50-1; **3d**, 24099-51-2; **3e**, 24099-52-3; **4b**, 21854-88-6; **4c**, 21854-89-7; **4d**, 24099-55-6; **4e**, 24099-56-7.

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## Reactions of *gem*-Dithio Compounds

JOSEPH V. BURAKEVICH, ANTHONY M. LORE, AND GERT P. VOLFF

Central Research Department, FMC Corporation,  
Princeton, New Jersey 08540

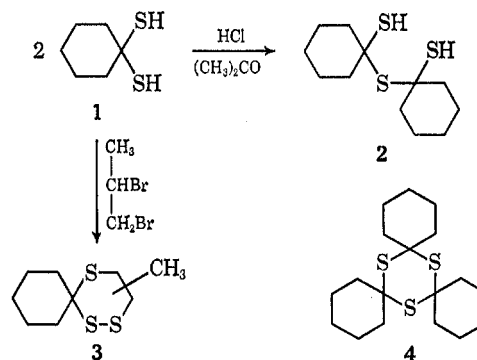
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The relatively stable *gem*-dithiol function is intriguing when compared with the analogous *gem*-diols, which undergo spontaneous dehydration to yield carbonyl groups. It was our desire to further extend the inter-

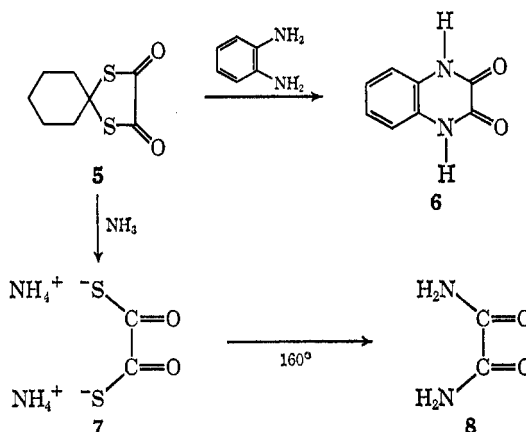
esting chemistry already reported on this system, and which often resulted from cleavage of the dithio group.<sup>1</sup>

Cyclohexane-1,1-dithiol (**1**) reacted in acidified acetone to yield bis(1-mercaptocyclohexyl) sulfide (**2**) in preference to a 1,3-dithietane which could arise through dithioketal formation with acetone. Compound **2** represents the dimer intermediate in the synthesis of 2,4,6-tris(pentamethylene)-1,3,5-trithiane (**4**), a known product of reaction of cyclohexane-1,1-dithiol with hydrogen chloride.<sup>1a</sup>

A displacement reaction between cyclohexane-1,1-dithiol and 1,2-dibromopropane in alkaline medium did not yield a dithioketal but afforded instead the trithiane **3**. This product must arise by capture of a sulfur from a second molecule of cyclohexane-1,1-dithiol.



The facile cleavage of *gem*-dithio compounds was observed in the following two reactions. 2,3-Dioxyquinoxaline (**6**) formed rapidly upon admixture of equimolar amounts of 2,2-pentamethylene-1,3-dithiolane-4,5-dione (**5**) and *o*-phenylenediamine in benzene. The substitution of excess ammonia for *o*-phenylenediamine in this reaction gave as an isolable intermediate, ammonium 1,2-dithiooxalate (**7**). Ammonium 1,2-dithiooxalate gave a quantitative yield of oxamide upon being heated to 160°. Although the products isolated from the reactions of 2,2-pentamethylene-1,3-dithiolane-4,5-dione (**5**) with *o*-phenylenediamine and with ammonia suggest different reaction mechanisms, this



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