charge for gc consisted to about 75% of the starting material **5** (*cf.* A above). This obnoxious behavior was observed in five runs as here described, and in gc of several samples from two runs as in A.

When the solvolytic procedure differed from that just described by addition of 2% of water to the solvent, rate of conversion of the intermediate was accelerated; the first peak in gc (identified as **8** by mass spectrum) was of approximately twice the height of the second.

Two samples of diester **8** were hydrolyzed to acid, which was reesterified to give the original ester, as an additional confirmation that **8** is not the hemiketal of the cyclic β-keto ester. For this purpose, 50 mg of **8** collected from gc was heated under reflux for 18 hr with 2 ml of a solution prepared from 4.3 ml of concentrated H_2SO_4, 7.3 ml of glacial acetic acid, and 7.6 ml of water. The reaction product, which was acidic, was esterified as in A except that reaction time was 4 hr. Gc of the product on the column used for the above analyses, at 198°, gave three peaks in the tracing, not overlapping significantly, with retention times of 6.3, 10, and 12.5 min, with areas (in the same order) in the approximate ratio of 4:3.5:1. The first peak proved to be the diester **8** (mass spectrum), while the compounds giving longer retention times were not encountered in other phases of this work, and have not been investigated.

One sample of cyclic product **5** was hydrolyzed in aqueous acid as described for hydrolysis of the diester **8**, above. The product of hydrolysis, which was entirely acidic material, was esterified as described just above. Gc showed two peaks of short retention time and a major peak of retention time expected for **8**; mass spectrum of the collected product verified this identity.

Cyanoethylation Product from Acetone (11).—Application of cyanoethylation to acetone in DME solvent, with solid KOH as catalyst, yielded a red, waxy material, from which no homogeneous product could be isolated. The procedure previously described[9], using a solution of KOH in *tert*-butyl alcohol, yielded the product described by Bruson and Riener, but in about one-fourth the yield. Our recrystallized sample consisted of colorless crystals, mp 149–154° (lit.[9] mp 154°).

Registry No.—**3**, 34917-90-3; **4**, 34886-35-6; **5**, 34886-36-7; **8**, 34886-37-8; **9**, 34886-38-9; **11**, 34886-39-0; 2-octanone, 111-13-7.

The Synthesis and Properties of 2-(2-Cyanoethylidene)-1,3-dithiane and Its Isomeric Ketene Thioacetal[1a]

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The preparation of 2-formyl-1,3-dithiane from 2-lithio-1,3-dithiane and dimethylformamide is reported. Wittig reaction of this versatile aldehyde gave, under different conditions, both "normal" coupling (**1**) and the rearranged ketene thioacetal **6**. Base-catalyzed treatment of **1** gave exclusively **6**, indicating the thermodynamic preference for the ketene thioacetal structure. Alkylation of **1** or **6** *via* its lithio salt gave only products derived from the carbanion α to the cyano group (**11**); yet at equilibrium the conjugation of the double bond favored the ketene thioacetal structure. These results suggest that there is considerable relief of ring strain when the 2 position is sp^2 hybridized. A further effect to account for these results may lie in enhanced overlap by 3p orbitals with the 2p orbitals of carbon when two adjacent sulfur atoms are present.

The synthetic utility of 1,3-dithianes as nucleophilic acylating agents is now well documented[2] by a variety of transformations leading to aldehydes and ketones. As part of another study, it was necessary to prepare 2-(2-cyanoethylidene)-1,3-dithiane (**1**) as a highly functionalized intermediate for further synthesis. The most direct approach seemed to involve the Wittig coupling of cyanomethylphosphorane (**2**) with 2-formyl-1,3-dithiane (**3**, R = H). Although 2-methyl-2-formyl-1,3-dithiane (**3**, R = Me) has been reported[2] from 2-lithio-2-methyl-1,3-dithiane (**4**, R = Me) and dimethylformamide, there was no mention of the preparation of **3** (R = H). The latter synthesis proved to be less than straightforward. When the lithio salt of 1,3-dithiane **4** (R = H) was treated with dimethylformamide, a complex mixture was obtained. However, when the previously prepared lithio dithiane was added to excess dimethylformamide at −10°, a viscous oil was isolated which exhibited both hydroxyl and formyl bands in the infrared. Distillation of this material afforded 2-formyl-1,3-dithiane in 81% yield. Thus, the viscous crude product is considered to be the dimer **5** arising from an aldol-type process which underwent thermal reversal to the desired product. The formyl dithiane slowly dimerized at room temperature although it is quite stable at −20° for several days.

When the formyl dithiane was added to a THF solutaining 1.1 equiv of cyanomethylphosphorane **2**,[3] the product was not the desired olefin **1** but instead the isomeric ketene thioacetal **6** (Figure 1, top). This product is undoubtedly the result of an isomerization by excess base (phosphorane or butyllithium from which it was prepared) present in the reaction medium. Base-catalyzed or thermal (~200°) equilibration attempts did not lead to any detectable quantities of the cyanovinyl dithiane **1**. The Wittig reaction was repeated using 0.9 equiv of the phosphorane so that no excessive base would be present. Indeed, this resulted in a 63% yield of the cyanovinyl dithiane **1** completely devoid of any isomeric material. To confirm the base-catalyzed lability of **1**, it was treated with 0.2 equiv of sodium ethoxide in ethanol at −20° and allowed to stand overnight at this temperature. Recovery after neutralization provided pure **6**. The isomerization was carried out at low temperature due to the instability of dithiane anions at ambient temperatures,[2] resulting in extensive decomposition of **1**. These results may be interpreted by assuming that the presence of *two* adjacent sulfur atoms causes sufficient 3p–2p π overlap in **6** to outweigh the 2p–2p π overlap in **1**. The importance of

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(1) (a) This study was supported by the National Institutes of Health (NIGMS-17941-02). (b) Address correspondence to this author at the Department of Chemistry, Colorado State University, Fort Collins, Colo. 80521.

(2) For an excellent review on this subject, see D. Seebach, *Synthesis*, **1**, 17 (1969).

(3) G. Schiemenz and E. Engelhard, *Ber.*, **94**, 578 (1961).

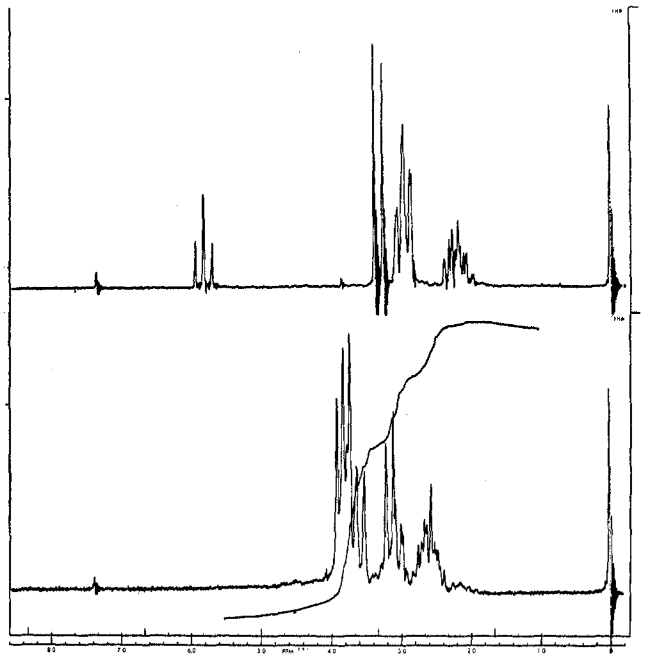
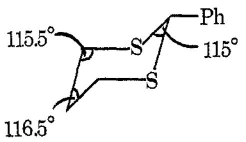


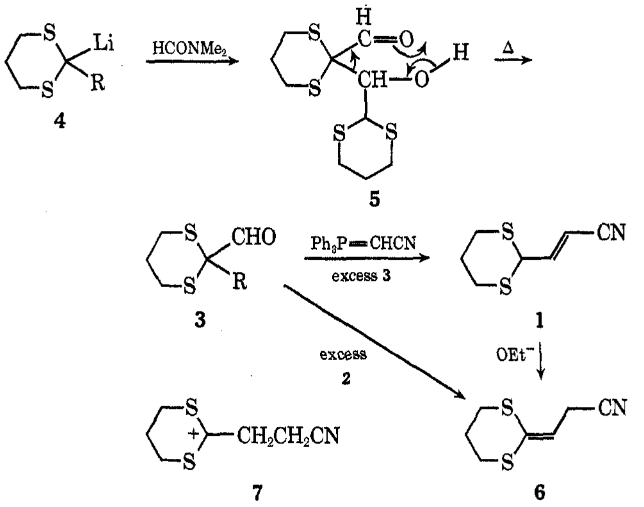
Figure 1.—(Top) 60-MHz spectrum of **6** in deuteriochloroform. (Bottom) 60-MHz spectrum of **6** in deuteriochloroform 5 min after addition of 20 equiv of trifluoroacetic acid.

3p–2p π overlap in vinyl sulfides has been questioned[4] and rightly so due to the unfavorable alignment of 3p and 2p orbitals on adjacent atoms. An alternative explanation for this phenomenon is based upon the large bond angles found for 1,3-dithianes from X-ray studies[5] on 2-phenyl-1,3-dithiane.



If the 2 position were allowed to rehybridize from an sp^3 to an sp^2 carbon, this would widen the S–C–S angle to approximately 120° and shorten the S–C bond distance, resulting in a decrease in the already strained C–C–C (116.5°) and C–C–S (115.5°) angles. There would also be considerable alteration in the dihedral angles between adjacent protons. Thus, it is concluded that the isomerization of **1** to **6**, which appears to be 99+% in favor of the latter (based upon nmr) and amounts to a $\Delta F°$ of 2.7–3.0 kcal/mol, could be the result of angle strain relief and added to this the 3p–2p π overlap by the two adjacent sulfur atoms. An X-ray study on **6** would shed some light on the relative importance of the angle strain theory.

The cyanovinyl dithiane **1** was also found to slowly isomerize to the ketene thioacetal **6** on standing or distillation, although this could be due to traces of base present. Fortunately, the crystalline cyanovinyl dithiane could be purified by passing through a silica gel column. Of further interest was the observation that the cyanovinyl dithiane **1** was perfectly stable to acidic conditions with no evidence of isomerization to **6**. This was convincingly demonstrated by addition of excess trifluoroacetic acid to a solution of **1** in deuteriochloroform. After 18 hr, there was no change in its nmr spectrum.



On the other hand, the ketene thioacetal **6** reacted within 5 min with excess trifluoroacetic acid, as evidenced by the disappearance of the vinyl signal to give the stable cation **7** (Figure 1, bottom). This behavior has recently been noted for a series of related ketene thioacetals derived from 1,3-dithianes.[6] The rapid reaction of **6** with acid to give a stable cation must be reckoned with when considering the importance of 3p–2p π overlap in sulfur systems.

Due to the facile base-catalyzed isomerization of **1** to **6** an investigation into the site of alkylation of the carbanions was prompted.[7] One may anticipate a highly delocalized anion **8** upon proton removal from either **1** or **6** possessing three potential sites for alkylation (A, B, C). Alkylation at A would give rise to **9**, alkylation at C would give **10**, and alkylation at B would produce **11**. Precedent for alkylation at A has been described by Seebach,[2] whereas ketenimine formation from alkylation of α carbanions of nitriles has been reported by Newman.[8] Since protonation of **8** has already shown to proceed exclusively at B to give **6**, it was not surprising to learn that alkylation afforded exclusively **11**. The anion **8** was generated at −78° and treated at this temperature with ethyl iodide, producing a crude mixture of **11a** and **11b** containing >95% **11a** (R = Et) (Figure 2, top). The yield of ethylated material was 74%. In addition, there was obtained a small quantity of geminal diethylated material (6–8%) due presumably to the slight inequity in the amount of butyllithium employed. Since the isolation of alkylated material did not involve any aqueous work-up, but simply solvent evaporation, only neutral material was recovered and there was little opportunity for equilibration of the products. This kinetically controlled mixture was equilibrated with a catalytic amount of sodium in ethanol at −20°. It was surprising to learn that the equilibrium mixture did in fact contain approximately 25% of the cyano-

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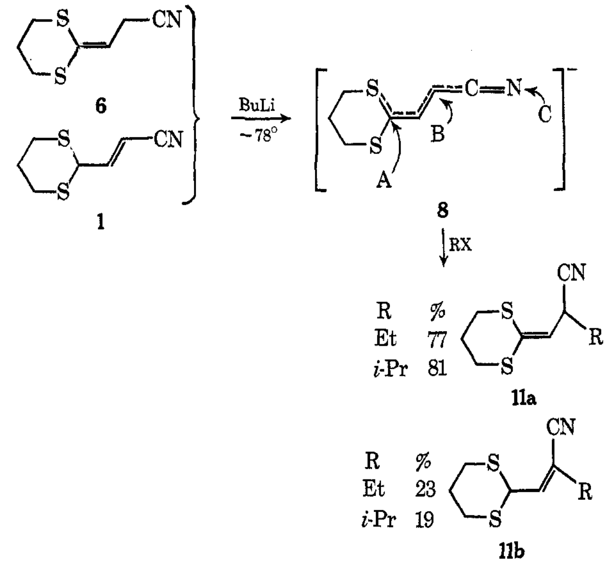
(4) For discussions relating to the importance of 3p–2p π bonding in sulfur compounds, see M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966); R. L. Autrey and P. W. Scullard, *ibid.*, **90**, 4924 (1968), and earlier references cited in these reports.

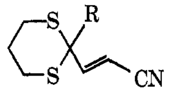
(5) H. T. Kalff and C. Romers, *Acta Crystallogr.*, **20**, 490 (1966).

(6) F. A. Carey and J. R. Neergard, *J. Org. Chem.*, **36**, 2731 (1971).

(7) A recent study on the resonance-stabilized anion of 2-styryl-1,3-dithianes [D. L. Coffen, T. E. McEnter, and D. R. Williams, *Chem. Commun.*, 913 (1970)] described alkylation at *two sites* in the molecule, contrary to what was found in this study for **1** and **6**.

(8) M. S. Newman, T. Fukunaga, and T. Miwa, *J. Amer. Chem. Soc.*, **82**, 873 (1960).





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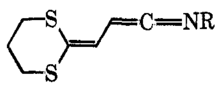

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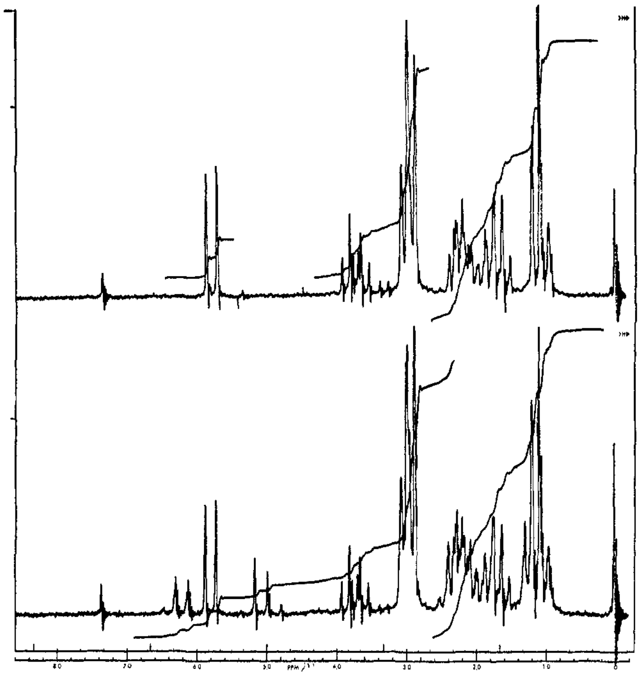


Figure 2.—(Top) 60-MHz spectrum of **11a** before equilibration with sodium ethoxide. (Bottom) 60-MHz spectrum showing **11a** and **11b** after equilibration.

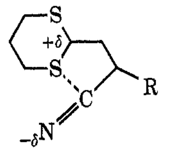
vinyl dithiane, **11b** (R = Et). From Figure 2 (bottom), the doublets at 5.1 ($J = 11$ cps) and 6.2 ppm (J = 11 cps) arising from the protons α to sulfur and at the vinyl carbon, respectively, in **11b** are clearly visible. The gas chromatogram of **11a**, which showed only a single peak, exhibited two discernible peaks in the ratio 77:23 after equilibration, indicating that the composition of the mixture was thermally unaffected. Repeated alkylations of **1** and **6**, using varying amounts of base, afforded prior to equilibration 75–95% of **11a** and 5–25% of **11b** (by nmr assessment) with similar ratios observed on vpc examination. This further supports the assumption that the kinetic product compositions are thermally inert. Treatment of these various mixtures with sodium ethoxide–ethanol at −20° as mentioned above converted them to the equilibrium value (77:23). Thus, the presence of the ethyl group has lowered the energy difference between the isomeric dithianes. The reason for this fact is not clearly visible. One factor could be that the steric bulk of the ethyl group in **11** is responsible since it is absent in **6** and **1**. The introduction of a larger alkyl group should then increase the proportion of **11b** over **11a**. With this in mind, the anion **8** was similarly alkylated with isopropyl bromide and resulted in a 31% yield of **11a** and **11b** (R = *i*-Pr). The ratio of **11a** to **11b** both in the crude and equilibrated material was found to be 81:19. This is not significantly different from the ratios observed for the ethylated derivatives and one must therefore conclude that the size of the alkyl groups plays little or no role in the equilibrium composition.

The minor components in the equilibrated system, **11b**, were assigned structures with the alkyl group and the dithiane ring trans to each other. Although, *a priori*, this would be a reasonable assignment in view of the fact that the two largest groups would be at maximum distance, the nmr spectrum of **11** (**a** and **b**) support this configuration. The vinyl protons in **11b** (R = Et, *i*-Pr) appear as a doublet ($J = 11$ cps) at 6.2–6.3 ppm, whereas the β-vinyl proton in **1** appears at 6.9 ppm as a pair of doublets. The J value for the α- and β-vinyl protons in **1** is 16 cps, indicative of the trans configuration; the β-vinyl proton is therefore cis to the cyano group. Since the vinyl protons in **11b** are at considerably higher field than that found in **1**, it is reasonable to assume that they are trans to the cyano group and out of its deshielding region.

The possibility of sulfur interaction with the cyano group in **11b** to account for its increased stability and presence in the equilibrium mixture was considered. Either 3p–2p bonding as in **12** or 3d–2p bonding as in **13** could conceivably enhance the stability of this system since, as mentioned above, the cyano group is cis to the dithiane moiety. These effects were precluded when 2-formyl-1,3-dithiane (**3**) was treated with the phosphorane derived from ethyl α-bromobutyrate, producing, after equilibrium, an 82:18 mixture containing proportions of the ketene thioacetal **14a** and vinyl dithiane **14b** in close agreement with that obtained from the nitrile. It should be noted that the initially isolated esters obtained from this reaction indicated by the nmr spectrum a high proportion of **14b** (∼90% kinetic product). Distillation in order to purify the material then produced the 82:18 mixture mentioned earlier (thermodynamic product). The similar isomer distribution in **11** and **14** would tend to dispute any unusual interaction of the cyano group in the alkylated vinyl dithianes, since the carboethoxy group, presumably trans to the dithiane, could not engage in such behavior.

It, therefore, seems likely that the effect of alkyl substitution on the cyano- or carboethoxyvinyl dithiane (**11** and **14**, respectively) with regard to their double bond positions rests mainly on the accepted fact that increasing the alkyl substitution on carbon–carbon double bonds increases their thermodynamic stability.

The results of this study invite further investigation into its potential synthetic utility. For example, the readily available 1-formyl-1,3-dithiane would allow



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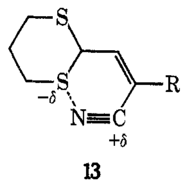

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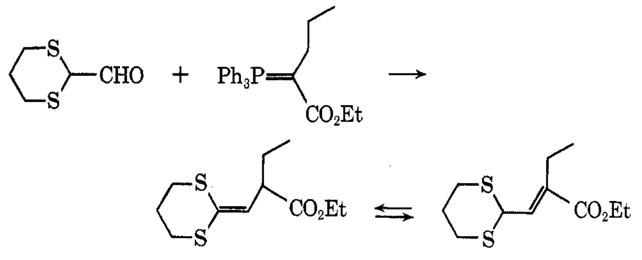
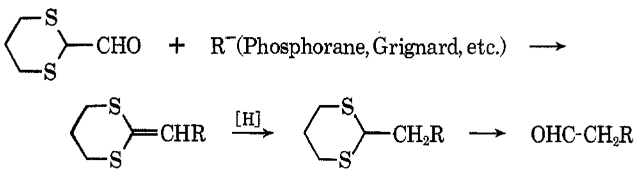


14a 82% **14b** 18%

coupling with a variety of Wittig-type reagents or other nucleophilic species (RLi, RMgX, etc.) to afford directly the ketene thioacetals, which may be reduced and cleaved[2] to the aldehydes (Scheme I).

SCHEME I



The scheme, if successfully implemented, would in effect provide a versatile and useful two-carbon homologation of alkyl and aryl halides to aldehydes, which has not been available through the dithiane route.[9,9a]

Experimental Section

Nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as internal standard. Chemical shifts are reported in parts per million (δ). Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer and peaks are reported in wavenumbers (cm^{-1}). The gas chromatography was performed on Hewlett-Packard 5750 instruments using 0.25 in. × 8 ft columns. Collection of samples was made with a small U-shaped pyrex collecting tube. 1,3-Dithiane was either prepared by the method of Corey[10] or purchased from Aldrich Chemical Co. Mass spectra were obtained using an AEI MS-9 at 70 eV. Microanalysis were performed by Midwest Microlab, Indianapolis, Ind.

2-Formyl-1,3-dithiane (3, R = H).—A solution containing 24.0 g (0.20 mol) of 1,3-dithiane in 400 ml of anhydrous tetrahydrofuran was cooled with stirring under nitrogen to −30° (Dry Ice–isopropyl alcohol) and treated dropwise with 59.2 g (0.20 mol) of 26 wt % *n*-butyllithium in hexane. After 1 hr of additional stirring the solution was transferred by syringe and added dropwise to a flask containing previously cooled (−10°) dimethylformamide (60 ml). The mixture was allowed to stir for 2 hr at −10° and then stored overnight at 0°. The resulting suspension was poured into ice water (400 ml) and the mixture was extracted several times with pentane. The aqueous layer was neutralized with dilute (1 *N*) hydrochloric acid and then extracted several times with ether. The ethereal extracts were dried ($MgSO_4$) and concentrated to give a viscous, cloudy oil which was distilled: bp 83–85° (0.45 mm); yield 24.0 g (81%) of colorless liquid; infrared (neat) 2675 (CHO), 1715 (C═O), 912 cm^{-1} (dithiane); nmr ($CDCl_3$) δ 9.6 (d, 1, J = 2 Hz, -CHO), 4.2 (s, 1, >CHCHO), 2.4–3.4 (m, 4, $-CH_2S-$), 1.8–2.3 (m, 2, $-CH_2-$). The product was stored at −20° to prevent dimerization, which occurs slowly at room temperature.

Anal. Calcd for $C_5H_8OS_2$: C, 40.51; H, 5.44; O, 10.79. Found: C, 40.60; H, 5.48; O, 10.49.

2-(2-Cyanovinyl)-1,3-dithiane (1).—Triphenylcyanomethylphosphonium chloride was prepared in 80% yield by heating chloroacetonitrile and triphenylphosphine (50% excess) in benzene overnight, collecting the phosphonium salt, washing with benzene, and drying *in vacuo*. Butyllithium (2.59 g, 8.5 mmol) as a 21 wt % solution in hexane was added at 0° to a suspension of the phosphonium salt (3.38 g, 10.0 mmol) in 40 ml of anhydrous tetrahydrofuran under a nitrogen atmosphere. The yellow suspension was stirred for 1 hr at room temperature and then cooled to −30° (Dry Ice–acetone). To this was rapidly added 1-formyl-1,3-dithiane (3, R = H, 1.48 g, 10.0 mmol) in 5 ml of tetrahydrofuran. The mixture was allowed to warm slowly to room temperature with stirring. After 2 hr, the solvents were removed by rotatory evaporation and the residue was triturated several times with warm ether or pentane. The ethereal (or pentane) solution was concentrated, affording an orange oil which solidified on standing. Elution of this material through neutral silica gel with ether–hexane (1:1) gave a colorless, crystalline product: yield 0.90 g (63%); mp 63–65°; infrared (KBr) 3040 (═CH), 2215 (C≡N), 1618 (C═C), 960 cm^{-1} (*trans*-CH═CH); nmr ($CDCl_3$) δ 6.9 [d (J = 16 Hz) of d (J = 6 Hz), 1, C**H**═CHCN], 5.7 [d (J = 16 Hz) of d (J = 2 Hz), 1, -CH═C**H**CN], 4.6 [d (J = 6 Hz) of d (J = 2 Hz), 1, <C**H**CH═CHCN], 2.6–3.1 (m, 4, CH_2S), 1.7–2.2 (m, 2, $-CH_2-$).

Anal. Calcd for $C_7H_9NS_2$: C, 49.08; H, 5.30; N, 8.17. Found: C, 49.08; H, 5.12; N, 8.23.

The crude product was also purified by recrystallization from ether–pentane but gave a slightly lower melting product, mp 61–63°. The latter is presumably contaminated with the isomeric dithiane, 6, although not detectable in the nmr spectrum.

2-(2-Cyanomethylvinylidene)-1,3-dithiane (6).—Butyllithium (7.78 g, 25.5 mmol) as a 21 wt % hexane solution was added to a suspension of triphenylcyanomethylphosphonium chloride (9.26 g, 27.4 mmol) in 60 ml of dry tetrahydrofuran at 0–3°. After the yellow suspension was stirred for 1 hr at room temperature, 1-formyl-1,3-dithiane (3.44 g, 23.2 mmol) in 10 ml of tetrahydrofuran was added dropwise and the mixture was stirred for 2 hr. The solvents were removed by rotatory evaporation and the oily residue was distilled, producing 2.5 g (63%) of a colorless oil: bp 108–110° (0.1 mm); infrared (neat) 3020 (═CH), 2245 (C≡N), 1579 ($-S_2C$═C); nmr ($CDCl_3$) δ 5.81 (t, 1, J = 7 Hz, C═CH), 3.33 (d, 2, J = 7 Hz, $-CH_2CN$), 2.8–3.1 (m, 4, CH_2S), 1.9–2.4 (m, 2, $-CH_2-$). The product was stored at −20° since it tends to darken on standing at 0–25° after several days.

Anal. Calcd for $C_7H_9NS_2$: C, 49.08; H, 5.30; N, 8.17. Found: C, 49.03; H, 5.22; N, 8.19.

Equilibration of 2-(2-Cyanovinyl)-1,3-dithiane (1) to 2-(2-Cyanomethylvinylidine)-1,3-dithiane (6).—A solution containing 206 mg (1.20 mmol) of 1 in 10 ml of absolute ethanol was cooled to −30° and treated with 2 ml of ethanolic sodium ethoxide in which 10 mg of sodium was dissolved. The pale yellow solution was stored for 30 hr at −20°, after which it had turned orange in color. The cold solution was neutralized with dilute acetic acid, at which point the orange color had returned to pale yellow. The solvents were evaporated *in vacuo* and the residue was taken up in chloroform, the latter solution washed with dilute bicarbonate and then with water, dried ($MgSO_4$), and concentrated. An oily residue remained (178 mg, 86%) whose ir and nmr spectra were identical with those of 6. When the equilibration was attempted at room temperature, the solution took on a deep brown color and several products were formed suggesting decomposition of 1 or 6 under these conditions.

Alkylation of 1 or 6 with Ethyl Iodide.—In a typical experiment, *n*-butyllithium (534 mg, 1.75 mmol, 21 wt %) was added to 1 or 6 (300 mg, 1.75 mmol) in 6 ml of anhydrous tetrahydrofuran at −78°. The solution immediately became yellow and a suspension formed. After the solution was stirred at this temperature for 30 min under nitrogen, ethyl iodide (546 mg, 3.50 mmol) in 1 ml of tetrahydrofuran was added. The mixture was stirred for 1 hr at −78° and then allowed to warm to room temperature. The solvents were removed by rotary evaporation and the residual material was triturated several times with hot hexane. Con-

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[9] Two-carbon homologations of alkyl halides to aldehydes are available from other systems; *cf.* A. I. Meyers, G. R. Malone, and H. W. Adickes, *Tetrahedron Lett.*, **No. 42**, 3715 (1970), and earlier references cited therein.

[9a] NOTE ADDED IN PROOF.—The preparation of ketene thioacetals from 2-lithio-2-trimethylsilyldithianes has recently been reported by Professor D. Seebach (University of Giessen) in *Angew. Chem., Int. Ed. Engl.*, in press, and Professor F. A. Carey, *J. Org. Chem.*, **37**, 1926 (1972).

[10] D. Seebach, E. J. Corey, and N. R. Jones, *J. Org. Chem.*, **33**, 300 (1968).

centration of this solution left an orange-colored oil, 258 mg (74%), a portion of which was injected into the gas chromatograph (240°, UCW-98 column). The ratio of **11a** to **11b** varied among several such alkylations from 75–95% **11a** to 5–25% **11b** depending upon the amount of butyllithium and the care exercized in the work-up to exclude moisture. Since the products were very sensitive to base, equilibration conditions were difficult to circumvent. The highest proportion (<95%) of **11a** (Figure 2) was accomplished in the above described experiment: nmr ($CDCl_3$) δ 5.80 (1, d, J = 10 Hz, $=CH$), 3.75 [1, d (J = 10 Hz) of t (J = 7 Hz), CHCN], 2.8–3.1 (m, 4, CH_2S), 2.1–2.4 (m, 2, $-CH_2CH_2S$), 1.75 (2, p, J = 7 Hz, $\mathbf{CH_2}CH_3$), 1.1 (3, t, J = 7 Hz, CH_3); infrared (neat) 2239 cm^{-1} (unconjugated $C\equiv N$); m/e 199 (calcd 199). The gas chromatogram indicated a small amount of a second component poorly resolved from the main peak of **11a**.

Equilibration of **11a** in sodium ethoxide–ethanol at −20° for 30 hr gave after recovery (as described for equilibration of **1** to **6**) a product which exhibited two distinct peaks in the gas chromatogram (UCW-98 column, 240°) integrating at 23:77. The nmr ($CDCl_3$) for this equilibrated product is shown in Figure 2 (bottom). The infrared (neat) shows two clearly separated bands at 2240 (unconjugated $C\equiv N$) and 2219 cm^{-1} (conjugated $C\equiv N$).

Alkylation of 1 or 6 with Isopropyl Bromide.—To 150 mg (0.88 mmol) of **6** or **1** in 2 ml of anhydrous tetrahydrofuran cooled to −78° under nitrogen was added 267 mg (0.88 mmol) of 21 wt % *n*-butyllithium in hexane. After 30 min 221 mg (1.8 mmol) of isopropyl bromide in 1 ml of tetrahydrofuran was added and the reaction was allowed to warm to room temperature. The solvents were evaporated and the residue was triturated several times with 15-ml portions of hot hexane. Filtration of the hexane solution followed by concentration left a yellow oil, 58 mg (31%). Vpc examination (UCW-98, 250°) revealed two distinct peaks (19 and 81%). Collection from the vpc gave m/e 213 (calcd 213), **11a** and **11b** (R = *i*-Pr): infrared (neat) 2240, 2220 cm^{-1} (unconjugated and conjugated CN); nmr ($CDCl_3$) δ 6.2 [d, J = 11 Hz, 0.2 H, $\mathbf{CH}=C(CN)C_3H_7$], 5.85 (d, J = 9 Hz, 0.8 H, $-S_2C=CH$), 5.1 (d, J = 11 Hz, 0.2 H, $-S_2CH-$), 3.7 [d (J = 9 Hz) of d (J = 9 Hz), 0.8 H, -CHCN], 2.9–3.1 (m, 4, CH_2S), 1.6–2.6 [m, 3, $\mathbf{CH_2}CH_2S$, $\mathbf{CH}(CH_3)_2$], 0.9–1.4 [m, 6, $(CH_3)_2C$].

Equilibration of this mixture with sodium ethoxide–ethanol at −20° for 30 hr gave no significant changes in the vpc, ir, and nmr analyses.

Wittig Coupling of 2-Formyl-1,3-dithiane with the Phosphorane of Ethyl α-Bromobutyrate (14a and 14b). A. *N*-Propyltriphenylphosphonium Bromide.—A solution of triphenylphosphine (48 g) and 1-bromopropane (22.4 g) in dry xylene was heated under reflux for 20 hr. Upon cooling, the solid was removed by filtration, washed with dry ether, and dried: yield 63 g (90%); nmr ($CDCl_3$) δ 7.6–8.2 (m, 15), 3.5–4.0 (m, 2, $-CH_2P^+Ph_3$), 1.1–2.1 (m, 5, CH_3CH_2).

B. 1-Carboethoxy-*n*-propyltriphenylphosphonium Chloride.[11]—*n*-Propyltriphenylphosphonium bromide (28.4 g, 73.6 mmol) as a suspension in dry benzene (50 ml) at 0° under nitrogen was treated with *n*-butyllithium (38 ml, 61 mmol) as a 15 wt % solution in hexane. The mixture was stirred for 1 hr, a solution of ethyl chloroformate (3.33 g, 30.5 mmol) in 5 ml of benzene was added, and stirring was continued for an additional 1 hr at room temperature. The phosphorane thus formed *in situ* was then treated with a benzene solution (5 ml) of 2-formyl-1,3-dithiane (5.0 g, 33 mmol). The mixture was stirred at room temperature for 16 hr and then poured into ice water. The benzene layer was separated and the aqueous solution was extracted with ether. Combination of the organic extracts, drying ($MgSO_4$), and concentration produced a residue, 6.4 g, which was distilled, bp 110–114°, (0.1 mm). The gas chromatogram (UCW-98, 240°) showed that two components in the ratio 82:18 were present: nmr ($CDCl_3$) δ 6.65 (d, J = 10 Hz, 0.18 H, $CH=C$ in **14b**), 5.82 (d, J = 10 Hz, 0.82 H, $-S_2C=CH$ in **14a**), 4.82 (d, J = 11 Hz, 0.18 H, $-S_2CH$ in **14b**), 4.15 (two overlapping quartets for $-OCH_2CH_3$ in **14a**, **14b**), 3.40 [d (J = 7 Hz) of t (J = 10 Hz), 0.82 H, $-\mathbf{CH}(C_2H_3)CO_2Et$ in **14a**], 2.8–3.1 (m, 4, SCH_2), 2.0–2.5 (m, 2, $\mathbf{CH_2}CH_2S$), 0.85–1.9 (m, 8); m/e 246 (calcd 246).

Registry No.—**1**, 34906-11-1; **3** (R = H), 34906-12-2; **6**, 34906-13-3; **11a**, 34906-14-4; **11b**, 34906-15-5; **14a**, 34906-16-6; **14b**, 34906-17-7.

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[11] H. J. Bestmann and H. Schulz, *Angew. Chem.*, **72**, 27 (1961), has described the *in situ* preparation of α-alkylcarboethoxy phosphoranes.

The Structure of Aroyl Isocyanide Trimers[1]

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The structure of the trimer of benzoyl isocyanide prepared by the action of silver cyanide on benzoyl bromide is shown to be 7-benzoylimino-2,5-diphenyloxazolo[5,4-*d*]pyrimidin-7-one (**2**) on the basis of chemical and spectroscopic evidence. The scope and limitation of the trimerization reaction is discussed.

The trimer of benzoyl isocyanide was first reported in 1895 by Nef[2] who prepared it by treating benzoyl bromide with silver cyanide. Diels and Stein[3] repeated this work in 1907 and on the basis of chemical evidence proposed the azetine structure **1**. In a review of trimethylenimines,[4] Moore noted that structure **1** was quite unlikely for the trimer. The benzoyl isocyanide trimer is also formed[5] as a minor product (2%) in the thermolysis of 2-azido-5-phenyl-1,3,4-oxadiazole along with benzoyl cyanide (35%).

Results

The benzoyl isocyanide trimer has been shown to be 7-benzoylimino-2,5-diphenyloxazolo[5,4-*d*][1,3]oxazine (**2**) on the basis of spectral and chemical evidence. The mass spectrum of the trimer afforded a molecular ion at m/e 393 consistent with $(PhCONC)_3$. The nmr spectrum indicated the presence of aromatic hydrogens only. The ir spectrum was devoid of triple-bond absorption and exhibited maxima at 1718 (sh), 1700, 1660, and 1640 cm^{-1}. Considered in conjunction with the chemical evidence presented below only structures **2** and **3** are consistent with the data. Structure **2**, a primary adduct, is favored over Dimroth rearrangement

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[1] Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 12–17, 1971.

[2] J. U. Nef, *Ann.*, **287**, 303 (1895).

[3] O. Diels and H. Stein, *Ber.*, **40**, 1655 (1907).

[4] J. A. Moore in "Heterocyclic Compounds with Three and Four Membered Rings," Part II, R. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 916.

[5] P. A. S. Smith in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y. 1970, p 149; H. Dounchis, Ph.D. Thesis, The University of Michigan, Ann Arbor, Mich, 1967.