

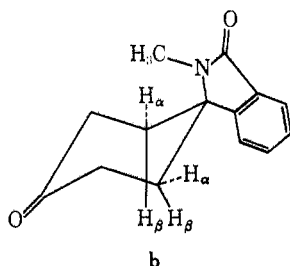
cause of the discrepancy in melting point, the compound was fully characterized: mass spectrum m/e 229 (parent ion); ir (CHCl_3) 1680 (γ -lactam $\text{C}=\text{O}$) and 1713 cm^{-1} (cyclohexanone $\text{C}=\text{O}$); reported 1676 and 1713 cm^{-1} ; nmr (CDCl_3) δ 1.9 (m,

2, C-H¹⁴), 2.3–3.1 (m, 6, $-\text{C}-\text{CH}_2-$ and C-H), 3.09 (s, 3, N-CH₃), and 7.60–7.95 (m, 4, ArH).

Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.15; H, 6.63; N, 5.99.

Following the procedure of Fieser,¹⁵ a solution of 2.29 g (0.01 mol) of the above product in 3.2 ml of ethanedithiol was treated with 2.2 ml of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and the solution was kept at ambient temperature for 1 hr. Ice water and Et_2O were added, and the organic solution was extracted with four 50-ml portions of 10% NaOH. The dried (MgSO_4) solvent was removed under reduced

(14) Assuming the product to have the conformation shown in b in which



the phenyl portion of the phthalimidine moiety assumes a more or less equatorial configuration, this multiplet can be assigned to the two equivalent equatorial protons H_α. A model shows these protons to be shielded (relative to the equivalent pair of axial protons H_β) by the positive anisotropic effect of the benzene ring and the amide carbonyl.

(15) L. F. Fieser, *J. Amer. Chem. Soc.*, **76**, 1945 (1954).

pressure, and the residue was crystallized from 15 ml of *i*-PrOAc. The product, 1.94 g (64%), showed biphasic melting. Inserted at 100°, it melted at 161–163°. Inserted at 145°, it melted, resolidified, and melted again at 161–162°. The mother liquors from the above crystallization were stripped to yield 0.65 g of solid, one peak in the glc identical with the major crop: total yield 85%; ir (CHCl_3) 1675 cm^{-1} (γ -lactam $\text{C}=\text{O}$); nmr (CDCl_3) δ 1.17–2.84 (m, 8, four CH₂ groups), 3.07 (s, 3, N-CH₃), 2.38 (m, 4, S-CH₂CH₂-S), and 7.17–8.00 (m, 4, ArH).

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{NOS}_2$: C, 62.91; H, 6.27; N, 4.59. Found: C, 62.88; H, 6.27; N, 4.49.

A 0.6-g (0.02 mol) sample of the above thioketal was stirred and refluxed with 3–4 g of Raney nickel in 10 ml of absolute ethanol. After 5 hr, glc analysis indicated that all of the thioketal had been converted to a material with lower retention time. The metal was filtered off and washed with EtOH, and the filtrates were stripped *in vacuo*. The residual oil (0.34 g, 81% crude yield) was homogeneous on glc. Crystallization from heptane gave 0.14 g (33%) of crystals: mp 87–88.5°; mass spectrum m/e 215 (parent ion); uv $\lambda_{\text{max}}^{\text{EtOH}}$ 222 m μ (ϵ 9660), 230 (9360), 243 (5870), 269 sh (3090), and 231 (2200); nmr (CDCl_3) δ 1.20–2.40 (m, 10, five CH₂ groups), 3.04 (s, 3, N-CH₃), and 7.30–8.00 (m, 4, ArH).

Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.94; H, 7.63; N, 6.39.

Registry No.—1b, 23659-57-6; 2a, 15836-66-5; 2b, 20141-84-8; 2c, 23659-74-7; 2c dithioketal, 23659-74-7; 2d, 23659-69-0; 3a, 26278-31-9; 3b, 26278-32-0; 3b·H₂SO₄, 26322-31-6; 3c, 26278-33-1; 3c HClO₄ salt, 26278-34-2; 3d, 26322-30-5; 2'-methylspiro[cyclohexane-1,3'-phthalimidin]-4-one, 26278-35-3.

The Cycloaddition of Aroyl and Sulfonyl Cyanides with 5,5-Dimethoxy-1,2,3,4-tetrahalocyclopentadienes

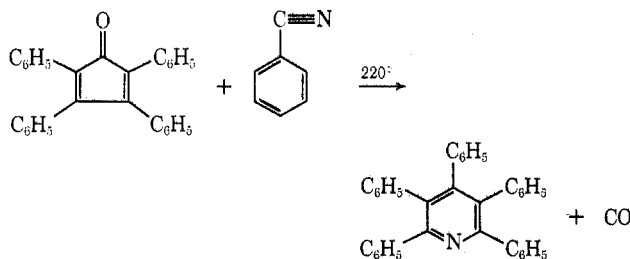
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The cycloaddition of aroyl and sulfonyl cyanides with 5,5-dimethoxy-1,2,3,4-tetrahalocyclopentadienes is facilitated by electron-withdrawing substituents. The sulfonyl cyanides have been shown to be more reactive than the aroyl cyanides providing further evidence that delocalization of the π charge density of the cyano group facilitates the cycloaddition reactions. The effect of solvent on the reaction of benzoyl cyanide and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene is also described.

The dienophilicity of the cyano group is well known and the subject has been reviewed.² The first observation of the dienophilic properties of the cyano group was reported by Dilthey³ who synthesized pentaphenylpyr-



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(b) Organic Chemicals Department, The Dow Chemical Company, Midland, Michigan 48640. (c) E. C. Britton Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640.

(2) G. J. Janz in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 97.

(3) J. Dilthey, *Ber.*, **66**, 1162 (1935).

idine from tetracyclone and benzonitrile. An extensive study of the cycloaddition reaction of perhalonitriles, *e.g.*, $\text{CF}_3\text{C}\equiv\text{N}$ with butadiene in the gas phase at 350–400°, was carried out by Janz and coworkers.⁴ Yields of the pyridines were essentially quantitative. Alder also cited an example of the dienophilic properties of the cyano group in which cyanofornic ester was found to react with butadiene to give 2-picolinic acid ester derivatives.⁵ Our interest in this area originated from the literature report^{6a} that 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (2a) would undergo reaction with benzoyl cyanide (1) to give a methyl picolinate. This paper describes our results concerning the effect of substituents on the benzoyl cyanide, the effect of solvent on the reaction, and structural proof of the side reaction products. In addition, the reaction is described for a

(4) G. J. Janz and A. R. Monohan, *J. Org. Chem.*, **29**, 569 (1964).

(5) K. Alder, "Newer Methods of Preparative Organic Chemistry," Wiley-Interscience, New York, N. Y., 1948.

(6) (a) T. Jawarski and W. Polaczowska, *Rocz. Chem.*, **31**, 1337 (1957);

(b) T. Jaworski and B. Korybut-Daszkiwicz, *ibid.*, **41**, 1521 (1967).

TABLE I^c
 REACTION CONDITIONS AND PHYSICAL PROPERTIES OF TRIHALOPICOLINATES

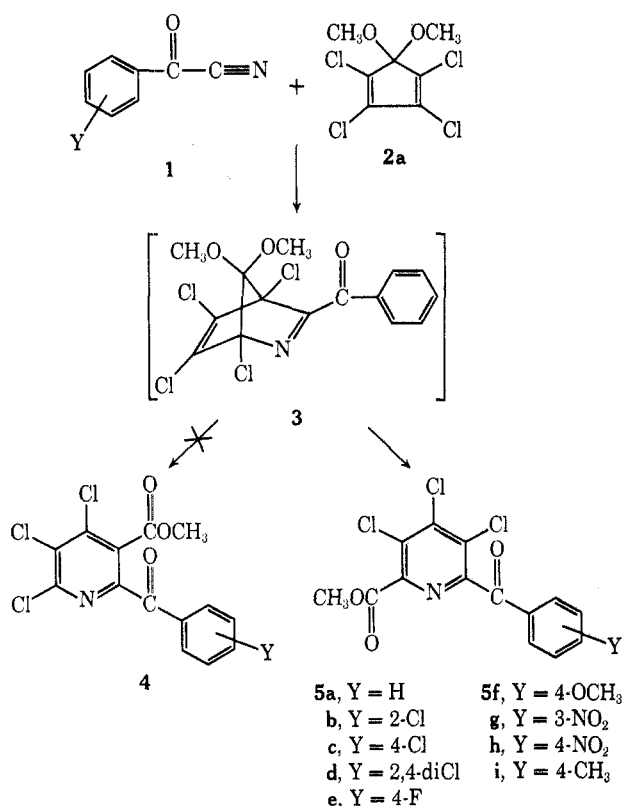
| Compd | Solvent | Temp, °C | Time, hr | Mp, °C | Yield, % | Mol wt ^b |
|-------|---------------------------|----------|----------|---------|------------------|---------------------|
| 5b | None | 190 | 7 | 132-134 | 9 | 344 (M - Cl) |
| 5c | None | 190 | 13.5 | 132-134 | 40 | 379 |
| 5d | None | 190 | 9 | 135-136 | 16 | 378 (M - Cl) |
| 5e | None | 190 | 17 | 133-135 | 30 | 357 |
| 5f | None | 190 | 32 | 105-106 | 13 | 376 |
| 5g | None | 190 | 9 | 122-125 | 31 | 389 |
| 5h | None | 190 | 9 | 130-131 | 11 | 389 |
| 5i | None | 190 | 32 | 151-153 | 10 | 357 |
| 16d | <i>o</i> -Dichlorobenzene | 165 | 48 | 127-129 | ... ^c | 461 |
| 16e | <i>o</i> -Dichlorobenzene | 165 | 15 | 131-132 | 74 | 545 |
| 16f | <i>o</i> -Dichlorobenzene | 160 | 5 | 173-175 | 60 | 556 |
| 16a | None | 150 | 20 | 105-106 | 76 | 362 (M - 2Cl) |
| 16b | None | 150 | 10 | 107-109 | 76 | 334 (M - HCl) |
| 16c | None | 140 | 7 | 135-137 | 81 | 424 |

^a Satisfactory analytical values (± 0.35 for C, H, N, and halogen) were reported for all compounds in this table: Ed. ^b The molecular weight, number, and kind of halogen were determined for each product except for the noted cases which did not give a parent peak. ^c Some decomposition of the ketal, **2b**, occurred; no attempt was made to optimize the yield.

new class of cyanides, the sulfonyl cyanides,⁷ and with the recently reported diene 5,5-dimethoxy-1,2,3,4-tetrabromocyclopentadiene.⁸

Results and Discussion

The reaction of ketal **2a** with benzoyl cyanide was repeated and found to give product with mp 145-147, in agreement with that reported by Jawarski.^{6a}

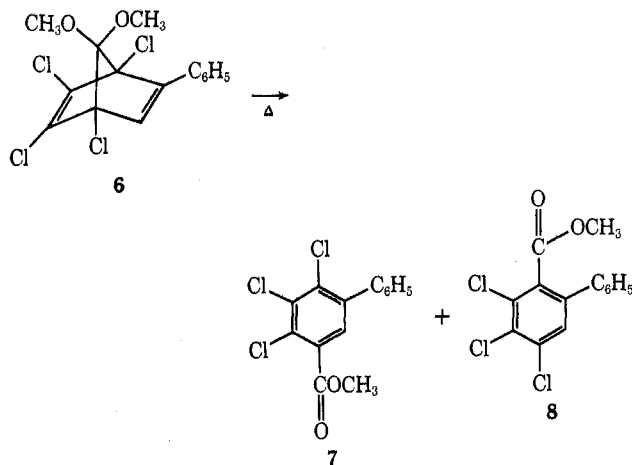


The necessity of establishing rigorously the positions of the three halogens is predicated by previous work on the thermal decomposition of 1,2,3,4-tetrachloro-7,7-

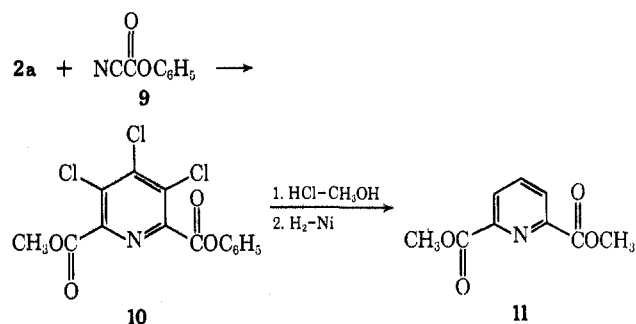
(7) (a) A. VanLeusen, A. Iedema, and J. Strating, *Chem. Commun.*, **18**, 440 (1968); (b) R. G. Pews and F. P. Corson, *ibid.*, 1187 (1969); (c) J. M. Cox and R. Ghosh, *Tetrahedron Lett.*, 3351 (1969).

(8) R. G. Pews, C. W. Roberts, and C. R. Hand, *Tetrahedron*, **26**, 1711 (1970).

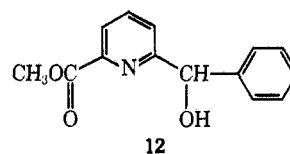
dimethoxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene (**6**) by LeMal and coworkers⁹ who demonstrated that both esters **7** and **8** were formed. Assignment of structure **5a**,



methyl 6-(benzoyl)-3,4,5-trichloropicolinate, is based on analogy with the reaction of **2a** and phenyl cyanofornate^{6b} (**9**), to give **10** and subsequent conversion of **10**

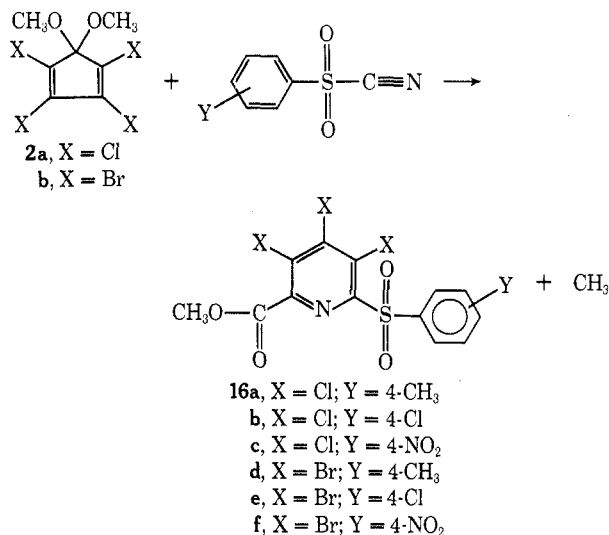


to **11**. In a similar manner **5a** was reduced to 6-(α -hydroxybenzyl) picolinate (**12**). The structure of **12** was

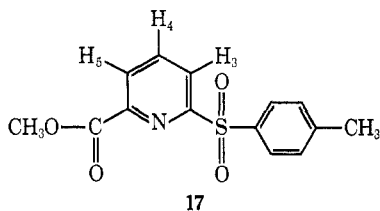


(9) D. M. LeMal, E. P. Gosselink, and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 582 (1966).

activity of the sulfonyl cyanides, *i.e.*, lower reaction temperatures, allowed the synthesis of some brominated picolinates derived from ketal **2b**. All attempts to carry out the cycloaddition of **2b** and aroyl cyanides were unsuccessful due to decomposition of **2b**. The spectral and physical properties of the pyridyl sulfones are summarized in Tables I and II.



As previously discussed for the reaction of **2a** with **1**, the reaction of **2a** with the sulfonyl cyanides could lead to two products. The substitution pattern of methyl 6-(4'-toluenesulfonyl)picolinate was characterized by reductive dehalogenation with palladium on calcium carbonate to **17**. The nmr spectrum of the three pyri-



dine protons consisted of doublets of doublets centered at δ 8.10, 8.21, and 8.32, tentatively assigned to H₄, H₃, and H₅, respectively. The coupling constants were determined as $J_{3,4} = 7.80$ Hz, $J_{4,5} = 7.75$ Hz, and $J_{3,5} = 1.05$ Hz. The coupling constants of protons in 2,3 positions of a pyridine fall in the range of 5–6 Hz, while those of protons in adjacent 3,4 or 4,5 positions fall in the range of 7–9 Hz.¹⁰ The 1.05 cps coupling constant is consistent with coupling between protons in the 3 and 5 position. The nmr spectrum is consistent with only structure **17**.

The results of the present work have provided further evidence for the dienophilicity of the cyano group. The specific reaction of 4-nitrobenzenesulfonyl cyanide with ketal **2a** appears to be the most facile 1,4 cycloaddition reaction of a cyano group reported to date.

Experimental Section

Infrared spectra were obtained with a Beckman IR-9 spectrometer. The mass spectra that are recorded in Table I were obtained on a CEC-21-110B (direct probe) instrument. Nmr spectra were recorded on either a Varian A-60A or HA-100 spec-

(10) (a) W. Brugel, *Z. Electrochem.*, **66**, 159 (1962); (b) W. Brugel, "Nuclear Magnetic Resonance Spectra and Chemical Structure," Vol. 1, Academic Press, New York, N. Y., 1967, p 156.

trophotometer. The melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Methods of preparation for many of the starting materials have been described in the literature. These compounds and the appropriate references are as follows: 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene⁹ (**2a**), 5,5-dimethoxy-1,2,3,4-tetrabromocyclopentadiene⁸ (**2b**), 2',3',4',5'-tetrachloro-1,3-dioxolan-2-spirocyclo-2',4'-diene (**15**),⁹ methyl 6-(benzoyl)-3,4,5-trichloropicolinate^{6a} (**5a**), 2-chlorobenzoyl cyanide,¹¹ 4-chlorobenzoyl cyanide,¹² 4-fluorobenzoyl cyanide,¹² 4-methoxybenzoyl cyanide,¹² 4-methyl benzoyl cyanide,¹¹ 3-nitrobenzoyl cyanide,¹⁰ 4-nitrobenzoyl cyanide,¹¹ 4-methyl benzenesulfonyl cyanide,¹⁰ 4-chlorobenzenesulfonyl cyanide,^{7c} and 4-chlorobenzenesulfonyl cyanide.^{7c} 2,4-Dichlorobenzoyl cyanide has not been reported in the literature. This compound prepared from the corresponding acid chloride and cuprous cyanide following the general procedure described by Oakwood and Weisberger¹³ had mp 79–80°. 4-Nitrobenzenesulfonyl cyanide has not been reported in the literature. This compound, prepared from the corresponding sodium sulfinate and cyanogen chloride in acetonitrile at room temperature, had mp 118–119°.

General Procedure for the Cycloaddition Reaction. A. Aroyl Cyanides.—In a typical experiment, ketal **2a** (22.6 g, 0.86 mol) and 4-chlorobenzoyl cyanide (**1c**) (14.2 g, 0.086 mol) were heated at 190° for 13.5 hr. The unreacted **1c** and **2a** were removed from the reaction mixture by vacuum distillation. The residue was slurried with hexane to give a solid. On recrystallization from hexane, 13.0 g (40%) of product was obtained mp 132–134°. In some cases, column chromatography on silica gel was necessary. In these cases, the dimeric materials from **2a**, **13**, and **14** eluted before the product.

B. Sulfonyl Cyanides.—In a typical experiment, ketal **2a** (26.4 g, 0.1 mol) and *p*-toluenesulfonyl cyanide (18.1 g, 0.1 mol) were heated at 150° for 20.0 hr. The reaction mixture was cooled, dissolved in 30 ml of ethyl acetate, and poured into 100 ml of cold, stirred hexane. There was obtained after filtration and drying, 29.6 g (76%) of product mp 105–106.5.

Reduction of Methyl 6-(Benzoyl)-3,4,5-trichloropicolinate (5a).—Methyl 6-(benzoyl)-3,4,5-trichloropicolinate (1.0 g, 0.0029 mol) was suspended in methanol (25 ml) and was hydrogenated for 8 hr over palladium on calcium carbonate (5%, 0.75 g) in a Paar hydrogenation apparatus (Model 3911). The catalyst was removed from the solution by filtration and the methanol by evaporation. The residue was distilled to give 0.44 g of a yellow oil: bp ~170° (0.03 mm); ir (CDCl₃) 3610 (OH), 3425 (OH), 1749 (C=O), 1727 cm⁻¹ (C=O); nmr (CDCl₃) δ 3.97 (s, 3, OCH₃), 4.81 (s, 1, OH), 5.85 (s, 1, HCO), 7.1–7.5 (m, 5, C₆H₅), and pyridine protons centered δ 7.3 (H₄) 7.71 (H₃), and 7.95 (H₅) with first-order coupling constants $J_{3,4} = 7.5$ Hz, $J_{3,5} = 1.4$ Hz, and $J_{4,5} = 7.5$ Hz; mass spectrum, molecular ion peak at *m/e* 243.

Reduction of Methyl 6-(4'-Toluenesulfonyl)-3,4,5-trichloropicolinate (16a).—Methyl 6-(4'-toluenesulfonyl)-3,4,5-trichloropicolinate was reduced as described above to methyl 6-(4'-toluenesulfonyl)picolinate in 48% yield: mp 123–126°; ir (split mull) 1731 (C=O), 1561 (C=N ring), 1319 and 1139 cm⁻¹ (SO₂); mass spectrum *m/e* 227, 212, 196, 169; nmr (CDCl₃) δ 2.37 (m, 3, aromatic CH₃), 3.92 (s, 3, OCH₃), 7.29 to 7.96 (m, 4, C₆H₄), and pyridine protons as determined by computer simulation with chemical shifts of 8.10 (H₄) 8.21 (H₃), and 8.32 \pm 0.02 (H₅), and $J_{3,5} = 1.05$, $J_{3,4} = 7.80$, and $J_{4,5} = 7.75 \pm 0.05$ Hz.

Anal. Calcd for C₁₄H₁₃NO₄S: C, 57.80; H, 4.47; N, 4.82. Found: C, 57.73; H, 4.47; N, 4.88.

4,7-Methanoindene-1,8-dione. 2,3,3a,4,5,6,7,7a-Octachloro-4,7-dihydrotramethyl Acetal (13).—5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (13.0 g, 0.05 mol) was heated in a sealed tube for 16 hr at 200°. The contents, after recrystallization from methanol gave 9.0 g (69%) product, mp 258–260°.

Anal. Calcd for C₁₄H₁₂O₄Cl₈: C, 31.84; H, 2.27; Cl, 53.76. Found: C, 31.95; H, 2.29; Cl, 53.75.

The mass spectrum did not give a molecular ion. Peaks at *m/e* 489 and 493 containing seven and eight chlorines were present and are indicative of loss of -Cl and -OCH₃ respectively. The infrared spectra showed strong bands in 1100–1200 cm⁻¹ in

(11) M. R. Zimmermann, *J. Prakt. Chem.*, **66**, 353 (1902).

(12) O. Achmatowicz and O. Achmatowicz, Jr., *Rocz. Chem.*, **35**, 783 (1961).

(13) T. S. Oakwood and C. A. Weisberger, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 112.

support of the acetal structure. Double bond absorptions were also present at 1600–1650 cm^{-1} . The nmr spectrum showed four singlets of equal intensity at 3.5 ppm which are in agreement for the diketal.

4,7-Methanoindene-1,8-dione. **2,3,3a,4,5,6,7,7a-Octachloro-4,7-dihydro-8-dimethyl Acetal (14).**—This compound was isolated from the cycloaddition reaction of the aroyl cyanides with **2a**, or from the pot residue on the distillation of **2a** has mp 228–231°.

Anal. Calcd for $\text{C}_{12}\text{H}_6\text{O}_3\text{Cl}_8$: C, 29.90; H, 1.25; Cl, 58.89. Found: C, 29.65; H, 1.18; Cl, 58.75.

The mass spectrum gave an ion at m/e 443 and showed the presence of seven chlorines in agreement with the loss of one chlorine from the parent ion. The nmr spectrum (CDCl_3) showed two peaks of equal intensity at δ 3.76 and 3.86 ppm. The carbonyl band at 1740 cm^{-1} is consistent with the α,β -unsaturated ketone.

Registry No.—**5b**, 26278-86-4; **5c**, 26278-87-5; **5d**, 26278-88-6; **5e**, 26278-89-7; **5f**, 26278-90-0; **5g**, 26278-91-1; **5h**, 26278-92-2; **5i**, 26278-93-3; **13**, 26278-94-4; **14**, 26322-41-8; **16a**, 26278-95-5; **16b**, 26278-96-6; **16c**, 26278-97-7; **16d**, 26278-98-8; **16e**, 26278-99-9; **16f**, 26279-00-5; methyl 6-(benzoyl)picolinate, 26279-01-6; methyl 6-(4'-toluenesulfonyl)picolinate, 26279-02-7.

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Rearrangement of Chloroformates of Cyclic Amine-Alcohols

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Chloroformates of 3- and 4-piperidinols, 3-pyrrolidinols, and 3-azetidins undergo facile rearrangements to cyclic carbamates: 2-oxazolidinones and tetrahydro-1,3-oxazin-2-ones. The alkyl substituents on the ring nitrogen atom seem to affect the yields of products. Best yields were obtained with *N*-benzyl derivatives. Bicyclic intermediates are proposed to account for the rearrangements.

An elegant synthesis of 2-oxazolidinones by the rearrangement of chloroformates (**2**) of 3-pyrrolidinols was described by Lunsford, *et al.*¹ They have shown that in the course of rearrangement the pyrrolidine ring opens in a specific manner so that only 5-(2-chloroethyl)-2-oxazolidinones (**4**) are formed. The structure of **4** was verified by pmr and unambiguous synthesis. No isolation of the other possible rearrangement prod-

uct tetrahydro-1,3-oxazin-2-ones (**5**) was recorded. Yields of **4** varied from 34 to 89% depending on the *N* substituent. The highest yields were obtained with the *N*-cyclohexyl derivative **4** ($\text{R} = \text{C}_6\text{H}_{11}$) (see Table I). However, no yield was reported on the *N*-benzyl compound **4a**.¹

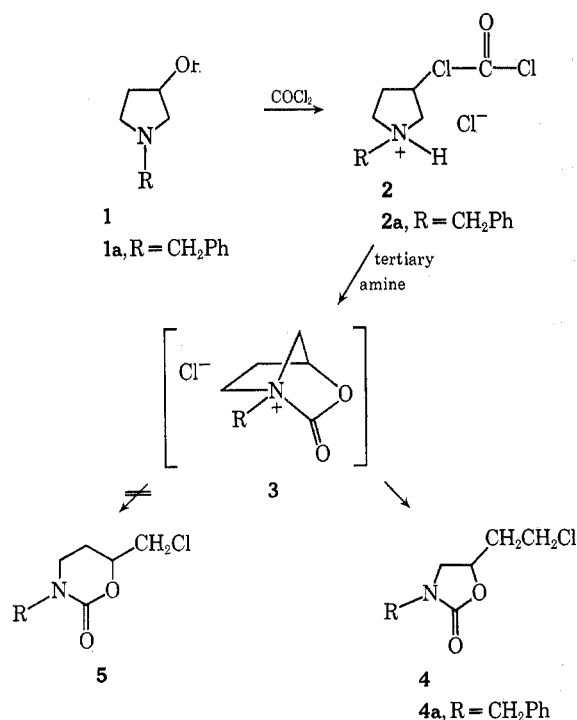


TABLE I
REARRANGEMENT PRODUCTS OF CHLOROFORMATES OF
FOUR-, FIVE-, AND SIX-MEMBERED CYCLIC AMINE ALCOHOLS

| Chloroformate | Product | R | Yield, % |
|---------------|---------|------------------------|-----------------|
| 2 | 4 | Me | 52 ^a |
| | | Et | 56 ^a |
| | | <i>n</i> -Bu | 34 ^a |
| | | Cyclohexyl | 89 ^a |
| | | CH_2Ph | 94 |
| 7 | 9 | Me | 0 |
| | | Et | 0 |
| | | CH_2Ph | 40 |
| 11 | 13 | Me | 70–77 |
| | | CH_2Ph | Quant |
| 14 | 16 | Me | 50 ^b |
| | | Cyclohexyl | Quant |

^a Reference 1. ^b Reference 2.

We have repeated this reaction. Thus, **2a** was prepared from the hydrochloride of *N*-benzyl-3-pyrrolidinol (**1a**) and heated with triethylamine in toluene. Compound **4a** was obtained in 94% yield. No attempt was made to detect any **5** which might have formed in the same rearrangement reaction. The results of Lunsford and of ours indicate some effect of the *N* substituents upon the yields of **4**. Similar substituent effects have been observed in the rearrangement of chloroformates of other cyclic amine-alcohols, which are described below.

* To whom correspondence should be addressed: Merck Sharp and Dohme Research Laboratories, Rahway, N. J. 07065

(1) M. L. Fielden, W. J. Weststead, and C. D. Lunsford, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p P5. We thank Dr. C. D. Lunsford for providing us with a long abstract.