Base-Catalyzed Reactions of Isocyanates. The Synthesis of 2,4-Dialkylallophanates

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The reaction of methyl isocyanate with phenols, thiophenols, and thiols in the presence of potassium *t*-butoxide occurs readily to afford, depending on the stoichiometry, either the corresponding carbamates and thiocarbamates or the corresponding 2,4-dialkylallophanates and 2,4-dialkylthioallophanates. Trace amounts of triisocyanurate were found in the allophanate-forming reactions. Under the same conditions, however, the reaction of aliphatic alcohols with methyl isocyanate affords a mixture of the carbamate, allophanate, and trimethyl isocyanurate. The independent synthesis of the allophanates from the corresponding phenols or thiophenols and the appropriate 2,4-dialkylallophanoyl chloride served to confirm the structural assignments.

The formation of carbamates from isocyanates and phenols occurs at a much slower rate than does formation from isocyanates and alcohols. Although catalysts such as triethylamine,[1] dibutyltin diacetate,[2] and dibutyltin dilaurate[3] have been used with success, the exceedingly long reaction times which are required, particularly in cases where the phenol has a bulky substituent such as the *t*-butyl grouping, render these catalysts unsatisfactory.

The phenolate ion is known to react more readily with isocyanates than does phenol itself. Therefore, a base capable of generating the phenolate ion, potassium *t*-butoxide, was selected. Although alkoxides effectively catalyze the trimerization of isocyanates,[4] this triisocyanurate-forming reaction was found to occur at a *very* slow rate if the isocyanate was added dropwise to a solution of potassium *t*-butoxide and the phenol in benzene at temperatures below 80°. Using this procedure several substituted phenols (see Table I), including the highly substituted 2,6-di-*t*-butyl-4-methylphenol, were readily converted to the corresponding carbamate (I). The bases, sodium methoxide and sodium 2,6-di-*t*-butyl-4-methylphenolate, were also used successfully.

TABLE I

CARBAMATES[a]

$ROCONHR_1$

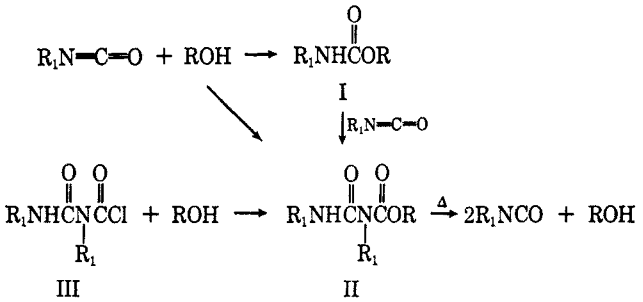
I

R	R_1	Yield, %	Mp, °C
C_6H_5	CH_3	69[b]	78–80[c]
$4\text{-}O_2NC_6H_4$	CH_3	93.5	158–161[d]
2,6-(*t*-Bu)-4-MeC_6H_2	CH_3	91.7	202–203[e]
2,6-(*t*-Bu)-4-MeC_6H_2	C_6H_5	97.5	133–134[f]
α-$C_{10}H_{11}$	CH_3	78.5	132–135[g]

[a] Potassium *t*-butoxide (1% by weight) was used as the catalyst. [b] Recrystallized from benzene; the crude yield is quantitative. [c] M. J. Kolbezen, R. L. Metcalf, and T. R. Fukuto, *J. Agr. Food Chem.* **2**, 864 (1954): mp 85–86°. [d] M. J. Kolbezen, *et al.*, *ibid.*, 864 (1954): mp 160–162°. [e] A. H. Haubein, U. S. Patent 3,140,167 (1964): mp 203–204°. [f] *Anal.* Calcd for $C_{22}H_{29}NO_2$: N, 4.12. Found: N, 4.17. [g] H. H. Moorefield, U. S. Patent 2,904,463 (1959); *Chem. Abstr.* **54**, 808 (1960): mp 142°.

Both the alkoxide-catalyzed reaction of I with a second equivalent of isocyanate and of the phenol with 2 equiv of isocyanate afforded aryl 2,4-dialkylallophanates (II), compounds not previously reported. Although Kogon[5] prepared 2,4-diarylallophanates from the reaction of carbanilates with aryl isocyanates in the presence of metal catalysts, similar reactions with alkyl isocyanates and alkyl carbamates failed to afford II.

The allophanates (II) which were prepared, along with the methods of synthesis, are summarized in Table II. The structure of compounds II was established by independent synthesis from the appropriate phenols and 2,4-dialkylallophanoyl chlorides (III)[6]



and by infrared and nuclear magnetic resonance (nmr) spectroscopic studies. The infrared spectra of the allophanates (II), listed in Table II, exhibited absorption at 3367 (NH) and 1724 and 1689 cm^{-1} (C=O), whereas the carbamates (I), listed in Table I, exhibited absorption at 3436–3472 (NH) and 1724–1748 cm^{-1} (C=O). Both classes of compounds show a well-defined doublet at 2.7 ppm in the nmr spectra of I and at 2.8–2.85 ppm in the nmr spectra of II, which is caused by coupling of the N-methyl protons with the neighboring NH proton, with a coupling constant of $J \simeq 5.0$ cps.[7,8] Double irradiation in the low-field NH region (5.7 ppm in I, and 8.73 ppm in II) causes the N-methyl doublet to collapse to a singlet. Therefore, hindered rotation around the nitrogen–carbon bond as cause for the doublet formation is ruled out.

Both the reaction of II with a third equivalent of isocyanate and the reaction of a phenol with 3 equiv of isocyanate afforded the triisocyanurate, and *not* the linear biuret N-carboxylic acid ester.

The allophanates (II) on being heated in an oil bath above 200°, regenerated the starting phenol and isocyanate, a reaction analogous to the dissociation of

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(1) D. S. Tarbell, R. C. Mallatt, and J. W. Wilson, *J. Am. Chem. Soc.*, **64**, 2229 (1942).

(2) J. R. Kilsheimer and H. H. Moorefield, U. S. Patent 3,081,340 (March 1963); *Chem. Abstr.*, **59**, 2743 (1963).

(3) G. K. Kohn, J. E. Moore, and J. N. Ospenson, U. S. Patent 3,076,741 (Feb 1963); *Chem. Abstr.*, **59**, 5075 (1963).

(4) A. Michael, *Ber.*, **38**, 22 (1905).

(5) K. C. Kogon, *J. Org. Chem.*, **26**, 3004 (1961).

(6) H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *ibid.*, **29**, 2401 (1964).

(7) A coupling constant of $J \simeq 5$–5.5 cps has been observed for N-methyl groups in amine salts of strong acids.[8]

(8) J. C. N. Ma, and E. W. Warnhoff, *Can. J. Chem.*, **43**, 1849 (1965).

TABLE II

ALLOPHANATES[a]

$ROCON(R_1)CONHR_2$

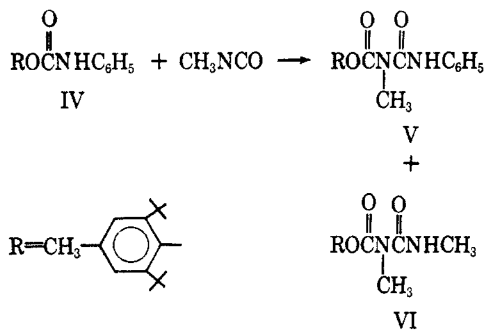
II

R	R_1	R_2	Method of synthesis[b]	Yield, %	Mp, °C	Formula	Calcd,[c] % C	H	N
C_6H_5	CH_3	CH_3	A	92.5	96–98	$C_{10}H_{12}N_2O_3$	57.74	5.89	13.60
$2\text{-Cl-}4,5(CH_3)_2C_6H_2$	CH_3	CH_3	B	55.8	117–118	$C_{12}H_{15}ClN_2O_3$	53.46	5.77	10.45
$3\text{-}t\text{-}BuC_6H_4$	CH_3	CH_3	A	99.3	79–80	$C_{14}H_{20}N_2O_3$	63.52	7.60	10.59
			C	98.5	70–74				
$4\text{-}CH_3\text{-}2,6(t\text{-}Bu)C_6H_2$	CH_3	CH_3	A	89.4	195–197	$C_{19}H_{30}N_2O_3$	68.36	9.01	8.20
			B	59.0	195–197				
$4\text{-}CH_3\text{-}2,6(t\text{-}Bu)C_6H_2$	C_6H_5	CH_3	B	15.6	178–180	$C_{24}H_{32}N_2O_3$	72.82	8.10	7.13
$\alpha\text{-}C_{10}H_{11}$	CH_3	CH_3	B	50.7	124–126	$C_{14}H_{14}N_2O_3$	64.90	5.45	10.66
$4\text{-}R^2NHCO(R^1)NCOOC_6H_4$	CH_3	CH_3	C[d]	31.6	253–255	$C_{14}H_{18}N_4O_6$	49.65	5.40	16.86

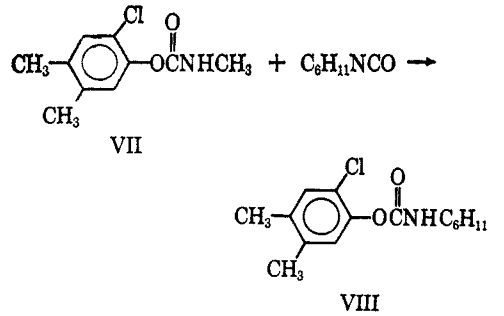
[a] Potassium *t*-butoxide (1% by weight) was used as the catalyst, except in method C. [b] A, ROH + $2R_1NCO$; B, $ROCONHR_1$ + R_2NCO; C, ROH + $R_2NHCON(R_1)COCl$. [c] All analytical data are within 0.3% of the calculated values. [d] Also obtained was 13.7% of 4-hydroxyphenyl 2,4-dimethylallophanate, mp 183–184°. *Anal.* Calcd for $C_{10}H_{12}N_2O_4$: N, 12.50. Found: N, 12.58.

allophanoyl chlorides to isocyanates and hydrogen chloride.[6]

The addition of an isocyanate, other than the one used in preparing the carbamate itself, to the carbamate (I) in the presence of potassium *t*-butoxide afforded not only the expected allophanate (II), but also products formed *via* dissociation and recombination. Methyl isocyanate, for example, on reacting with 2,6-di-*t*-butyl-4-methyl carbanilate (IV) gave 15.6% of the mixed allophanate (V) and 9% of the 2,4-dimethylallophanate (VI), along with starting material (16.5%).

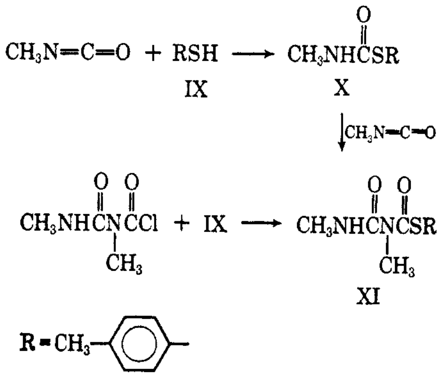


Similarly, cyclohexyl isocyanate, on reaction with the carbamate VII gave a mixture of the various expected and "exchange" products, from which 3,4-dimethyl-2-chlorophenyl cyclohexylcarbamate (VIII) could be isolated in 23% of theory.



The thermal dissociation of carbamates derived from phenols is well known, and this reaction may in fact be facilitated by base.[9]

The reactions of thioalcohols and thiophenols with isocyanates are known to be slower than that of the phenols. Farkas and Mills[10] report that the reaction of thiophenol with ethyl isocyanate at 30° and in the presence of triethylamine proceeds at a rate too slow to be measured. Again the use of an alkoxide as catalyst effected rapid formation of the carbamates (X) and the allophanates (XI). Compounds XI also were synthesized from IX and 2,4-dimethylallophanoyl chloride.



The thiocarbamate (X) and the thioallophanate (XI) afforded from methyl isocyanate and toluenethiol (IX) showed absorption in the infrared at 3436 (NH), 1661 (C=O), 3344 (NH), and 1709 and 1689 cm⁻¹ (C=O), respectively. As did the spectra of I and II, the nmr spectra of X and XI exhibited a doublet at 2.7 and 2.73 ppm, respectively, owing to coupling of the N-methyl group with the neighboring NH proton, which appears at 8.2 ppm in XI.

Similarly, 1-dodecanethiol was allowed to react with 2 equiv of methyl isocyanate in the presence of potassium *t*-butoxide and afforded *n*-dodecyl 2,4-dimethylthioallophanate (XII) in 99.5% of theory. The infrared spectra of XII exhibited NH absorption at 3344 cm^{-1} and C=O at 1709 and 1689 cm^{-1}, and the nmr spectra a singlet at 3.25 ppm and a doublet at 2.8 ppm.

Aliphatic alcohols and methyl isocyanate, on the other hand, on reacting in the presence of potassium *t*-butoxide, gave a mixture of carbamates, allophanates, and trimethyl isocyanurate. The quantitation of these mixtures was easily accomplished by integration of their nmr spectra. The singlet of trimethyl isocyanurate appeared at 3.28 ppm, the singlet of the allophanates at 3.12 ppm, and the doublet of the car-

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(9) N. M. Bortnick, L. S. Luskin, M. D. Hurwitz, and Q. W. Rytina, *J. Am. Chem. Soc.*, **78**, 4358 (1956).

(10) A. Farkas and G. A. Mills, *Advan. Catalysis*, **13**, 439 (1962).

TABLE III

REACTION OF ALCOHOLS WITH METHYL ISOCYANATE[a]

Alcohol	Carbamate		Allophanate		Trimethyl isocyanurate[e]
	Bp, °C (mm)	Yield,[b] %	Bp, °C (mm)	Yield,[b] %	yield,[b] %
Methanol	42–47 (1.2)[d]	28	47[e,f]	33	39
Isopropyl alcohol	42–46 (0.2)[g]	22	63–65 (0.2)[h]	47.5	30
t-Butyl alcohol	41–45 (0.1)[i]	22	67–71 (0.1)[j]	17	61

[a] Reaction in benzene, using 2 equiv of methyl isocyanate in the presence of 1% (by weight) of potassium *t*-butoxide. [b] Yields are based on the methyl isocyanate consumed. [c] A melting point value of 178°, lit [A. Hofmann and O. Olshausen, *Ber.*, **3**, 269 (1870)] mp 176°. [d] K. H. Slotta and R. Tschesche [*ibid.*, **60**, 1023 (1927)] reported bp 61° (10 mm). [e] Melting point, in °C. [f] K. H. Slotta and R. Tschesche [*Ber.*, **60**, 295 (1927)] reported mp 47°. [g] K. H. Koenig, H. Pommer, H. Adolphi, and H. Stummeyer [Belgium Patent 633,594 (1963); *Chem. Abstr.* **61**, 1763 (1964)] reported bp 31–33° (0.2 mm). [h] *Anal.* Calcd for $C_7H_{14}N_2O_3$: C, 48.26; N, 8.10; N, 16.08. Found: C, 48.11; H, 7.89, N, 15.76. [i] *Anal.* Calcd for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68. Found: C, 55.00; H, 10.12; N, 11.20. [j] *Anal.* Calcd for $C_8H_{16}N_2O_3$: C, 51.05; H, 8.57; N, 14.88. Found: C, 50.82; H, 8.45; N, 14.57.

bamates at 2.7 ppm (the doublet of the allophanate appeared at 2.8 ppm). The product distributions obtained from the reaction of methyl isocyanate with methanol, isopropyl alcohol, and *t*-butyl alcohol are shown in Table III.

A mechanism consistent with the obtained results involves the ambident allophanate ion as an intermediate.[11]

Experimental Section[12]

2,6-Di-*t*-butyl-4-methylphenyl Methylcarbamate. General Procedure.—The preparation of 2,6-di-*t*-butyl-4-methylphenyl methylcarbamate demonstrates the procedure used for the synthesis of the carbamates listed in Table I. Methyl isocyanate (5.7 g, 0.1 mole) was added dropwise and with stirring during 2 min at 20–50° to a solution of 0.22 g of potassium *t*-butoxide[13] and 22 g (0.1 mole) of 2,6-di-*t*-butyl-4-methylphenol in 25 ml of benzene. On cooling there was afforded 25.4 g (91.7%) of 2,6-di-*t*-butyl-4-methylphenyl methylcarbamate, mp 202–203° (benzene–ligroin).

Phenyl 2,4-Dimethylallophanate from Phenol and Methyl Isocyanate. General Procedure.—The preparation of phenyl 2,4-dimethylallophanate which follows is exemplary of the procedure followed for the synthesis of allophanates from phenols and methyl isocyanate (method A, Table II). Methyl isocyanate (12 g, 0.21 mole) was added dropwise and with stirring during 4 min at 21–58° to a solution of 0.188 g of potassium *t*-butoxide[13] and 18.8 g of phenol in 50 ml of benzene. The mixture was heated to reflux, an additional 12 g (0.21 mole) of methyl isocyanate was added, and the mixture was allowed to reflux for 15 min. Benzene (200 ml) was added to the reaction mixture and the trimethyl isocyanurate (3 g), mp 178°, which precipitated was removed by filtration. On evaporation of the benzene there was afforded 38.5 g (92.5%) of phenyl 2,4-dimethyl-allophanate, mp 96–98° (methanol).

2-Chloro-4,5-dimethylphenyl 2,4-Dimethylallophanate from 2-Chloro-4,5-dimethylphenyl Methylcarbamate and Methyl Isocyanate. General Procedure.—The preparation of 2-chloro-4,5-dimethylphenyl 2,4-dimethylallophanate which follows is exemplary of the procedure used for the synthesis of allophanates from carbamates and isocyanates (method B, Table II). A solution of 0.213 g of potassium *t*-butoxide and 21.35 g (0.1 mole) of 2-chloro-4,5-dimethylphenyl methylcarbamate[14] in 40 ml of benzene was stirred and heated to reflux, and 6 g (0.105 mole) of methyl isocyanate was added dropwise during 11 min. After the solution had been allowed to reflux for 9 min, 200 ml of benzene was added and the triisocyanurate (0.8 g) which precipitated was removed by filtration. On evaporation of the benzene there was afforded 28.2 g of a crude product from which 15.15 g (55.8%) of 2-chloro-4,5-dimethylphenyl 2,4-dimethylallophanate, mp 117–118° (methanol), was obtained.

3-*t*-Butylphenyl 2,4-Dimethylallophanate from 3-*t*-Butylphenol and 2,4-Dimethylallophanoyl Chloride. General Procedure.—The preparation of 3-*t*-butylphenyl 2,4-dimethylallophanate exemplifies the procedure followed in the synthesis of allophanates from phenols and 2,4-dimethylallophanoyl chloride (method C, Table II). To 15 g (0.1 mole) of 3-*t*-butylphenol and 10.1 g (0.1 mole) of triethylamine dissolved in 200 ml of benzene there was added dropwise and with stirring 15 g (0.1 mole) of 2,4-dimethylallophanoyl chloride.[6] The mixture was stirred for 1 hr at room temperature, and the 12.7 g (94%) of triethylamine hydrochloride which precipitated was removed by filtration. Evaporation of the solvent afforded 26 g (98.5%) of 3-*t*-butylphenyl 2,4-dimethylallophanate, mp 70–74°. The infrared and nmr spectra of this material were identical with the spectra obtained from the material prepared by method A.

Thermolysis of 2,6-Di-*t*-butyl-4-methylphenyl 2,4-Dimethylallophanate.—2,6-Di-*t*-butyl-4-methylphenyl 2,4-dimethylallophanate (15.2 g, 0.045 mole) was heated in an oil bath at 240–277° for 1 hr, 4.5 g (86.5%) of methyl isocyanate, bp 41–42°, being removed by distillation.

Reaction of 2-Chloro-4,5-dimethylphenyl Methylcarbamate (VII) with Cyclohexyl Isocyanate.—A solution of 0.107 g (5% by weight) of potassium *t*-butoxide and 21.35 g (0.1 mole) of VII in 50 ml of benzene was heated to reflux and a solution of 13.5 g (0.1 mole) of cyclohexyl isocyanate in 20 ml of benzene was added dropwise and with stirring. The reaction mixture was refluxed for 5 hr and then was cooled to room temperature. Evaporation of the solvent and recrystallization of the residue from methanol afforded 6.45 g (23%) of 2-chloro-3, 4-dimethylphenyl cyclohexylcarbamate (VIII): mp 123–124°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ (infrared spectrum) 3460 (NH) and 1739 (C=O) cm^{-1}.

Anal. Calcd for $C_{15}H_{20}ClNO$: C, 67, 77; H, 7.58; N, 5.27. Found: C, 67.72; H, 7.60; N, 5.32.

Reaction of 2,6-Di-*t*-butyl-4-methylphenyl Carbanilate (IV) with Methyl Isocyanate.—A solution of 0.085 g (5% by weight) of potassium *t*-butoxide and 16.95 g (0.05 mole) of IV in 30 ml of benzene was heated to reflux and a solution of 3.13 g (0.055 mole) of methyl isocyanate in 20 ml of benzene was added. The reaction mixture was refluxed for 3 hr and the solvent was evaporated. The residue was extracted with warm ligroin. On cooling the extract, 2.8 g (16.5%) of starting material (IV) precipitated. The mother liquor was evaporated and the residue was recrystallized from methanol to afford 3.1 g (15.6%) of 2,6-di-*t*-butyl-4-methylphenyl 2-methyl-4-phenylallophanate (V): mp 178–180°, $\lambda_{\max}^{\mathrm{CCl_4}}$ (infrared spectrum) 3247 (NH) and 1730 and 1695 cm^{-1} (C=O); nmr spectrum singlets at 1.33 (18 protons), 2.34 (3 protons), and 3.56 ppm (3 protons), and multiplets at 7.2 (8 protons) and 16.8 ppm (1 proton).

Evaporation of the methanol and fractional crystallization from methanol–water gave 1.5 g (9%) of 2,6-di-*t*-butyl-4-methylphenyl 2,4-dimethylallophanate (VI), mp 198–200°, which was identical with the material prepared from 2,6-di-*t*-butyl-4-methylphenol and methyl isocyanate.

***p*-Tolyl Methylthiocarbamate (X).**—To a solution of 0.124 g of potassium *t*-butoxide[13] and 12.4 g (0.1 mole) of *p*-toluenethiol (IX) in 20 ml of benzene there was added dropwise and with stirring during 6 min at 25–47° a solution of 5.7 g (0.1 mole) of methyl isocyanate in 20 ml of benzene. The solution was

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[11] H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press Inc., New York, N. Y., 1967, p 131.

[12] Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were determined in chloroform solution, using a Beckman IR-8 or Perkin-Elmer 21 spectrophotometer. Nmr spectra were obtained from samples in deuteriochloroform solution on a Varian A-60 instrument using tetramethylsilane as the internal standard.

[13] In all reactions, except where noted, the amount of potassium *t*-butoxide used was equal to 1% of the weight of the phenol, thiophenol, or thiol.

[14] A. Lemin, G. A. Boyack, and R. M. MacDonald, *J. Agr. Food Chem.*, **12**, 214 (1964).

allowed to cool and the 10.9 g of X, mp 78–81°, which precipitated, was collected by filtration. Evaporation of the solvent afforded an additional 7 g of product, mp 65–75°, which was recrystallized from benzene. The total yield of X was 17.9 g (98.8%).

Anal. Calcd for $C_9H_{11}NOS$: C, 59, 64; H, 6.11; N, 7.72. Found: C, 59.70; H, 6.15; N, 7.96.

p-Tolyl 2,4-Dimethylthioallophanate (XI). A. From p-Tolyl Methyl Carbamate (X) and Methyl Isocyanate.—A solution of 0.035 g (0.5% by weight) of potassium *t*-butoxide and 7 g (0.04 mole) of X in 20 ml of benzene was heated to reflux and a solution of 2.28 g (0.04 mole) methyl isocyanate in 10 ml of benzene was added during 6 min. The mixture was allowed to reflux for 20 min. Benzene (100 ml) was added and the 1.1 g (48.3%) of trimethyl isocyanurate, mp 174–175°, which precipitated, was removed by filtration. Evaporation of the solvent and recrystallization of the residue from methanol afforded 4.5 g (42.2%) of XI, mp 89–90°.

Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.43; H, 5.93; N, 11.75. Found: C, 55.51; H, 5.81; N, 11.80.

B. From p-Toluenethiol and 2,4-Dimethylallophanoyl Chloride.—To a solution of 6.1 g (0.41 mole) of 2,4-dimethylallophanoyl chloride[6] in 60 ml of benzene there was added 4.15 g (0.041 mole) of triethylamine and 5.1 g (0.041 mole) of *p*-toluenethiol. An exothermic reaction occurred immediately. The mixture was stirred for 30 min after which time the 4.75 g (84.3%) of triethylamine hydrochloride which had precipitated was removed by filtration. Evaporation of the solvent afforded 10.5 g of crude XI, mp 70–85°, which was recrystallized from benzene to give 5.9 g (60.5%) of XI, mp 89–91°. The infrared and nmr spectra were identical with those of the compound prepared by procedure A.

***n*-Dodecyl-2,4-Dimethylthioallophanate (XII).**—A solution of 6 g (0.105 mole) of methyl isocyanate in 10 ml of benzene was added dropwise and with stirring during 4 min at 28–43° to a solution of 0.1 g of potassium *t*-butoxide and 10.1 g (0.05 mole) of 1-dodecanethiol in 20 ml of benzene. Benzene (100 ml) was added and the very small amount of trimethyl isocyanurate which precipitated was removed by filtration. Evaporation of the solvent left 15.7 g (99.5%) of *n*-dodecyl 2,4-dimethylthioallophanate, a liquid.

Anal. Calcd for $C_{16}H_{32}N_2O_2S$: N, 8.84. Found: N, 8.70.

Reaction of Alcohols with Methyl Isocyanate. General Procedure.—The reaction of isopropyl alcohol with methyl isocyanate well exemplifies the procedure used for the products summarized in Table III. A solution of 22.8 g (0.4 mole) of methyl isocyanate in 20 ml of benzene was added dropwise and with stirring during 10 min to a solution of 0.12 g of potassium *t*-butoxide[13] and 12 g (0.2 mole) of isopropyl alcohol in 20 ml of benzene. The mixture was allowed to reflux for 30 min. Benzene (100 ml) was added and the 6.85 g (30%) of trimethyl isocyanurate which precipitated was removed by filtration. Evaporation of the solvent and fractional distillation of the residue afforded 7.2 g of isopropyl methylcarbamate [bp 42–46° (0.2 mm)]; 9.3 g of a mixture of isopropyl methylcarbamate (57%) and isopropyl 2,4-dimethylcarbamate (43%) [bp 46–63° (0.2 mm)]; and 7.5 g of pure isopropyl 2,4-dimethylallophanate, [bp 63–65° (0.2 mm)]. The total yields are listed in Table III.

The Synthesis of Unsaturated Esters by a Semicatalytic Reaction of Nickel Carbonyl

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Methyl 7-hydroxy-2,5-heptadienoate and dimethyl 2,5,8-decatriene-1,10-dioate were prepared from reactions of either *cis*-2-butene-1,4-diol or butadiene monoxide with acetylene, carbon monoxide, nickel carbonyl, and methanol in the presence of an acid and an inorganic halide. The reaction of butadiene monoxide was controlled to give high yields of the seven-carbon ester but the *cis*-2-butene-1,4-diol reaction could not be directed to this product alone. The isomeric distribution of products was established by a combination of polarography and ultraviolet and infrared absorption spectroscopy.

Chiusoli[1] has described a very facile technique for converting allylic compounds to 2,5-hexadienoates which involves the reaction of the allylic compound with acetylene, carbon monoxide, nickel carbonyl, and alcohol. It was of interest to us to apply this reaction to appropriately substituted butenes in order to prepare seven and ten carbon acids or esters of possible commercial importance.[2]

Diol Reaction.—The initial work was directed to converting the difunctionally allylic intermediates *trans*-1,4-dichloro-2-butene and *cis*-2-butene-1,4-diol by reaction at one allylic substituent to methyl 7-substituted-2,5-heptadienoate (I) or by reaction at both allylic substituents to dimethyl 2,5,8-decatriene-1,10-dioate (II) (eq 1). Compound I after hydrogenation and amidation could serve as an intermediate to enantholactam and nylon 7 while compound II on hydrogenation and saponification would give sebacic acid. Chiusoli[1a,c] has reported, however, that 1,4-dichloro-2-butene undergoes a rapid reaction with nickel carbonyl that results in the formation of *cis*-2-butene and butadiene but no carbonylation products. Our experience with this reaction verifies his observation. Over a wide variety of conditions, including the addition of *trans*-1,4-dichloro-2-butene to an established carbonylation reaction of allyl chloride, the *trans*-1,4-dichloro-2-butene reacts solely with nickel carbonyl to produce nickel chloride and butadiene.[3] The use of Chiusoli conditions in the reaction of *cis*-2-butene-1,4-diol[1b] also results in butadiene as the sole product even when the molar ratios of diol to hydrogen chloride or sulfuric acid are very high. The failure of these reactions is directly due to having halogen as both allylic

$$\left.\begin{array}{l}\mathrm{ClCH_2CH{=}CHCH_2Cl}\\ \quad\text{or}\\ \mathrm{HOCH_2CH{=}CHCH_2OH + HCl}\end{array}\right\} \xrightarrow[\mathrm{HC{\equiv}CH,\ CH_3OH}]{\mathrm{Ni(CO)_4,\ CO}}$$

$$\begin{array}{c}\mathrm{RCH_2CH{=}CHCH_2CH{=}CHCOOCH_3}\\ \text{Ia, R = OH}\\ \text{b, R = Cl}\\ \Big\downarrow{\scriptstyle \mathrm{Ni(CO)_4,\ CO}\atop\scriptstyle \mathrm{HC{\equiv}CH,\ CH_3OH}}\\ \mathrm{H_3COOCCH{=}CHCH_2CH{=}CHCH_2CH{=}CHCOOCH_3}\\ \text{II}\end{array} \quad (1)$$

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[1] (a) G. P. Chiusoli, *Chim. Ind.* (Milan), **41**, 506 (1959); (b) G. P. Chiusoli, *ibid.*, **41**, 762 (1959); (c) G. P. Chiusoli and L. Cassar, *Angew. Chem. Intern. Ed. Engl.*, **6**, 124 (1967); (d) G. P. Chiusoli and G. Bottaccio, Belgian Patent 630, 619 (1963).

[2] (a) Our interest in this particular area of nickel carbonyl chemistry stemmed from research at Rohm and Haas on the semicatalytic acrylate reaction.[2b] During studies on the application of various alcohols to the process, the reaction of allyl alcohol was independently observed to give the allyl ester of 2,5-hexadienoic acid. (b) H. T. Neher, E. H. Specht, and A. Neuman (Rohm and Haas Co.), U. S. Patent 2,582,911 (1952).

[3] Identification of butadiene was established by preparation of the maleic anhydride adduct which was compared with an authentic sample.