all of this material was concentrated into the last fraction containing the more soluble components. (The τ 3.49 peak was not observed in the nmr spectrum of the original reaction precipitate.)

Kinetic Studies.—Each reaction mixture was carried out in a constant-temperature water bath at 29 ± 1°. To solutions of 12.7 g (0.050 mol) of **1** in 500 ml of acetic anhydride at 29° were added the respective amounts [6.0 ml(0.092 mol), 4.5 ml (0.069 mol), or 3.0 ml (0.046 mol)] of concentrated nitric acid (68%) in 7.5 ml of glacial acetic acid. Periodically, 5-ml aliquots were removed and added to 25-ml portions of water. Each sample was shaken for 4 min until the acetic anhydride was decomposed. The solids from each sample were removed by filtration and washed with water. The entire precipitate in each case was analyzed by nmr. The nmr analyses (DMSO-d_6) were carried out by relative integration of the bridgehead proton areas at τ 4.34 for **1**, 4.05 and 4.10 for **2**, and 3.78, 3.82, and 3.86 for **3** and **4**.

Competitive Nitrations. 9,10-Dihydro-9,10-ethanoanthracene (7) *vs.* **Triptycene (1).**—A mixture of 516 mg (0.0025 mol) of **7**, 636 mg (0.0025 mol) of **1**, and 565 mg of eicosane (internal standard) was dissolved in a small amount of methylene chloride, and an aliquot was removed for vpc analysis. After removal of the solvent, 25 ml of nitromethane and 25 ml of acetic anhydride were added, and the reaction mixture was placed in a 29° constant-temperature bath. Upon addition of 0.16 ml (0.0025 mol) of concentrated nitric acid (68%), the reaction was allowed to proceed for 5 hr at 29° before the product was added to water, which hydrolyzed the acetic anhydride. The mixture was extracted with methylene chloride, and the resulting solution was dried with sodium sulfate and concentrated to a small volume for vpc analysis. The vpc analyses were carried out on a 4-ft 10% silicone rubber SE-52 column at 250°. The results showed 53% of **7** and 69% of **1** remaining at the end of the reaction. By using the expression, $\log([A]/[A_0])/\log([B]/[B_0]) = k_A/k_B$, where [A] and [B] refer to final concentrations of **7** and **1**, respectively, and where $[A_0]$ and $[B_0]$ refer to initial concentrations; $k_7/k_1 \cong 1.7$.

9,10-Dihydro-9,10-ethanoanthracene (7) *vs.* **2-Nitrotriptycene (2).**—An experiment similar to the one above was carried out with 258 mg (0.00125 mol) of **7**, 374 mg (0.00125 mol) of **2**, 300 mg of eicosane, 0.16 ml (0.0025 mol) of concentrated nitric acid, 25 ml of nitromethane, and 25 ml of acetic anhydride. The results of the vpc analyses (240°, programmed at 10°/min to hold at 300°) showed 28% of **7** and 92.5% of **2** remaining at the end of the reaction, so that $k_7/k_2 \cong 16$ and $k_1/k_2 \cong 9$.

Registry No.—**1**, 477-75-8; **3**, 18339-75-8.

Acknowledgments.—The authors wish to thank Mr. Walter J. Kirk, Engineering Division, Kodak Park, for analog computer advice and service, and Dr. Thomas H. Regan and Mr. Robert L. Young, for nmr spectra.

Reactions of Acyl Isocyanates

L. R. SMITH, A. J. SPEZIALE, AND JOAN E. FEDDER

Agricultural Division, Research Department, Monsanto Company, St. Louis, Missouri 63166

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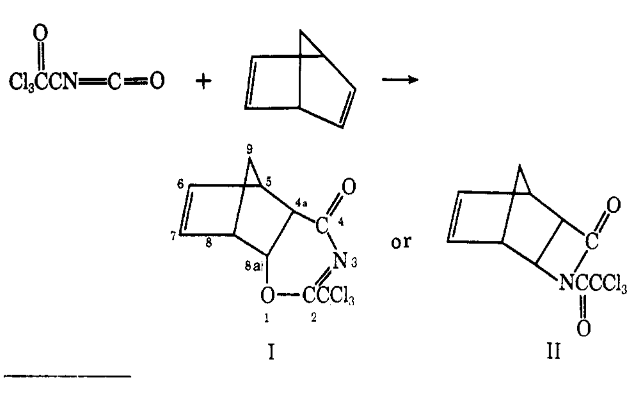
The reaction of norbornadiene with trichloroacetyl isocyanate is shown to proceed *via* a novel cyclization to give tetrahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxan-4-one. The structure of this product and the mechanism of its formation is discussed. Similar reactions occurred with norbornene and dicyclopentadiene. Enamines and vinyl ethers reacted with acyl isocyanates to give adducts in which the isocyanate had, in effect, replaced the β proton of the enamine or vinyl ether. Adducts of acyl isocyanates with indole and pyrrole are reported. Reactions of N,N-disubstituted formamides with trichloroacetyl isocyanate proceeded with the loss of carbon dioxide and formation of acyl formamidines. Conventional reactions of acyl isocyanates with nucleophiles are reported.

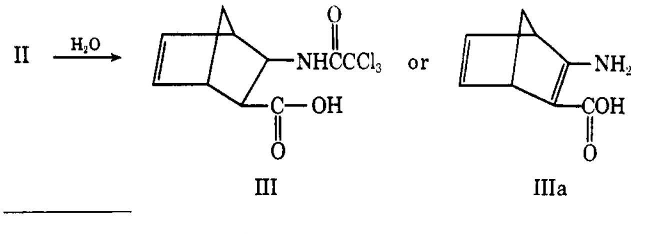
The discovery of a facile preparative route to acyl isocyanates from the reaction of amides with oxalyl chloride[1] prompted us to investigate their reactions. Of particular interest were reactions involving the unique diene [-(C=O)N=C<] and dienophile (-N=C<) systems present in acyl isocyanates.

The electron-deficient dienophiles, maleic anhydride and dimethyl acetylenedicarboxylate, did not react with trichloroacetyl isocyanate. The nucleophilic olefin norbornadiene, however, gave a 1:1 adduct I, mp 83–85°. Hydrolysis and spectral data indicate that the adduct is 4a,5,8,8a-tetrahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (I) rather than the alternate structure II or some product involving molecular rearrangement.



The infrared absorptions of the adduct at 1706 and 1603 cm^{-1} are quite consistent for the C=O and C=N groups in I. These values are not consistent for II, a fused β-lactam, which have been shown[2] to absorb at 1770 to 1789 cm^{-1}. The nmr spectrum of the adduct, along with tentative peak assignments and the spectra of related derivatives, is reported in Table I.

The hydrolysis of II should lead to the carboxylic acid III or IIIa assuming that a β-lactam would hydrolyze faster than a trichloroacetamide. Con-



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[1] A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 3742 (1962); **28**, 1805 (1963).

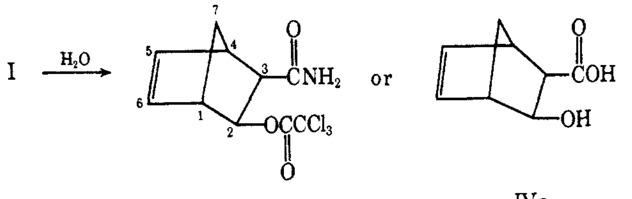
[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 204.

TABLE I

CHEMICAL SHIFT (τ)

	Carbon atom^{a,b}							
Structure^{c}	1 and 4	2	3	5 and 6	7	NH_2	$C(CH_3)_3$	Coupling constants, J, cps^{d}
I	6.62 m	5.07 d	7.23 d	3.45 m	8.38 m			$J_{2n,3n} = 15$
		5.22 d	7.38 d	3.85 m				$J_{2n,7s} = J_{3n,7s} = 2^{e}$
IV	6.93 m	4.73 d	7.25 d	3.45 m	7.97 m	3.85		$J_{2n,3n} = 15^{f}$
		4.88 d	7.40 d	3.85 m				$J_{2n,7s} = J_{2n,7s} = 3.5^{e}$
IX	6.97 m	4.66^{g}	7.17 s	3.70 m	6.17 m	2.20	8.74 s	$J_{2n,3n} = 15$
		4.81^{g}	*h*	4.00 m				
XI	7.16 m^{i}	4.97		8.55 m^{j}				
		5.12 d						

^{a} Refers to the norbornene system as in V. ^{b} d, doublet; m, multiplet; s, singlet. ^{c} Integration of peak areas are consistent with the proposed structures. ^{d} n, *endo* proton; 7s, 7 proton *syn* to the double bond. ^{e} Values from 1.6^{3g} to 3.1^{3f} have been reported. ^{f} This spectrum is not consistent with an *exo* ester and *endo* carboxamido structure which could be formed by epimerization of the carboxamido group since $J_{2n,3x}$ = 3.1^{3b}–4.4^{3g} (x, *exo* proton). ^{g} Peaks are somewhat broadened. ^{h} Obscured by C_1 and C_4 proton signals. ^{i} $H_{1,3,4}$. ^{j} $H_{5,6,7}$.

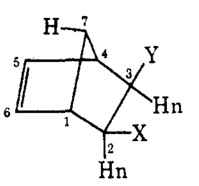


IV IVa

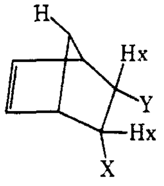
versely, the hydrolysis of I should lead to the amido ester IV (or IVa).

Refluxing the adduct in 75% acetone gave 3-carbamoyl-5-norbornen-2-yl trichloroacetate (IV) which had infrared absorption at 1745 (ester C=O) and 1684 cm^{-1} (amide C=O). The compound was not an acid as evidenced by its insolubility in sodium bicarbonate solution. The strongly basic hydrolysis of the adduct yields ammonia which would be expected from I but not from II.

The question of whether IV (and probably I) has the *exo* or *endo* configuration was investigated by use of nmr spectra (Table I). It has been shown that splitting does not occur between C_1 and C_2 (and C_3 and C_4) protons in *exo*-substituted norbornenes V.[3] It has been further shown that long-range splitting takes place between the C_2 and C_3 protons and the *syn*-C_7 proton.[3] Therefore the C_2 proton of V should appear as a quartet[4] due to splitting by the C_3 proton and the *syn*-C_7 proton (but not the C_1 proton). Similarly, the C_3 proton should appear as a quartet. In the case of *endo* substitution VI, the C_2 proton would appear as a quartet (splitting by C_1 and C_3 protons) and the C_3 proton would also appear as a quartet. Therefore, the question of whether IV has the *exo* or *endo* configuration cannot be resolved by a simple examination of its nmr spectrum alone. However, if the *syn*-C_7 proton is replaced, then long-range coupling cannot occur and, in the case of the *exo* configuration, the two C_2–C_3 quartets should become two doublets. In the case of the *endo* configuration, no change should occur in the absorption of the C_2 and C_3 protons.

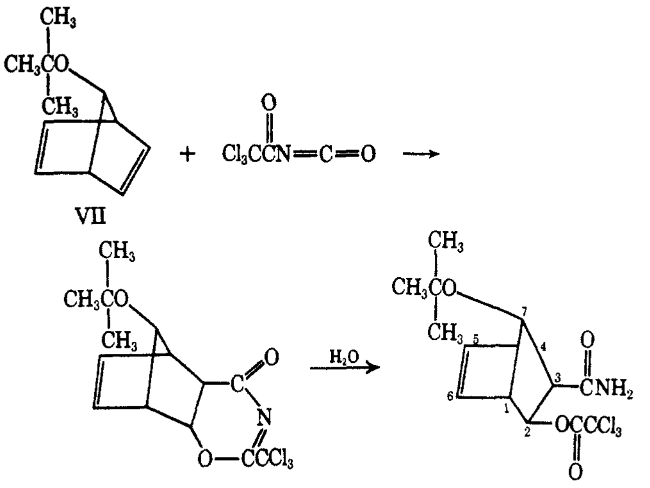


V



VI

The reaction of trichloroacetyl isocyanate with 7-*t*-butoxynorbornadiene[5] (VII) proceeded smoothly and, after hydrolysis, IX was isolated. The infrared absorptions of IX at 1751 and 1664 cm^{-1} indicate the presence of ester and amide carbonyl groups and serve to show that the structure of IX is similar to IV.



VII VIII IX

Since the nmr spectrum of IX (Table I) shows the C_2 and C_3 protons as doublets rather than doublets of doublets, it appears that IX has the *exo* configuration. Structures involving the *t*-butoxy group in a position *anti* to the double bond appear to be ruled out on steric grounds, the presence of small interactions of the 7a proton with the vinyl hydrogens,[3c] and because the nmr spectra of both such structures should show the C_2 and C_3 protons as doublets of doublets. If one can assume that IX and IV would be produced by similar reaction mechanisms, the *exo* configuration for IV is also indicated.

exo attack is the accepted mode of reaction of norbornene derivatives since the attacking species enters from the less hindered side of the olefin. The reaction

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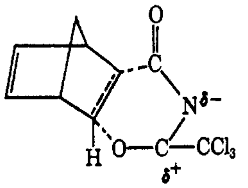
(3) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959); (b) J. Meinwald, Y. Meinwald, and T. Baker, *J. Amer. Chem. Soc.*, **85**, 2513 (1963); J. Meinwald and Y. Meinwald, *ibid.*, **85**, 2514 (1963); (c) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (d) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, No. 11, 559 (1964); (e) P. Lazlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964); (f) J. Davis and T. Van Auken, *ibid.*, **87**, 3900 (1965); (g) T. Van Auken and E. Rick, *Tetrahedron Lett.*, No. 22, 2709 (1968).

(4) A referee prefers "AMX doublet of doublets."

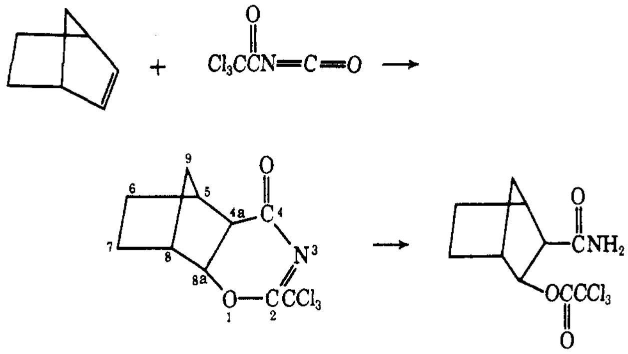
(5) Frinton Laboratories, South Vineland, N. J.

of trichloroacetyl isocyanate with norbornadiene would be expected to proceed by *cis* addition since strain considerations would not favor the formation of a *trans* product. The absence of structural rearrangement in the reaction suggests a four-center mechanism[3a] with little carbonium ion character developing in the transition state X.



X

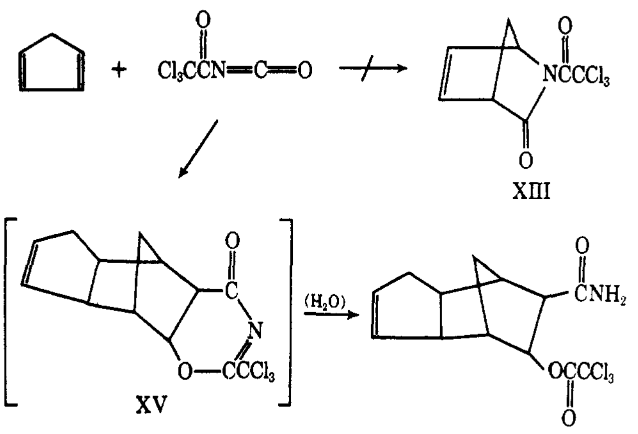
The reaction was extended to norbornene with similar results. Treatment of norbornene with trichloroacetyl isocyanate in refluxing toluene gave 4a,5,6,7,8,8a-hexahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (XI). The infrared spectrum of XI showed C=O and C=N absorption at 1692 and 1590 cm^{-1} confirming the oxazin-4-one structure. Hydrolysis of XI gave XII which had infrared absorption at 1742 (ester C=O) and 1645 cm^{-1} (amide C=O).



XI XII

Unstrained olefins such as cyclohexene and cyclopentene were unreactive toward acyl isocyanates. It appears that only very nucleophilic olefins are capable of undergoing this reaction. The apparent nucleophilic attack of the dienophile on the diene in this reaction is contrasted with the Diels–Alder reaction in which the dieneophile acts as an electrophilic reagent.[6]

In order to determine if trichloroacetyl isocyanate would also react as a dienophile it was treated with cyclopentadiene under reflux. The product isolated was not the simple adduct XIII but was rather 6-carbamoyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-5-yl trichloroacetate (XIV). The infrared spectrum of XIV showed absorption at 1745 (ester C=O) and 1661 cm^{-1} (amide C=O). The nmr spectrum was very complex with multiplets in the regions of τ 4.20, 4.85, 7.40, and 8.30. The same compound could be prepared by reaction of dicyclopentadiene with trichloroacetyl isocyanate. It appears that the cyclopentadiene underwent dimerization[6d] followed by four-centered reactions with the acyl isocyanate. Atmospheric moisture converted the benzoxozineone XV into the amido ester XIV.



XIII XV XIV

Enamines and vinyl ethers reacted with acyl isocyanates giving 1:1 adducts. For example, 1-morpholinocyclopentene and dihydropyran gave adducts with *o*-toluoyl isocyanate and trichloroacetyl isocyanate, respectively. The presence of an NH absorption in the infrared spectra of the adducts showed that the isocyanate had, in effect, replaced the β proton of the enamine or vinyl ether. Acyl isocyanates thus behave similarly to other isocyanato derivatives[7] in reaction with these unsaturates although azetidinones, reported to be also formed by reaction of sulfonyl isocyanates with enol ethers[7d] and thiazinones from thioacyl isocyanates and enamines,[6c] were not detected in the case of acyl isocyanates. Trichloroacetyl isocyanate appears to be more reactive than benzoyl isocyanate since it has been reported that the latter compound does not react with enol ethers.[7d]

Acid hydrolysis of the adduct of 1-morpholinocyclopentene and *o*-toluoyl isocyanate gave the expected N-(2-oxocyclopentylcarbonyl)-*o*-toluamide.

The difference in the course of the acyl isocyanate reactions with enamines and vinyl ethers from that of norborenenes may be attributed to the fact that the enamines and vinyl ethers may react or rearrange by way of a stabilized zwitterion transition state[8] which allows prototropic shifts while the norbornenes probably react by way of a four-center reaction which does not. However, thioacyl isocyanates have been reported to give six-membered ring derivatives with enamines.[6c] In the latter case apparently ring closure is faster than a β-hydrogen shift—perhaps owing to the greater nucleophilicity of sulfur over oxygen.

Treatment of indole with chloroacetyl isocyanate gave a 1:1 adduct XVa. The expected substitution in the 3 position of indole was indicated by a comparison of the ultraviolet spectrum of the adduct with that of the adduct XVb from chloroacetyl isocyanate and 1,2-dimethylindole (Table II).

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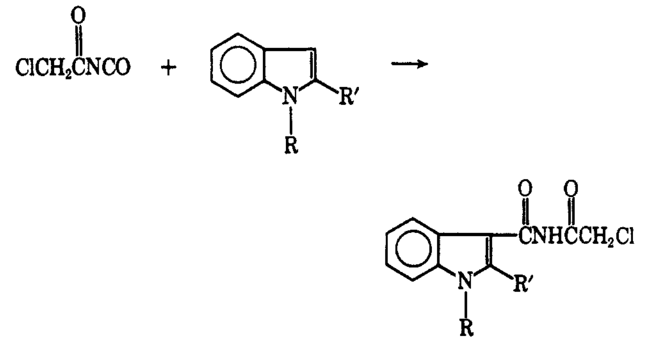
(6) Subsequent to the preparation of this manuscript related reactions of norbornadiene and norbornene with thiobenzoyl isocyanate were reported: (a) R. Weiss, *Ber.*, **100**, 685 (1967). See also (b) R. Neidlein, *Angew. Chem. Intern. Ed. Engl.*, **3**, 446 (1964); *Ber.*, **97**, 3476 (1964); (c) J. Goerdeler and H. Schenk, *Ber.*, **98**, 3831 (1965); (d) G. Collins, *J. Org. Chem.*, **29**, 1688 (1964).

(7) (a) G. Berchtold, *J. Org. Chem.*, **26**, 3043 (1961); (b) S. Hunig, K. Hübner, and E. Benzing, *Ber.*, **95**, 926 (1962); (c) G. DeStevens, H. Blatter, and R. W. J. Carney, *Angew. Chem. Intern. Ed. Engl.*, **5**, 35 (1966); (d) F. Effenberger and R. Gleiter, *ibid.*, **2**, 324 (1963); *Ber.*, **97**, 1576 (1964).

(8) Compare R. Scarpati, D. Sica, and C. Santacroce, *Tetrahedron*, **20**, 2735 (1964). See also ref 6c.

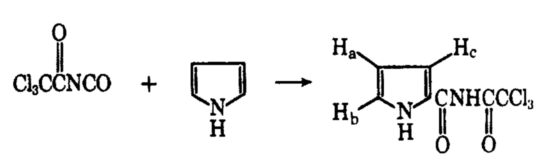


XVa, R = R′ = H
b, R = R′ = CH_3

TABLE II

	λ_{max}, mμ (log ε), C_2H_5OH
Indole adduct XVa	243 (4.36), 291 (3.81), 299 (3.85)
1,2-Dimethylindole adduct XVb	247 (3.98), 275 (3.96), 307 (4.09)

The expected 2 substitution of the adduct XVI of pyrrole and trichloroacetyl isocyanate was confirmed by a comparison of its nmr spectrum with that of pyrrole-2-carboxaldehyde.



XVI

Both the adduct and pyrrole-2-carboxaldehyde have septuplets in the region τ 2.8 (H_c) and 3.1 (H_b) and a sextuplet in the region 3.7 (H_a).[9]

Acyl isocyanates reacted similarly to phenyl[10a] and p-toluenesulfonyl[10b] isocyanates with N,N-disubstituted formamides giving acyl formamidines with the loss of carbon dioxide. For example, trichloroacetyl isocyanate with N,N-dimethylformamide gave N-trichloroacetyl-N′,N′-dimethylformamidine. This reaction probably proceeds *via* an oxazetanone intermediate, does not occur with N,N-disubstituted acetamides, and appears to be the only method of synthesizing *acyl* formamidines. Similar reactions have been reported for phenyl isocyanate with nitrosobenzene,[11] thioureas,[11] and aldehydes.[11,12]

TABLE III

ADDUCTS OF CHLOROACETYL ISOCYANATE WITH NUCLEOPHILES

Adduct with	Registry no.	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
Benzyl alcohol	18355-21-0	134–136	88	52.76	4.43	52.69	4.72
Methyl mercaptan	18355-22-1	134–135	67	28.66	3.61	28.78	4.18
N-Methylcyclohexylamine	18355-23-2	125–126	69	51.61	7.36	51.73	7.56
Benzamide	18355-24-3	191–192	60	49.91	3.77	49.95	3.87
Benzenesulfonamide	18355-25-4	131–134	97	41.46	3.48	41.28	3.35
1,3-Diphenylurea	18355-26-5	156–158	77	57.92	4.25	58.09	4.06
Ethyl carbamate	18426-00-1	136–138	56	34.54	4.35	34.66	4.50
Butyrolactam	18355-27-6	118–120	72	41.09	4.43	41.13	4.51
Thionacetamide	18355-28-7	120–121.5	75	30.85	3.63	30.95	4.10
2,4-Dichlorophenol	18355-29-8	118–120	72	38.26	2.14	38.55	2.36

Normal reactions occurred between acyl isocyanates and nucleophiles generally employed with alkyl and aryl isocyanates, *i.e.*, alcohols, phenols, thiols, and amines. The normal reaction also occurred at slightly higher temperatures with the less reactive prototropic reagents—amides, thionamides, carbamates, ureas, lactams, and sulfonamides. Some examples are reported in Table III.[13]

Displacement of the isocyanato group, as sometimes occurs with the isothiocyanato group of acyl isothiocyanates,[14] was not observed.

Experimental Section[15]

4a,5,8,8a-Tetrahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (I).—A solution of norbornadiene (4.6 g, 0.05 mol) and trichloroacetyl isocyanate (9.4 g, 0.05 mol) in toluene (75 ml) was refluxed for 24 hr. The toluene was removed *in vacuo* and recrystallization of the residue from methylene chloride–hexane gave 4a,5,8,8a-tetrahydro-2-(trichloromethyl)-5,8-methano-4H-1,3-benzooxazin-4-one (9.3 g, 0.033 mol, 66%): mp 83–85°, $\nu_{C=O}$ (cm^{-1}) 1706; $\nu_{C=N}$ 1603 (Nujol).

Anal. Calcd for $C_{10}H_8Cl_3NO_2$: C, 42.81; H, 2.87; Cl, 37.92; N, 4.99; mol wt, 280.54. Found: C, 42.49; H, 2.93; Cl, 37.98; N, 4.91, mol wt, 280.

3-Carbamoyl-5-norbornen-2-yl Trichloroacetate (IV).—A solution of 4a,5,8,8a-tetrahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (2.1 g, 0.0075 mol) was refluxed in 75% acetone for 0.25 hr. The addition of excess cold water caused a solid to separate. Recrystallization of the solid from methylene chloride–hexane gave 3-carbamoyl-5-norbornen-2-yl trichloroacetate (1.4 g, 0.0047 mol, 62%): mp 126–126°; ν_{NH} (cm^{-1}) 3425, 3058; $\nu_{C=O}$ 1742, 1684 (Nujol).

Anal. Calcd for $C_{10}H_{10}Cl_3NO_3$: C, 40.23; H, 3.38; Cl, 35.64; N, 4.69. Found: C, 40.43; H, 3.46; Cl, 35.43; N, 4.56.

7-*t*-Butoxy-3-carbamoyl-5-norbornen-2-yl Trichloroacetate (**IX**).—A solution of 7-*t*-butoxynorbornadiene[15] (8.25 g, 0.05 mol) and trichloroacetyl isocyanate (9.4 g, 0.05 mol) in toluene (100 ml) was refluxed for 24 hr. The toluene was removed *in vacuo* and the residue was refluxed with 90% acetone for 0.5 hr. The addition of water and chilling caused a tan solid to separate. Recrystallization of the solid from methylene chloride–hexane gave 7-*t*-butoxy-3-carbamoyl-5-norbornen-2-yl trichloroacetate (6.1 g, 0.017 mol, 34%): mp 187–188°; ν_{NH} (cm^{-1}) 3279, 3067; $\nu_{C=O}$ 1751, 1664 (Nujol).

Anal. Calcd for $C_{14}H_{18}Cl_3NO_4$: C, 45.36; H, 4.89; Cl, 28.70; N, 3.78. Found: C, 45.35; H, 4.84; Cl, 28.68; N, 3.74.

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(9) N. Bhacca, L. Johnson, and J. Shoolery, "Varian NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, p 98.

(10) (a) M. Weiner, *J. Org. Chem.*, **25**, 2245 (1960); (b) C. King, *ibid.*, **25**, 352 (1960).

(11) H. Staudinger and R. Endle, *Ber.*, **50**, 1042 (1917).

(12) E. Niwa, H. Aoki, H. Tanaka, K. Munakata, and M. Namiki, *ibid.*, **99**, 3932 (1966).

(13) See also G. Derkach and V. Belaya, *Zh. Obshch. Khim.*, **36**, 1942 (1966).

(14) D. Elmore and J. R. Ogle, *J. Chem. Soc.*, **289** (1957).

(15) Melting points are uncorrected. Infrared spectra were run on the Beckman IR-5A spectrometer; nmr spectra in deuteriochloroform on the Varian A-60 spectrometer.

4a,5,6,7,8,8a-Hexahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (XI).—A solution of norbornene (4.7 g, 0.05 mol) and trichloroacetyl isocyanate (9.4 g, 0.05 mol) in toluene (100 ml) was refluxed for 20 hr and the solvent was removed *in vacuo*. The solid residue was recrystallized from methylene chloride–hexane and gave 4a,5,6,7,8,8a-hexahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (9.0 g, 0.032 mol, 64%): mp 106–108, $\nu_{C=O}$ (cm^{-1}) 1692; $\nu_{C=N}$ 1590 (Nujol).

Anal. Calcd for $C_{10}H_{10}Cl_3NO_2$: C, 42.50; H, 3.57; Cl, 37.65; N, 4.96. Found: C, 42.48; H, 4.01; Cl, 37.79; N, 5.12.

3-Carbamoyl-2-norbornyl Trichloroacetate (XII).—A solution of 4a,5,6,7,8,8a-hexahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (XI) (2.5 g, 0.009 mol) in 75% acetone (50 ml) was refluxed for 0.25 hr. The addition of excess cold water caused a solid to separate. Recrystallization of the solid from methylene chloride–hexane gave 3-carbamoyl-2-norbornyl trichloroacetate (1.9 g, 0.0063 mol, 70%): mp 175–176°; ν_{NH} (cm^{-1}) 3300, 3096; $\nu_{C=O}$ 1742, 1645 (Nujol).

Anal. Calcd for $C_{10}H_{12}Cl_3NO_3$: C, 39.96; H, 4.03; Cl, 35.39; N, 4.66; mol wt, 300.58. Found: C, 39.72; H, 4.03; Cl, 35.18; N, 4.53; mol wt, 317.

6-Carbamoyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoinden-5-yl Tricloroacetate (XIV). A.—A solution of cyclopentadiene (3.3 g, 0.05 mol) and trichloroacetyl isocyanate (9.4 g, 0.05 mol) in toluene (50 ml) was refluxed for 10 hr and the toluene was removed *in vacuo*. The brown tarry residue was placed on a column of Woelm neutral alumina and elution with benzene gave a solid. Recrystallization of the solid from benzene and methylene chloride–hexane gave XIV (4.0 g, 0.012 mol, 24%), mp 130–132°. The infrared spectrum was identical with that of a sample prepared as follows.

B.—A solution of trichloroacetyl isocyanate (20.0 g, 0.11 mol) in dicyclopentadiene (100 ml) was refluxed for 4 hr and the dicyclopentadiene was distilled *in vacuo*. The residue was allowed to stand for 2 months and then was recrystallized once from benzene and once from methylene chloride–hexane. This produced XIV (14.0 g, 0.041 mol, 38%): mp 134–135°; $\nu_{C=O}$ (cm^{-1}) 1745, 1661 (Nujol).

Anal. Calcd for $C_{13}H_{14}Cl_3NO_3$: C, 46.11; H, 4.17; Cl, 31.41; N, 4.14. Found: C, 46.16; H, 4.24; Cl, 31.59; N, 4.07.

N-(2-Oxocyclopentylcarbonyl)-*o*-toluamide.—A solution of morpholinocyclopentene (7.7 g, 0.05 mol) in benzene (50 ml) was stirred at 0° while *o*-toluoyl isocyanate (8.1 g, 0.05 mol) in benzene (50 ml) was added. The solution was stirred for 1 hr and removal of the benzene *in vacuo* left an orange glass which was dissolved in methylene chloride–hexane and placed on a column of neutral alumina packed wet with hexane. Elution with benzene gave a yellow-gold tar. The tar was dissolved in 80% acetone and 3 drops of concentrated hydrochloric acid were added. The solution was refluxed for 1 hr and the acetone was removed *in vacuo*. The residue was extracted with methylene chloride and the extract was dried over anhydrous magnesium sulfate and treated with charcoal. The addition of hexane and chilling caused N-(2-oxocyclopentylcarbonyl)-*o*-toluamide to separate (2.55 g, 0.012 mol, 24%): mp 118–120°; ν_{NH} (cm^{-1}) 3205; $\nu_{C=O}$ 1724, 1695, 1653 (Nujol).

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.40; H, 6.14; N, 5.61.

α-Phenyl-N-trichloroacetyl-1-pyrrolidineacrilamide.—A solution of β-pyrrolidinostyrene (8.7 g, 0.05 mol) in benzene (50 ml) was stirred in an ice bath while a solution of trichloroacetyl isocyanate (9.4 g, 0.05 mol) was added dropwise. The solution was stirred for 1 hr and the benzene was removed *in vacuo*. The brown residue was recrystallized three times (with charcoal treatment) from benzene giving α-phenyl-N-trichloroacetyl-1-pyrrolidineacrilamide as a light yellow solid (6.7 g, 0.019 mol, 38%): mp 136–138°; ν_{NH} (cm^{-1}) 3289; $\nu_{C=O}$ 1739, 1664; $\nu_{C=C}$ 1563 (Nujol).

Anal. Calcd for $C_{15}H_{15}Cl_3N_2O_2$: C, 49.81; H, 4.18; N, 7.75. Found: C, 50.07; H, 4.31; N, 7.73.

5,6-Dihydro-N-chloroacetyl-4H-pyran-3-carboxamide.—A solution of dihydropyran (4.2 g, 0.05 mol) and chloroacetyl isocyanate (6.0 g, 0.05 mol) in toluene (70 ml) was stirred for 12 hr and refluxed for 1 hr. On cooling a solid separated which was filtered. Recrystallization of the solid from methylene chloride–hexane gave 5,6-dihydro-N-chloroacetyl-4H-pyran-3-carboxamide (2.1 g, 0.01 mol, 20%): mp 156–157°; ν_{NH} (cm^{-1}) 3289; $\nu_{C=O}$ 1709, 1664; $\nu_{C=C}$ 1600 (Nujol).

Anal. Calcd for $C_8H_{10}ClNO_3$: C, 47.18; H, 4.95; Cl, 17.41. Found: C, 46.98; H, 4.92; Cl, 17.65.

N′-Chloroacetylindole-3-carboxamide (XVa).—A solution of indole (5.9 g, 0.05 mol) and chloroacetyl isocyanate (6.0 g, 0.05 mol) in benzene (50 ml) was refluxed for 2 hr and a solid separated. The solid was filtered and was found to be a high melting amorphous material. The benzene solution on evaporation yielded a white solid which was recrystallized from methanol–benzene. This produced N′-chloroacetylindole-3-carboxamide (2.1 g, 0.009 mol, 18%), mp 205–206°. The compound gave a negative Ehrlich's test: ν_{NH} (cm^{-1}) 3226; $\nu_{C=O}$ 1709, 1681 (Nujol).

Anal. Calcd for $C_{11}H_9ClN_2O_2$: C, 55.82; H, 3.83; Cl, 14.98; N, 11.83. Found: C, 55.86; H, 3.88; Cl, 14.92; N, 11.29.

N′-Chloroacetyl-1,2-dimethylindole-3-carboxamide (XVb).—A solution of 1,2-dimethylindole (7.25 g, 0.05 mol) in benzene (50 ml) was stirred while a solution of chloroacetyl isocyanate (6.0 g, 0.05 mol) in benzene (25 ml) was added. The resulting purple solution was stirred and a solid separated. Hexane (25 ml) was added and a purple solid was removed by filtration. Three recrystallizations of the solid, with charcoal treatment, from methylene chloride–hexane gave N′-chloroacetyl-1,2-dimethylindole-3-carboxamide (7.6 g, 0.029 mol, 58%): mp 159–169.5°; $\nu_{C=O}$ (cm^{-1}) 1709, 1661 (Nujol).

Anal. Calcd for $C_{13}H_{13}ClN_2O_2$: C, 58.99; H, 4.95; N, 10.58; Cl, 13.40. Found: C, 58.41; H, 4.61; N, 10.46; Cl, 13.69.

N′-Trichloroacetylpyrrole-2-carboxamide (XVI).—A solution of freshly distilled pyrrole (3.35 g, 0.05 mol) in benzene (50 ml) was stirred while trichloroacetyl isocyanate (9.42 g, 0.05 mol) in benzene (25 ml) was added dropwise. The solution was stirred for 1 hr and the benzene was removed *in vacuo*. Recrystallization of the residue from methylene chloride–hexane gave a white solid (5.85 g, 0.023 mol, 46%): mp 142–144°; ν_{NH} (cm^{-1}) 3333; $\nu_{C=O}$ 1739, 1681 (Nujol).

Anal. Calcd for $C_7H_5Cl_3N_2O_2$: C, 32.90; H, 1.97; N, 10.97; Cl, 41.63. Found: C, 33.21; H, 2.23; N, 10.69; Cl, 42.04.

N-Trichloroacetyl-N′,N′-dimethylformamidine.—A solution of dimethylformamide (3.65 g, 0.05 mol) in benzene (50 ml) was stirred while trichloroacetyl isocyanate (9.4 g, 0.05 mol) was added. An immediate evolution of gas occurred and the solution was stirred for 1 hr and refluxed for 1 hr. The benzene was removed *in vacuo* and the solid residue was recrystallized from methylene chloride–hexane. This produced N-trichloroacetyl-N′,N′-dimethylformamidine (7.1 g, 0.033 mol, 66%), mp 55–56°.

Anal. Calcd for $C_5H_7Cl_3N_2O$: C, 27.61; H, 3.25; Cl, 48.90; N, 12.88. Found: C, 27.95; H, 3.36; Cl, 49.38; N, 13.07.

Reaction of Nucleophiles with Acyl Isocyanates (Table III).—The alcohol, thiol, amine, or amide was added to an equivalent amount of the acyl isocyanate (usually 0.05 mol) in methylene chloride (or ethylene chloride in the case of amides). The resulting solution was refluxed for 5 min to 8 hr and evaporated to a small volume. Hexane was added to precipitate the product which was recrystallized from methylene chloride–hexane.

Registry No.—I, 18354-89-7; IV, 18346-66-2; IX, 18346-67-3; XI, 18354-90-0; XII, 18354-91-1; XIV, 18354-92-2; XVa, 18354-93-3; XVb, 18354-94-4; XVI, 18354-95-5; N-(2-oxocyclopentylcarbonyl)-*o*-toluamide, 18354-96-6; α-phenyl-N-trichloroacetyl-1-pyrrolidineacrilamide, 18354-97-7; 5,6-dihydro-N-chloroacetyl-4H-pyran-3-carboxamide, 18354-98-8; N-trichloroacetyl-N′,N′-dimethylformamidine, 18354-99-9.