The Chemistry of Nitrogen Radicals. IX. Reactions of N-Halocyanamides and N-Halosulfonamides

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The photolytic rearrangement of N-*t*-butyl-N-halobutanesulfonamides to the corresponding 3-halobutanesulfonamides occurred in ~75% yield; cyclization of the products gave either the sultam (V) by ring closure at nitrogen or an isomeric cyclopropanesulfonamide (IV) by ring closure at the carbon α to the sulfone group. Additions of N-chloro-N-methylcyanamide and N-chloro-N-methylmethanesulfonamide to both conjugated and nonconjugated olefins in 45–75% yield are also reported. Photolytic reactions of N-*t*-butyl-N-chlorocyanamide in the presence of olefins gave carbodiimide derivatives as the principal products.

In recent years an increasingly active study of free-radical reactions of aliphatic N-halo compounds has shown that two types of synthetically important processes can be realized with a variety of N-halamines RN(hal)Y. Depending on the nature of the alkyl group R and the alkyl or electron-withdrawing group Y, either rearrangement of halogen into R or Y or addition of the N-halamine to unsaturated hydrocarbons may occur. Thus, rearrangement of chlorine into the N-alkyl group has been observed in protonated dialkyl-[1] or monoalkyl-N-chloramines,[2] N-chlorocarboxamides,[3] and N-chlorosulfonamides[4] to give the corresponding 4-chloroalkyl isomers. Rearrangement of halogen into the group Y has been reported for N-alkyl-N-halocarboxamides,[5,6] N-chlorocarboximides,[7] and most recently N-alkyl-N-chlorosulfonamides.[8] The addition of N-halo compounds across carbon–carbon double bonds has been carried out with dialkyl-[9–11] and monoalkyl-N-chloramines,[12] N-chlorourethanes,[13] an N,N-dichlorophosphoramidate,[14] N-bromosuccinimide,[15] and an N-chlorosulfonamide.[16] It is the purpose of this report to describe the addition of N-chlorosulfonamides and N-chlorocyanamides to a variety of olefins and to provide considerably more information on the rearrangement of N-halosulfonamides and the conversion of the products into cyclic derivatives than has heretofore[8] been disclosed.

Rearrangement of N-Halosulfonamides.—We have reported previously the rearrangement of N-halocarboxamides and the cyclization of the γ-halocarboxamides thus formed.[5] We now describe the analogous rearrangement of N-halosulfonamides and details of the selective preparation of two types of cyclization products from the rearranged N-halamides. Since the completion of this work, a limited study of N-chlorosulfonamide rearrangements has appeared,[8] which is in agreement with our results.

The preparations of the N-bromo- and N-chlorobutanesulfonamides were straightforward and are summarized in the Experimental Section. The photolytic rearrangements of the N-*t*-butyl compounds were more efficient than those of the N-methyl analogs and proceeded as follows. Irradiation of a 0.4 *M* solution of N-*t*-butyl-N-chlorobutanesulfonamide (**1a**) in a Vycor vessel using an external 100-W uv lamp produced a complete loss of electropositive chlorine in 1 hr in benzene or in 3 hr in carbon tetrachloride. Evaporation of either solution gave a solid, whose nmr spectrum contained the methyl doublet absorption of the γ-chloro isomer **2a** (Scheme I); from the relative areas of this doublet and the *t*-butyl peak, **2a** was found to comprise ~67% of the total N-*t*-butyl compounds present. This is consistent with the report[8b] that **1a** rearranged in benzene to give 62% **2a**, 15% δ-chloro isomer, and 20% parent amide. However, work-up gave ~75% yield of **2a** with no evidence of significant amounts of the δ-chloro isomer.

The Japanese workers[8] apparently did not pursue the chemistry of their rearrangement products except to obtain a very low yield of the sultam of N-*t*-butyl-3-chloropentanesulfonamide on treatment of the compound with alcoholic KOH. In our hands, the analog **2a** afforded a greater yield of either a sultam or a cyclopropane isomer, depending on the base used (Scheme I). The major product from methyllithium in tetrahydrofuran (THF) was 40% N-*t*-butyl-2-methylcyclopropanesulfonamide (**4**), whereas 60% sultam, 2-*t*-butyl-3-methyltetrahydroisothiazole 1,1-dioxide (**5**), resulted from freshly prepared sodium amide in THF.

The rearrangement of the N-bromosulfonamide **1b**

(1) R. S. Neale and M. R. Walsh, *J. Amer. Chem. Soc.*, **87**, 1255 (1965); R. S. Neale, M. R. Walsh, and N. L. Marcus, *J. Org. Chem.*, **30**, 3683 (1965); M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

(2) E. Schmitz and D. Murawski, *Chem. Ber.*, **99**, 1493 (1966).

(3) G. H. Coleman, C. C. Schulze, and H. A. Hoppens, *Proc. Iowa Acad. Sci.*, **47**, 264 (1940).

(4) S. M. Verma and R. C. Srivastava, *Bull. Chem. Soc. Jap.*, **40**, 2184 (1967).

(5) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

(6) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).

(7) R. C. Petterson and A. Wambsgans, *J. Amer. Chem. Soc.*, **86**, 1648 (1964).

(8) (a) M. Okahara, T. Ohashi, and S. Komori, *Tetrahedron Lett.*, 1629 (1967); (b) M. Okahara, T. Ohashi, and S. Komori, *J. Org. Chem.*, **33**, 3066 (1968).

(9) (a) R. S. Neale, *ibid.*, **32**, 3263 (1967); (b) R. S. Neale and N. L. Marcus, *ibid.*, **32**, 3273 (1967).

(10) F. Minisci, R. Galli, and G. Pollina, *Chim. Ind.* (Milan), **47**, 736 (1965).

(11) J. M. Surzur and P. Tordo, *Compt. Rend.*, **263**, 446 (1966).

(12) R. S. Neale and N. L. Marcus, *J. Org. Chem.* **33**, 3457 (1968).

(13) (a) T. A. Foglia and D. Swern, *ibid.*, **31**, 3625 (1966); (b) T. A. Foglia and D. Swern, *ibid.*, **32**, 75 (1967); (c) T. A. Foglia and D. Swern, *ibid.*, **33**, 766 (1968); (d) K. Schrage, *Tetrahedron*, **23**, 3033 (1967).

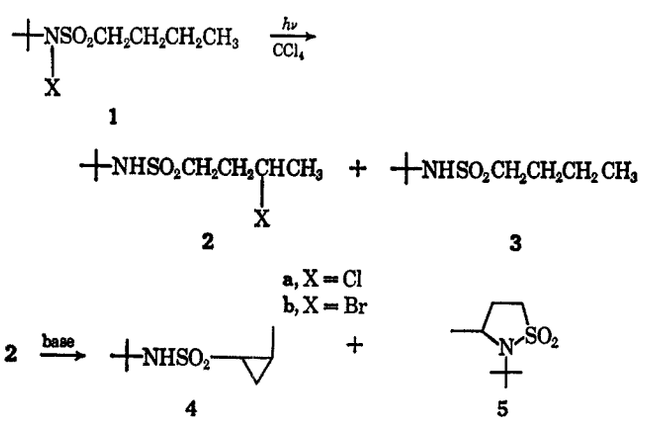
(14) A. Zwierzak and A. Koziara, *Angew. Chem. Intern. Ed. Engl.*, **7**, 292 (1968).

(15) L. H. Zalkow and C. D. Kennedy, *J. Org. Chem.*, **29**, 1290 (1964); W. J. Bailey and J. Bellow, *ibid.*, **20**, 525 (1955).

(16) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963).

in CCl_4 was complete in 45 min and afforded a mixture of **2b** and the parent amide (**3**). Although **2b** could not be separated from **3** by recrystallization, the mixture afforded the same cyclization products as the chloro analog (Scheme I).

SCHEME I



ir (cm^{-1}) 6124 (cyclopropyl), 3240 (NH), 1135 (SO_2); nmr (τ) 4.7 bs (0.88 H, NH), 7.6–8.1 m (1.06 H, SO_2CH), 8.67 s (t-C_4H_9), 8.88 d (CH_3), 8.3–9.1 m (total 14.00 H), 9.10–9.55 m (1.06 H)

ir (cm^{-1}) no NH; nmr (τ) 6.20 m (1.06 H, NCH), 6.6–8.3 m (3.94 H, SO_2CH_3 and CCH_2C), 8.60 s (t-C_4H_9), 8.68 d (CH_3, total both groups 11.65 H)

Compound 2	Base	% yield based on 2			
		2	3	4	5
a	CH_3Li in THF	0	~5	40	~5
b	CH_3Li in THF	0		53	~5
a	$NaNH_2$ in THF	0	5	5	60
b	$NaNH_2$ in THF	0	5	5	55
a	NaOH in CH_3OH	0	10	18	43
a	NaH in xylene	0	70	0	0
a	$AgBF_4$ in CH_2Cl_2	80	0	0	0
a	n-C_4H_9Li in heptane	75	0	0	0

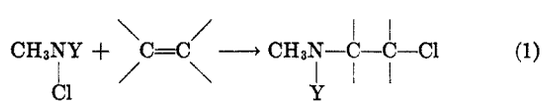
The structures of **4** and **5** were assigned as follows. Preparative glpc gave pure samples of **4** and **5**, which were found to be isomeric from their elemental analyses; neither fractional distillation nor column chromatography on Florisil effected a significant separation. Assignment of the cyclopropane structure to **4** was based on its nmr, ir, and near-ir spectra (Scheme I). The strong NH band also present in the parent amide **3** ruled out the five-membered, nitrogen-containing ring of **5**, and the near-ir band at 1.633 μ implied[17] the presence of a cyclopropyl group. The loss of HCl in forming **4**, shown by the elemental analysis, was further indicative of a cyclic structure for **4**, and the points of ring closure were confirmed from the nmr spectrum. Thus, the doublet methyl-group absorption disclosed the generation of a tertiary γ hydrogen. No peaks occurred between τ 6.8 and 7.0, which showed the absence of the characteristic 2 hydrogen SO_2CH_2 methylene group absorption in **3**, **2a** and **2b**, and **1a** and **1b**, but a single SO_2CH hydrogen was observed at higher field, consistent with its incorporation into a cyclopropane ring. Although three hydrogens absorbed in the cyclopropane region[16] at $\tau > 8.6$, the data do not permit an identification of the highest field hydrogen nor an assignment of the stereochemistry of the two ring substituents.

The isomeric sultam structure **5** was assigned on the basis of spectral data. In particular, the absence of an NH band in the ir spectrum, the presence of a doublet methyl peak in the nmr spectrum, and nmr absorption in the region expected for SO_2CH_2 were definitive. The nmr spectrum was comprised of a multitude of sharp peaks and was very similar to the spectra of the related five-membered ring analogs, 2-t-butylimino-5-methyltetrahydrofuran and the corresponding γ-valerolactone.[5]

Since N-chloro-N-methylvaleramide had previously rearranged to the 4-chloroalkyl isomer, although less efficiently than the N-t-butyl analog,[5] N-chloro-N-methylbutanesulfonamide was prepared and irradiated in benzene. The weight of the doublet CCH_3 absorption relative to the t-butyl peak in the nmr spectrum of the crude product showed the presence of about equal parts of the desired 3-chloroalkyl isomer and other products, but only N-methylbutanesulfonamide could be isolated (30–40% yield) by distillation or column chromatography. Treatment of the rearrangment mixture with either $NaNH_2$ or CH_3Li failed to yield isolable amounts of a cyclization product analogous to **4** or **5**.

Addition of N-Halamides to Olefins.—When we reported the rearrangement of N-halocarboxamides, we noted that both N-t-butyl- and N-methyl-N-chloroacetamide failed to react with olefins to yield an isolable 1:1 adduct.[5] Since the irradiation source was weak (100 W), we repeated the photolyses using styrene as a test olefin and a 450-W Hanovia immersion uv lamp in a Pyrex vessel; small amounts of new amide products were now obtained following chromatography on Florisil, but significant quantities of individual compounds could not be isolated. N-Chloroacetamide itself also failed to give an adduct, either as a heterogeneous mixture in CCl_4 or in CH_2Cl_2 solution.

In dramatic contrast to these results, however, N-chloro-N-methylcyanamide and -sulfonamide gave good to excellent yields of 1:1 adducts with a variety of olefins (eq 1 and Table I). These addition reactions



(1)

Y = CN, SO_2CH_3

appeared to be as facile as those of N-chlorourethans[13] or protonated N-chloramines;[9,12] analogy to these processes suggests that the present reactions were free radical in nature with the amino radical $CH_3\dot{N}Y$ as the chain-carrying species. However, there is reason to doubt that all of these additions did in fact involve *free* amino radicals.

Since a typical free-radical chain process involving alkyl radical intermediates should be inhibited by oxygen, our reactions were repeated in the presence of air. Although the N-chlorosulfonamide reactions were inhibited, better results were obtained with the N-chlorocyanamide in the presence of air than in its absence (Table I). The effect of weak uv irradiation, required in the N-chlorosulfonamide reactions, was

(17) The following ranges have been quoted: 1.624–1.650 μ by P. G. Gassman, *Chem. Ind.* (London), 740 (1962); 1.624–1.640 μ by H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964); and 1.637–1.659 μ by L. Skattebøl, *J. Org. Chem.*, **31**, 2789 (1966).

TABLE I

ADDITIONS OF N-HALAMIDES TO OLEFINS

RN(Cl)Y											
R	Y	*M*	Olefin	*M*	N_2 or air	Temp, °C	*hν*	Time, hr	Adduct[a]	Compd no.	% yield[b]
CH_3	SO_2CH_3	0.16	Butadiene	0.28	N_2	25	+	4.5	$CH_3SO_2N(CH_3)CH_2CH{=}CHCH_2Cl$	6	50
CH_3	SO_2CH_3	0.16	Isobutylene	0.28	N_2	25	+	2.0	$CH_3SO_2N(CH_3)CH_2C(CH_3)_2Cl$	7	70
CH_3	SO_2CH_3	0.16	Styrene	0.28	N_2	25	+[c]	2.5	$CH_3SO_2N(CH_3)CH_2CHClC_6H_5$	8	50
CH_3	SO_2CH_3	0.16	Styrene	0.28	Air	25	+	5.0			None
CH_3	CN	0.24	Butadiene	*d*	Air	10	−	0.9	$NCN(CH_3)CH_2CH{=}CHCH_2Cl$	9	52
CH_3	CN	0.24	Cyclopentadiene	0.53	Air	0	−	0.2	$RN(CN)CH_3$[f]	10	68[e]
$(CH_3)_2CH$	CN	0.29	Cyclopentadiene	0.59	Air	5	−	0.7	$RN(CN)CH(CH_3)_2$[f]	11	58
CH_3	CN	0.24	Isobutylene	0.28	N_2	25	+[g]	0.4	$NCN(CH_3)CH_2C(CH_3)_2Cl$	12	44
CH_3	CN	0.24	Isobutylene	0.28	Air	25	+	0.6	$NCN(CH_3)CH_2C(CH_3)_2Cl$		38
CH_3	CN	0.15	Styrene	0.28	Air	25	+	0.75	$NCN(CH_3)CH_2CHClC_6H_5$	13	76
CH_3	CN	0.19	Styrene	0.31	Air	25	−	1.25	$NCN(CH_3)CH_2CHClC_6H_5$		72

[a] Purified olefinic compounds were *cis–trans* mixtures except for *trans* **6**. [b] Purified compounds. [c] Reaction ceased when irradiation was interrupted but resumed on further irradiation. [d] Not determined. [e] Reaction run in benzene at 30° under air gave 13% **10**. [f] R =  [g] No reaction in the absence of irradiation.

TABLE II

NMR SPECTRA OF N-CHLOROCYANAMIDE AND N-CHLOROSULFONAMIDE ADDUCTS[a]

Compd no.	NCH_3	SO_2CH_3	CH_2Cl	CH_2N	Vinyl H	CCH_2C	CCH_3	C_6H_5
6	—7.20 s, 7.22 s—		5.90 m[b]	6.24 m[b]	4.0–4.5			
	(6.01)		(2.03)	(1.88)	(2.11)			
7	—6.90 s, 7.16 s—			6.62 s			8.35 s	
	(2.88, 3.26)			(1.95)			(5.90)	
8	—7.18 s, 7.27 s—		4.89 t	6.32 d				2.54 s
	(5.92)		(1.00)	(1.92)				(5.15)
9[c]	7.16 s		5.90 m[b]	6.38 m[b]	4.11 m			
	(3.06)		(1.98)	(1.98)	(2.04)			
10[d]	7.18, 7.21		4.8–5.3	5.5–5.9	3.7–4.2 m	6.8–8.2 m		
	(*e*)		—(diffuse; total 1.94)—		(1.97)	(*e*)		
11			4.80–5.35 m	5.40–6.00 m	3.75–4.35 m	6.0–8.2 m[f]	8.69 d, 8.75 d[g]	
			(0.83)	(0.88)	(1.71)	(3.45)	(6.13)	
12	6.94 s			6.74 s			8.36 s	
	(2.85)			(1.87)			(6.26)	
13[h]	7.25 s		4.97 t	6.58 d				2.63 s
	(3.03)		(1.01)	(2.07)				(4.87)

[a] Chemical shifts in τ values relative to tetramethylsilane (TMS); m = multiplet, t = triplet, d = doublet, s = singlet; area count in parentheses; CCl_4 solvent, except $CDCl_3$ for **7** and **8**. [b] Major pattern is a doublet of a doublet with additional splitting. [c] Areas include minor contribution of absorptions due to *cis* isomer (presumably) at τ 4.40 m, 5.2–5.6 m, 6.70 d, and 7.07 s. [d] Areas not measured. [e] Total of 5.08 H in the two groups. [f] Includes isopropyl methine hydrogen. [g] Ratio 4:1 presumably reflects ratio of *cis* to *trans* isomers. [h] Sample from chromatography before distillation; after distillation, new peaks were present at τ 2.85 (C_6H_5), 3.45 and 4.10 (vinyl H?, AB pattern, J = 14 cps), and 7.0 (NCH_3).

TABLE III

PHOTOLYSIS OF *t*-BUTYL-N-CHLOROCYANAMIDE IN THE PRESENCE OF OLEFINS IN CARBON TETRACHLORIDE AT 25° [a]

Olefin	Mol, *t*-BuNClCN/olefin	Sweep gas	Time, min	Work-up[b]	% yield of 1:1 adduct[c]	% yield of **17**	% yield of **18**
Cyclohexene	0.045/0.15	N_2	50	A	22	15	2
	0.045/0.15	Air	50	A	25	7	0
				B	20	6	0
	0.045/0.15	O_2	80	A or B	18	4	0
	0.015/0.15	N_2[d]	30	A	6	14	0
Styrene	0.045/0.11	N_2	45	B	6	32	4
	0.045/0.11	Air	55	B	8	0	14
1-Hexene	0.045/0.11	N_2	60	B	0	21	2
		Air	80	B	0	18	2

[a] Total solution, 300 ml; 15-min preirradiation of cyanamide solution prior to adding olefin to reactor; Hanovia 450-W uv immersion lamp. [b] A, Dimethyl sulfoxide (DMSO)–H_3PO_4–H_2O; B, oxalic acid–ether. [c] After hydrolysis; for structures see text. [d] No preirradiation.

equally ambiguous, since the N-chlorocyanamide additions to the conjugated olefins styrene, butadiene, and cyclopentadiene all proceeded spontaneously in the dark. It is therefore tempting to view these latter reactions as nonradical. However, the addition of N-chloro-N-methylcyanamide to isobutylene did require photolytic initiation, as did the recently reported[18] addition of N-chloro-N-methylethanesulfonamide to 1-hexene. Although normal radical chain processes must have been involved in the light-catalyzed but oxygen-sensitive reactions, molecular addition may have occurred in the others with the development of some free-radical character in the transition state. The latter possibility was discussed previously by Foglia and Swern[13c] regarding additions of N-chlorourethan to olefins.

The assignment of structure to the adducts shown in Table I followed from spectral analyses and, when the stability of the compounds permitted, elemental analyses. Only with the unsymmetrical olefins, isobutylene and styrene, did the question of the direction of the N-halamide addition across the double bond arise. Despite the lack of a clear-cut mechanism in the present reactions, we believe by analogy to the many related additions[9–16] that a species with amino radical character added to the double bond and that this was followed by attachment of chlorine to the carbon atom better able to stabilize the resulting radical-like intermediate. This assumption is supported by the following observations.

In the nmr spectra of the isobutylene adducts **7** and **12** (Table II), the methylene singlets (τ 6.62 in **7** and 6.74 in **12**) did not occur at sufficiently high field to rule out the group CH_2Cl, but they were more consistent with the values expected for a methylene group alpha to amide-type nitrogen. However, the presence of the tertiary chloride was strongly implied by the rapid, positive test in acidified, alcoholic silver nitrate observed at 25° with both **7** and **12**.

The nmr spectra of the styrene adducts **3** and **13** (Table II) were also consistent with the structures assigned. The low-field benzylic hydrogen appeared in both compounds as the expected triplet at τ 4.89 in **3** and 4.97 in **13**, whereas the methylene which we assign to NCH_2 appeared as a doublet at 6.32 and 6.58, respectively; all four absorptions had J = 7 cps. The low-field absorption occurred in the region expected for a benzylic methine hydrogen C_6H_5CHCl, but one cannot rule out a benzylic amide group in either adduct on this basis, since the benzylic hydrogen in a carboxamide model compound, α-(benzoylamino)ethylbenzene, absorbed at τ 4.7 in $CDCl_3$. However, the higher-field absorption at 6.3–6.6 seems too high for CH_2Cl attached to a carbon with two electron-withdrawing groups; for example, the methylene absorption in 1,1,2-trichloroethane appears in τ 6.03.[19] The rapid, positive tests obtained with silver nitrate solution at 25° again provided the better evidence for structures containing labile, benzylic chlorine substituents.

When the N-*t*-butyl analogs of both types of N-chloramide were photolyzed in the presence of olefins, the facile additions realized with the N-methyl compounds were not observed. Although interesting results were obtained with the N-chlorocyanamide (see next section), the sulfonamide gave only the parent N-*t*-butylmethanesulfonamide (50–80%) and some chlorinated olefin on reaction in carbon tetrachloride with cyclohexene, norbornene, or styrene. This contrasts with the N-halosulfonamide rearrangements above and with N-halocarboxamide rearrangements,[5] in which the N-*t*-butylamides gave superior results to the N-methyl compounds.

Reactions of N-*t*-Butyl-N-chlorocyanamide.—The reactions of N-*t*-butyl-N-chlorocyanamide (**15**) with olefins (Table III) were considerably more interesting than those of the corresponding sulfonamide. When **15** was irradiated in the presence of cyclohexene under nitrogen, electropositive chlorine was lost and an originally very small band at 2130 cm^{-1} in the ir spectrum of a concentrated sample grew significantly with time. When the reaction was complete, the new band was more intense than the strong NCN band at 2220 cm^{-1} which characterized both *t*-butylcyanamide and its N-chloro derivative **15**. Since the ambident radical species **14** was a possible intermediate in the reaction and the 2130-cm^{-1} band strongly suggested[20]

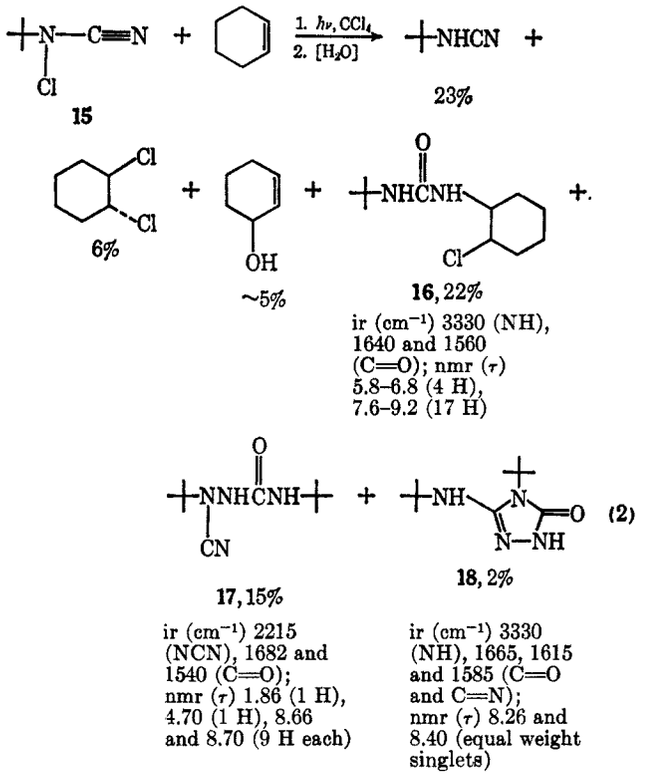
14a **14b**

(18) T. Ohashi, M. Suzie, M. Okahara, and S. Komori, *Tetrahedron Lett.*, 4195 (1968).

(19) Nmr Spectra Catalog, Spectrum No. 2, Varian Associates, 1962.

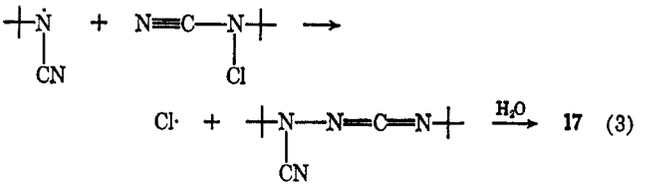
(20) G. D. Meakins and R. J. Moss, *J. Chem. Soc.*, 993 (1957), quote the range 2140–2125 cm^{-1} for the aliphatic carbodiimide *anti*-symmetric stretching frequency.

the carbodiimide group –N=C=N–, the reaction solution was concentrated under vacuum and treated with reagents known to hydrolyze diimides to the corresponding ureas. Products were obtained as shown in eq 2; *t*-butylcyanamide was a major product of every reaction studied (Table III), but its yield was not usually determined quantitatively.



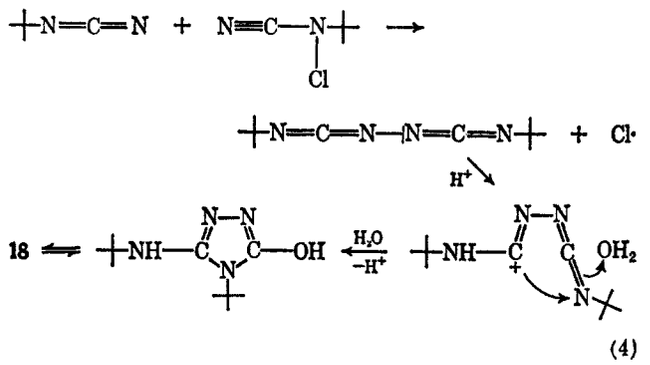
The structures of the adduct **16** and compounds **17** and **18** (or a tautomer of **18**) were deduced from their elemental analyses and the following data. The ir spectrum of **16** contained bands consistent with that of a secondary amide or urea, the nmr spectrum in d_6-DMSO included four low-field hydrogens and an N-*t*-butyl singlet, and a heavy precipitate of silver chloride was obtained from **16** and alcoholic silver nitrate after brief warming. The alternative structure t-$C_4H_9N(R)CONH_2$, in which the other nitrogen is alkylated, was ruled out by the absence of the second NH stretching band characteristic[21] of primary amides and because the NCN group of the required precursor was not expected to hydrolyze; under the conditions used, *t*-butylcyanamide was hydrolytically stable. The chlorine was assumed to reside on the other carbon of the double bond, but the data do not distinguish between a *cis* or *trans* addition in the present case.

Compounds **17** and **18** were found from their elemental analyses to be isomeric and derived from two molecules of **15**; both melted with the evolution of a gas, presumably nitrogen, and contained basic nitrogen. Only the structures shown appear possible from the spectral data. Compound **17** showed both the NC≡N and secondary amide ir bands, and the d_6-DMSO nmr spectrum contained two 1 H singlets and two *t*-butyl singlets. The N-cyanosemicarbazide **17** is the logical hydrolysis product of a dimer of **14a** with **14b.** However, the precursor of **17** might also have formed by attack of **14a** on the nitrile nitrogen of **15,** followed by (or concurrently with) elimination of a chlorine atom (eq 3). The latter alternative may be the more



probable, since the yields of **17** sometimes became appreciable (Table III). Since the uv maximum of **15** (286 mμ) falls well below the limit of transparency of the Pyrex reactor (~300 mμ) and is weak (ε 265), a facile photodissociation of **15** and recombination of amide radicals appears improbable. Tailing in **15** to 415 mμ, however, can account for the apparently inefficient photolability observed.

The ir spectrum of compound **18** contained three bands in the double-bond stretching region, and two different *t*-butyl peaks were revealed in the nmr spectrum. NH absorption was present in the ir, although missing from the nmr spectrum in d_6-DMSO, but the molecular weight confirmed a dimeric structure, $(C_4H_9NCN)_2H_2O$. Compound **18** is a reasonable cyclohydration product of a dimer of **14b,** but the bisdiimide precursor could also have formed by an addition–elimination process (eq 4).

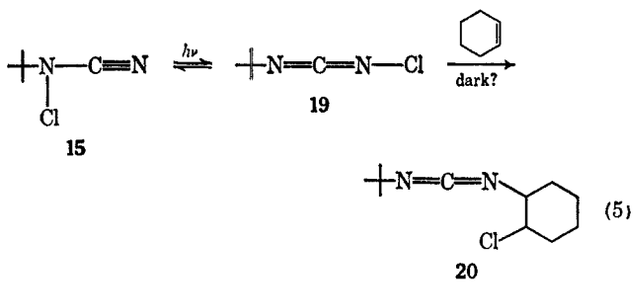


Several photolyses of **15** were carried out in the presence of cyclohexene in an effort to find the conditions most favorable to the synthesis of the adduct **16.** Irradiation of the chlorocyanamide in CCl_4 for 15 min prior to the introduction of the olefin caused less than 10% loss of active chlorine but a five-fold growth in the minor diimide band originally present; apparently, **15** was isomerizing to the diimide **19** (eq 5). This process is the opposite of the reported photolytic isomerization of carbodiimides RN=C=NR′ to the cyanamides.[22] When the lamp was extinguished and cyclohexene then added, ~25% of the active chlorine disappeared within 5 min, and the reaction was brought to completion by renewed irradiation. This dark reaction suggests that the photolytically produced **19** added spontaneously to cyclohexene

(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, p 206.

(22) J. H. Boyer and P. J. A. Frints, *Tetrahedron Lett.*, 3211 (1968).

(eq 5). Curiously, a second dark reaction could not be detected, even if only a limited amount (10 mol %) of olefin was added following the first preirradiation. This implies that the isomerization **15** ⇄ **19** was easily inhibited by small amounts of olefins or reaction products.

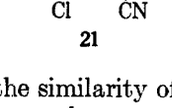


(5)

If the 1:1 adduct **20** did form in a dark reaction, the unexpected failure of air to inhibit adduct formation with cyclohexene or styrene becomes reasonable. However, the yield of **17** was lower in the presence of air in two of the three cases shown in Table III, although the yield of **18,** which we feel must arise by a mechanism closely related to that which gives **17,** was actually increased in the case of styrene. These results will require further study to explain with conviction. Equally puzzling was the result of a reaction carried out with one-third the usual amount of **15** but without preirradiation (Table III); the yield of adduct **16** was severely reduced, but that of **17** was unaffected.

Two further changes in reaction conditions were also without useful effect. Runs made under the conditions of entries 1 or 2 of Table III failed to produce any adduct when the solvent used was benzene (N_2, 60 min), pyridine (air, 40 min), or acetonitrile (air, 40 min), and irradiation under air of a 1:2 mixture of **15** and cyclohexene in the absence of a solvent gave only 9% **16** and no **17** or **18.**

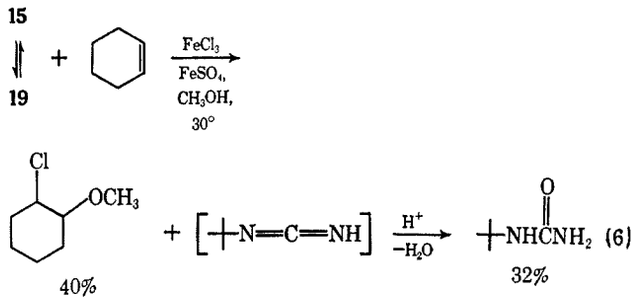
In addition to the three olefins shown in Table III, **15** was also photolyzed in the presence of norbornene, 1,3-cyclooctadiene, cyclopentadiene, methylenecyclohexane, tetramethylethylene, or trimethylvinylsilane. None of these afforded an isolable 1:1 adduct. The adduct (**21**) from styrene (Table III) was assigned the structure shown from a positive silver nitrate test for



21

labile chlorine and the similarity of its spectral data to those of related compounds.

Finally, it was interesting to find evidence of *t*-butylcarbodiimide itself as a major product of a reaction in methanol between **15** and cyclohexene under conditions known to effect the metal-catalyzed addition of N-chlorodialkylamines to olefins.[10] The products isolated following chromatography on Florisil were 40% 1-chloro-2-methoxycyclohexane, a few per cent 1,2-dichlorocyclohexane, and 32% *t*-butylurea (eq 6). None of the urea was produced when *t*-butylcyanamide was subjected to the conditions of work-up. We therefore believe that the urea arose from *t*-butylcarbodiimide, which is the expected product if **19** were acting as an ionic chlorinating agent similar to N-chlorosuccinimide. About 10% of the urea was also obtained from the photolytic reaction of methylenecyclohexane under nitrogen using either method of diimide hydrolysis.



(6)

Experimental Section

Preparation of N-Halamides. N-*t*-Butyl-N-chlorobutanesulfonamide (1a).—The parent sulfonamide (**3**) was prepared from *t*-butylamine and butanesulfonyl chloride (Aldrich Chemical Co.) in benzene: bp 115–120° (0.9 mm), $n^{23}D$ 1.4545 [lit.[8a] bp 155–156° (6 mm), $n^{20}D$ 1.4530]. To 0.20 mol of **3,** 0.3 g of $K_2CO_3 \cdot 1.5H_2O$, and 300 ml of CCl_4 was added dropwise 0.20 mol of *t*-butyl hypochlorite (Frinton Laboratories) and the mixture was heated under reflux for 4 hr. Evaporation of the solvent and distillation through a 600 × 6 mm column packed with a tantalum wire spiral afforded 94% **1a,** bp 86° (0.5 mm), $n^{23.5}D$ 1.4698; NH absorption was absent from the ir spectrum of the product (lit.[1] $n^{20}D$ 1.4718).

Anal. Calcd for $C_8H_{18}ClNO_2S$: Cl, 15.57. Found (iodometric titration): Cl, 15.55, 15.58.

N-Bromo-N-*t*-butylbutanesulfonamide (1b).—A 1.1 *M* solution of *t*-butyl hypobromite was prepared as described previously,[5] except that the hypobromite was extracted into one 50-ml and two 25-ml portions of CCl_4, washed with two 20-ml portions each of water and saturated sodium carbonate, and dried over anhydrous potassium carbonate. The sulfonamide **3** (0.08 mol) and 73 ml of the hypobromite solution were stirred in 100 ml of CCl_4 for 90 min to give **1b,** which was then irradiated. After 90 min, no NH absorption was present in an evaporated sample removed from a stirred mixture of 0.08 mol each of **3** and the hypobromite in 100 ml of CCl_4.

When a similar preparation of the crude N-methyl analog was attempted, no loss of NH occurred after 4 hr at room temperature, and only randomly brominated material was produced on heating the sulfonamide–hypobromite mixture under reflux for 3 hr.

N-Chloro-N-methylbutanesulfonamide.—A mixture of 0.2 mol of N-methylbutanesulfonamide, bp 150–155° (0.03 mm), $n^{25}D$ 1.4550, and 0.21 mol of *t*-butyl hypochlorite in 200 ml of CCl_4 was heated under reflux for 2 hr in the presence of 0.5 g of $K_2CO_3 \cdot 1.5H_2O$. The product was obtained in 98% yield: bp 70–73° (0.05 mm), $n^{25}D$ 1.4685.

Anal. Calcd for $C_5H_{12}ClNO_2S$: Cl, 19.10. Found (iodometric titration): Cl, 19.00, 18.98.

N-*t*-Butyl-N-chloromethanesulfonamide.—On chlorination of the parent sulfonamide, mp 39–42° (lit.[23] mp 40–41°), and attempted distillation of the N-chloro derivative at 1 mm, decomposition occurred at a bath temperature of 88°; this N-halamide was therefore used without purification.

N-Chloro-N-methylmethanesulfonamide.—N-Methylmethanesulfonamide, bp 78–79° (0.03 mm), $n^{25}D$ 1.4501 (lit.[24] $n^{25}D$ 1.4493), was chlorinated in the usual manner and distilled: bp 64–65° (1 mm), $n^{23}D$ 1.4737, mp 32–33°, yield 92%.

Anal. Calcd for $C_2H_6ClNO_2S$: Cl, 24.70. Found (iodometric titration): Cl, 24.60, 24.65.

N-*t*-Butyl-N-chlorocyanamide (15).—*t*-Butylcyanamide was used as received from Aldrich Chemical Co. [lit.[25] bp 114–115.5°

(23) V. I. Markov and S. I. Burmistrov, *Zh. Obshch. Khim.*, **33,** 1647 (1963); *Chem. Abstr.*, **59,** 11232*h* (1963).

(24) J. Vaughan and P. Sears, *J. Phys. Chem.*, **62,** 183 (1958).

(25) E. Schmidt, D. Ross, J. Kittl, and H. H. von Diisel, *Ann.*, **612,** 11 (1957).

(14 mm), mp 12–13°]. A solution of 19.6 g (0.20 mol) in 250 ml of CCl_4 was treated with 23 g (0.212 mol) of *t*-butyl hypochlorite and 0.5 g of $K_2CO_3 \cdot 1.5H_2O$ at room temperature for 3 hr. The yellow solution was filtered and evaporated, and the residue was distilled to afford 21.5 g (81%) of **15**: bp 53.5–54° (8 mm), $n^{24}D$ 1.4433, ir 2215 cm^{-1} (NCN) with a weak band at 2080 cm^{-1}.

Anal. Calcd for $C_5H_9ClN_2$: Cl, 26.76. Found (iodometric titration): Cl, 26.54.

N-Chloro-N-methylcyanamide.[26]—A dried solution containing 0.28 mol of cyanogen bromide in 350 ml of anhydrous ether was introduced into a dry flask equipped with a coarse glass-fritted gas dispersion tube projecting to but not below the surface of the liquid. The ether solution was cooled to −30° with mechanical stirring under a nitrogen atmosphere, and methylamine was slowly added through the dispersion tube. When 1.8 mol of amine/mol of cyanogen bromide had been added (2 hr), a precipitate of methylamine hydrobromide was removed by rapid filtration as the filtrate containing methylcyanamide was maintained at −10° or below. It is important that three variables be controlled in order to realize a good yield of methylcyanamide: stringently dry conditions, a reaction temperature of −30° (colder temperatures require excessive reaction times), and a dilution of cyanogen bromide equal to or greater than that indicated.

The cyanamide was chlorinated as follows. The ether solution was concentrated to about one-half its volume in a rotary evaporator at water aspirator pressure but *without* a water bath; this removed any residual methylamine. The resulting solution was diluted with 75 ml of CCl_4 in a reaction flask, cooled to −10°, treated with the theoretical amount of *t*-butyl hypochlorite in 30 ml of CCl_4, and allowed to warm to room temperature over 2 hr. Distillation gave N-chloro-N-methylcyanamide in variable yields of 36–60%: bp 44–46° (30 mm), $n^{24}D$ 1.4393. Occasionally the pot residue decomposed rather suddenly as the distillation neared completion.

Anal. Calcd for $C_2H_3ClN_2$: Cl, 38.06. Found (iodometric titration): Cl, 38.00, 37.95.

N-Chloro-N-isopropylcyanamide.—Ten drops of isopropylamine were added to a dried solution of 30 g of cyanogen bromide in 250 ml of ether at −15°. When a precipitate of the amine hydrobromide appeared, dropwise addition of the remaining 30 g of amine was continued at −15°. The reaction was complete after 45 min. The reaction mixture was then filtered, diluted with CCl_4, and evaporated at 20° to remove ether. The residue was further diluted to 200 ml with CCl_4 and treated with 0.25 mol of *t*-butyl hypochlorite in 50 ml of CCl_4 at 0°. After warming to 25° and stirring for 45 min, the solution was evaporated to a residue which was distilled to give the product in 50% yield: bp 64–65°, $n^{24}D$ 1.4410. The spectral data were as anticipated; a chlorine analysis was not obtained.

Caution. When the amine was added in its entirety to the cyanogen bromide solution at −30°, no reaction occurred as judged by the absence of the precipitate of amine hydrobromide. On warming to −20° after 30 min, still no reaction was evident. However, at −10° the reaction took place with sufficient violence to shatter the reaction vessel and surrounding apparatus.

Rearrangement of N-Chloro-N-*t*-butylbutanesulfonamide (1a).—A solution of 0.08 mol of **1a** in 200 ml of benzene was irradiated at 28–30° for 55 min with a 100-W Hanovia uv lamp; the Vycor vessel was the same as that described previously,[5] and a nitrogen purge of the solution was implemented for 20 min prior to irradiation. On evaporation of the solution a solid was left which was recrystallized from ether–pentane. **N-*t*-Butyl-3-chlorobutanesulfonamide (2a)** was obtained in two fractions: 12.7 g (67%), mp 58–60°, and 2.3 g (12%), mp 47–54°. A further recrystallization afforded **2a** with mp 63–65°. The major impurity was identified as the parent amide **3** on comparison of the appropriate nmr spectra. No evidence of the 4-chloro isomer was found; in particular, no triplet absorption due to the $-CH_2Cl$ group was present in the nmr spectra of the reaction product or recrystallization fractions. The nmr spectrum of **2a** was definitive of the 3-chloro isomer, however: NH, τ 4.90 bs (0.90 H); CHCl, 5.66–6.05 m (0.86 H); SO_2CH_2, 6.84 unsymmetrical quartet (1.94 H); CCH_2C, 7.5–8.3 m (2.07 H); CH_3, 8.42 d (3.24 H), $(CH_3)_3C$, 8.62 s (ratio of area to total of the other 9 H was 0.94).

(26) R. Kitawaki, M. Yamashita, and K. Sugino, *Nippon Kagaku Zasshi*, **78**, 567 (1957); *Chem. Abstr.*, **53**, 5124*g* (1959).

Anal. Calcd for $C_8H_{18}ClNO_2S$: C, 42.19; H, 7.97; Cl, 15.57; N, 6.15; S, 14.08. Found: C, 42.21; H, 7.90; Cl, 15.72; N, 5.94; S, 13.97.

Rearrangement of N-Bromo-N-*t*-butylbutanesulfonamide (1b).—The bromamide was prepared *in situ* as noted above and irradiated in CCl_4 solution; the reaction proceeded identically with that of the N-chloro analog to give a solid, mp 55–65°, after crystallization from ether–pentane (60% yield based on **2b**). Recrystallization gave a sample of **2b**, mp 65–67°, whose nmr spectrum contained the CCH_3 triplet from about 20% of the parent amide **3**; **3** could not be removed by further recrystallization. This mixture, cyclized as described below, contained **2b** in a final yield of 45%. The nmr spectrum of **2b** was similar to that of **2a**: NH, τ 4.72; CHBr, 5.5–6.0; SO_2CH_2, 6.80 unsymmetrical quartet; CCH_2C, ~7.0–8.0; CH_3, 8.22 d; $(CH_3)_3C$, 8.60 s.

2-*t*-Butyl-3-methyltetrahydroisothiazole 1,1-Dioxide (5).—To 0.02 mol of **2a** in 200 ml of dry tetrahydrofuran was added a slurry of 0.02 mol of $NaNH_2$[27] in benzene. The mixture was stirred under reflux for 3 hr in a nitrogen atmosphere, cooled, filtered, and evaporated to a residue which was chromatographed on Florisil. A fraction containing **5** in 60% yield along with 5% **3** and 5% **4** was analyzed by glpc. An analytical sample of **5**, $n^{25}D$ 1.4773, was collected from the product of a similar cyclization of **2b**. The assignment of structure was given in the results section.

Anal. Calcd for $C_8H_{17}NO_2S$: C, 50.23; H, 8.96; N, 7.32; S, 16.76. Found: C, 50.09; H, 9.27; N, 7.21; S, 16.91.

N-*t*-Butyl-2-methylcyclopropanesulfonamide (4).—To 0.02 mol of **2b** in 200 ml of dry tetrahydrofuran was added 0.02 mol of methyllithium as a 2 *M* solution in ether (Lithium Corp. of America). The mixture was stirred at 60° under nitrogen for 4 hr, cooled, evaporated, and treated with ether to precipitate lithium chloride. The concentrated residue had the same ir and nmr spectra as the material obtained when an ether solution of the crude product was washed with water to remove the salt. Both thin layer and gas chromatography showed the presence of **4** and **5**, but **4** predominated by at least fivefold. Short-path distillation [bp 94° (0.12 mm)] did not separate **4** from **5**; the analytical sample of **4**, $n^{24}D$ 1.3106, and the yield were therefore obtained by glpc.

Anal. Calcd for $C_8H_{17}NSO_2$: C, 50.23; H, 8.96; N, 7.32; S, 16.76. Found: C, 50.54; H, 9.48; N, 7.29; S, 16.68.

Other Cyclization Procedures for 2a and 2b (see Scheme I). Sodium Hydroxide in Methanol.[28]—To a mixture of 0.034 mol of **2b** and 0.2 g of N,N-dimethylaniline in 50 ml of anhydrous methanol was added 0.04 mol of NaOH in 50 ml of methanol. The mixture was heated under reflux for 24 hr, cooled, evaporated to one-half the volume, and diluted with ether. This precipitated 3.4 g of NaBr. The filtrate was concentrated and analyzed by glpc (see Scheme I).

Sodium Hydride.—A mixture of 0.02 mol of **2a** and a slight excess of NaH were heated at 130° in xylene for 6 hr. Routine work-up afforded only **3**, identified by ir, nmr, and glpc.

Silver tetrafluoroborate in methylene chloride or acetone, which has been used to cyclize γ-chlorocarboxamides,[29] failed to effect any reaction of **2a** even after heating for 4 hr.

The Addition of N-Halamides to Olefins.—The preparations of adducts **6–13** (Table I) are summarized below; their nmr spectra are summarized in Table II.

N-(4-Chloro-2-butenyl)-N-methylmethanesulfonamide (6).—The reaction vessel was a 300-ml-capacity Pyrex cylinder, ~8 × 30 cm, fitted with a porous glass disk gas inlet near the bottom, a side arm leading to a condenser near the top, and a standard taper joint at the top into which was inserted a Pyrex immersion well with water jacket to accommodate a 450-W Hanovia uv lamp. To this vessel was added 0.044 mol of N-chloro-N-methylmethanesulfonamide and 200 ml of CCl_4. Following a nitrogen gas purge of 20 min, 75 ml of a CCl_4 solution containing 0.08 mol (initially) of butadiene was added. Irradia-

(27) Freshly prepared material (A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1957, p 195) was required; little product resulted on use of commercially available $NaNH_2$.

(28) A. D. Bliss, W. K. Cline, and O. S. Sweeting, *J. Org. Chem.*, **29**, 2412 (1964).

(29) G. L. Schmir and B. A. Cunningham, *J. Amer. Chem. Soc.*, **87**, 5692 (1965).

tion was then carried out for 4.5 hr as agitation was provided by a slow stream of nitrogen rising through the solution. The product was obtained by rotary evaporation of the solution under aspirator vacuum and chromatography on Florisil using methylene chloride and ether as eluents. The adduct **6** was obtained in 72% yield and contained a compound, presumably *cis* **6**, which did not survive distillation. The distilled sample, which darkened on standing, was *trans* **6**, bp 120–125° (1 mm), n^{22}D 1.4948; its ir and nmr spectra were definitive on comparison with the spectra of the analogous dialkylchloramine adducts,[9a] especially the *trans*-CH=CH doublet at 970 (strong) and 945 (medium) cm^{-1}.

Anal. Calcd for $C_6H_{12}ClNO_2S$: C, 36.45; H, 6.12; Cl, 17.94; N, 7.09; S, 16.22. Found: C, 36.48; H, 6.33; Cl, 18.15; N, 7.09; S, 16.45.

N-(2-Chloro-2-methylpropyl)-N-methylmethanesulfonamide (7).—Crude **7** was obtained similarly in 80% yield from isobutylene except that chromatography was not required. Analytically pure **7**, mp 54–55°, resulted after three recrystallizations from hexane.

Anal. Calcd for $C_6H_{14}ClNO_2S$: C, 36.10; H, 7.05; N, 7.02. Found: C, 35.90; H, 7.00; N, 7.26.

N-(2-Chloro-2-phenylethyl)-N-methylmethanesulfonamide (8).—A mixture of 0.044 mol of N-chloro-N-methylmethanesulfonamide and 0.08 mol of freshly distilled styrene (the excess was probably not required) in 280 ml of CCl_4 was purged with nitrogen and irradiated, then stripped to 14 g of a residue which was chromatographed on Florisil. After 3.4 g of a mixture of chlorinated styrenes was eluted with hexane, elution with CH_2Cl_2 and ether gave 6.9 g of a solid, mp 78–81°. Recrystallization from 1:5 CH_2Cl_2–ether gave **8**, mp 79.5–81°.

Anal. Calcd for $C_{10}H_{14}ClNO_2S$: C, 48.48; H, 5.70; N, 5.65. Found: C, 48.41; H, 5.72; N, 5.62.

When the reaction was repeated in the presence of a slow stream of oxygen, no amide adduct could be isolated. When the chloramide was stirred with styrene in CCl_4 under nitrogen for 18 hr, no loss of electropositive chlorine occurred, but one-half was lost in 75 min when irradiation was begun. No further loss occurred in a dark period of 2.5 hr; the reaction was completed in 2 hr by renewed irradiation to give 40% **8**.

N-(4-Chloro-2-butenyl)-N-methylcyanamide (9).—A solution of 0.06 mol of N-chloro-N-methylcyanamide in 250 ml of CCl_4 at 0° was stirred under gaseous butadiene, which was introduced at a rate sufficient to maintain 15–30°. After 50 min (ambient light only) the reaction was complete, and the mixture was stripped and chromatographed on Florisil. The combined adduct-containing fractions appeared to contain a mixture of both *cis* and *trans* isomers. Distillation was facile but the product decomposed in a few days even at <0°, which prevented a successful elemental analysis; the distillate was predominantly *trans* **9**, bp 121–122° (18 mm), n^{23}D 1.4856. The structure of **9** was obvious, as in the case of **6**, by comparison of the ir and nmr spectra with those of analogous compounds. An attempt to produce the corresponding acetate from the chloride **9** according to a procedure found useful for the dialkylamino analog[10] was unsuccessful.

3-N-Cyano-N-methylamino-5-chlorocyclopentene (10).—When 0.08 mol of freshly distilled cyclopentadiene was added slowly to 0.036 mol of N-chloro-N-methylcyanamide stirred in 150 ml of CCl_4 in an ice bath, a rapid reaction ensued to give a product which was chromatographed on Florisil and distilled: bp 84.5–86° (0.1 mm), n^{23}D 1.5074. The twin peaks for the NCH_3 group in the nmr spectrum suggest that the product was a *cis–trans* mixture, although the myriad of lines in the total spectrum defied simple analysis. Neither a picrate (from ethanol or acetone[30]) nor a hydrochloride (from ether or pentane) could be prepared.

Anal. Calcd for $C_7H_9ClN_2$: C, 53.68; H, 5.79; Cl, 22.64; N, 17.89. Found: C, 53.70; H, 5.72; Cl, 22.22; N, 17.81.

3-(N-Cyano-N-isopropyl)-5-chlorocyclopentene (11).—A reaction carried out with N-chloro-N-isopropylcyanamide and cyclopentadiene as in the preceding example gave a product that was eluted from Florisil mainly in hexane and the remainder in CH_2Cl_2. Distillation in a semimicroapparatus gave an unstable mixture of *cis* and *trans* **11**, bp 86–95° (0.1 mm), n^{23}D 1.4944. The nmr spectrum of **11** consisted of two distinct spectra in relative importance of 4:1; that these corresponded to isomers was evident from the measured areas when similar groups were ascribed to the same type of hydrogen; however, an impurity was also suggested by too great an absorption in the high-field region. A picrate could not be prepared. There seems no reason to doubt, however, that the main component of the product was **11**, by analogy with so many similar additions.

N-(2-Chloro-2-methylpropyl)-N-methylcyanamide (12).—Irradiation of 0.06 mol of N-chloro-N-methylcyanamide and 0.07 mol of isobutylene in CCl_4 using the 450-W lamp gave **12** after chromatography on Florisil and distillation: bp 71–72° (0.5 mm), n^{23}D 1.4567. Only 15% **12** was obtained under air on irradiation with a 100-W source after a 2-hr dark period, during which no reaction occurred. A sample of **12** was distilled from CaO without evidence of dehydrohalogenation.

Anal. Calcd for $C_6H_{11}ClN_2$: C, 49.15; H, 7.56; Cl, 24.18; N, 19.11. Found: C, 49.04; H, 7.63; Cl, 24.03; N, 19.11.

N-(2-Chloro-2-phenylethyl)-N-methylcyanamide (13).—The adduct was obtained under an atmosphere of air: bp 120° (0.03 mm), n^{22}D 1.5603; the same yield of **13** was obtained whether or not the solution was irradiated (Table I). Since the nmr spectrum of the distilled product contained some extraneous peaks in the vinyl region which were not present in the sample eluted from Florisil, the contaminant was thought to be a dehydrohalogenation product. However, attempts to induce this reaction failed with the following: sodium hydride, which gave no discrete product; refluxing triethylamine in benzene (no reaction); distillation from molten NaOH (tar); or treatment with methyllithium (tar). Acid-catalyzed reactions were not attempted. The chromatography sample, although providing a definitive nmr spectrum, gave an unsatisfactory elemental analysis.

The Reaction of N-Chloro-N-*t*-butylcyanamide with Cyclohexene (Table III, Entry I).—A solution of 6.0 g of the N-chlorocyanamide in 280 ml of CCl_4 was irradiated with the 450-W uv lamp for 15 min in a slow stream of nitrogen. The lamp was then turned off, 15 ml of cyclohexene was added, and the irradiation was resumed after 5 min. The solution was evaporated under aspirator vacuum at 30° when the titre for electropositive chlorine had reached zero. A residue (10 g) resulted which contained carbodiimide compounds (see results section); these were treated in one of two ways to effect their hydrolysis (Table III). Method A is illustrated here; method B is illustrated in the experiment described below.

The residue was heated with 4 ml of DMSO, 1 ml of H_3PO_4, and 1.5 ml of isopropyl alcohol/g of crude product for 45 min, followed by the addition of 2 ml of water/g of original residue. The mixture was shaken intermittently for 45 min as a precipitate of the urea **16** formed. This procedure is similar to that in which dicyclohexylcarbodiimide, DMSO, and an acid are used in the oxidation of alcohols to carbonyl compounds.[31] The precipitate was collected and washed with 5 ml of chilled 5:1 ether–acetone; the 3.0 g of crude **16** thus obtained was recrystallized using 10 ml of acetone/g to afford 2.3 g of **15** in two crops, mp 151–153°. Several recrystallizations afforded an analytical sample, mp 155–156.5°. The characterization of **N-*t*-butyl-N-2-chlorocyclohexylurea** and of the new compounds described below was discussed in the results section.

Anal. Calcd for $C_{11}H_{21}ClN_2O$: C, 56.76; H, 9.10; N, 12.04. Found: C, 56.45; H, 9.00; N, 12.19.

The filtrate from the collection of crude **15** was poured into 225 ml of water. The combined ether extracts (50 ml, then 5–25-ml portions) of this solution were washed with water and dried. Evaporation under vacuum left 3.2 g of a residue containing N-*t*-butylcyanamide, *trans*-1,2-dichlorocyclohexane, and 2-cyclohexenol (eq 2); the yields were estimated by glpc analysis.

The aqueous phase on separation from the ether extracts was basified with 12 *N* NaOH and immediately extracted with ether. The ether extracts were washed with water, dried over Na_2SO_4, concentrated, and evaporated to leave 2.1 g of material that partially crystallized on standing. The crystals (0.70 g) were collected after 1 day at 25° using a small amount of ether diluent: mp 173–175°. Crystallization of 0.4 g from 12 ml of hot benzene on the addition of 1 ml of hot hexane gave **N-*t*-butyl-N′-(N-*t*-butyl-N-cyanoamino)urea (17)**, mp 174–175.5° dec (evolution of a gas).

Anal. Calcd for $C_{10}H_{20}N_4O$: C, 56.58; H, 9.50; N, 26.39. Found: C, 56.34; H, 9.70; N, 26.44.

(30) J. Berger and A. D. Sorensen, *Acta. Chem. Scand.*, **20**, 2002 (1966).

(31) M. G. Burdon and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 4656 (1965); A. H. Fenselau and J. G. Moffatt, *ibid.*, **88**, 1762 (1966); K. E. Pfitzner, J. P. Marino, and R. A. Olofson, *ibid.*, **87**, 4658 (1965).

The filtrate from the collection of **17** was evaporated. After 1 day, crystals again appeared (0.05 g) and were collected: mp 220–226°. These and similar crystals obtained in other experiments were combined and 0.4 g was recrystallized from 30 ml of ethanol to afford pure **3-*t*-butylamino-4-*t*-butyl-1,2,4(1H)-triazolone (18)**, mp 239–240°.

Anal. Calcd for $C_{10}H_{20}N_4O$: C, 56.58; H, 9.50; N, 26.39; mol wt, 212.3. Found: C, 56.39; H, 9.38; N, 26.23; mol wt, 212.8.

The Reaction of N-Chloro-N-*t*-butylcyanamide with Styrene under Nitrogen.—A reaction was carried out as in the preceding example except that 0.14 mol of styrene was introduced after the preirradiation of the chloramide. The dark reaction with styrene had consumed 27% of the active chlorine in the 10 min before irradiation was again begun. Hydrolysis of 5 g of the 22.5 g of crude products obtained was carried out using method B (Table III), whereby the hydration of carbodiimides with oxalic acid under nonaqueous conditions was performed.[32] To the sample in 30 ml of ether was added oxalic acid in an amount calculated as 1.1 mol/mol of sample, assuming the latter to be comprised entirely of a 1:1 adduct of the chloramide and the olefin. A gas was evolved during the first 2 hr as the mixture was stirred at room temperature and then left without stirring for 48 hr. (When cyclohexene reaction products were hydrolyzed, the adduct urea precipitated in pure form during this time.) The solution was then diluted with ~200 ml of ether, neutralized using saturated $NaHCO_3$ solution, dried, and evaporated. **17** separated on standing: 0.35 g (32%), mp 177–178° dec. The decomposition point of **17** depended on the rate of heating.

After removal of **17**, the residue was chromatographed on alumina. Following the elution of 0.8 g of styrene and chlorinated styrenes with hexane, 0.15 g of material was eluted with CH_2Cl_2. The crystals of **21** which formed in this fraction were washed with pentane and analyzed directly: mp 62.5–64.0°. The nmr spectrum of the product was consistent with its formulation as **N-(2-chloro-2-phenylethyl)-N-*t*-butylcyanamide**: τ 2.67 (C_6H_5), 5.01 (CHCl), 6.62 (doublet of doublets, J = 7.5, 2.0 cps, NCH_2), 8.82 (*t*-butyl). Another compound appeared to be present in trace amounts by the presence of small peaks at τ 2.8, 8.68, 8.75, 9.2, and 9.9. The elemental analysis was nevertheless excellent for **21**, and it is therefore implied that the impurity is an isomer, perhaps the aziridine salt resulting from cyclization.

Anal. Calcd for $C_{13}H_{17}ClN_2$: C, 65.95; H, 7.24; Cl, 14.98; N, 11.83. Found: C, 65.84; H, 7.16; Cl, 14.94; N, 12.16.

A slightly larger amount of **21** was obtained in a similar way when a reaction was run in air (Table III); a sample following chromatography on Florisil gave three times the residue obtained from alumina, but the material gave a mixture of products on distillation. Most significant regarding the reactions of styrene in the presence of air was the elimination of **17** as a product and the isolation of the isomer **18** in unusually enhanced yield, following the oxalic acid treatment (Table III); **18** was eluted from alumina with methanol after the other products had been eluted with less polar solvents.

Iron-Catalyzed Reaction of N-Chloro-N-*t*-butylcyanamide with Cyclohexene in Methanol.—A procedure was approximated which is known to yield adducts of olefins and dialkyl-N-chloramines.[10] To 6.0 g (0.045 mol) of the chloramide and 15 ml (0.15 mol) of cyclohexene in 50 ml of methanol was added 7 g of $FeCl_3 \cdot 6H_2O$ as a slurry in methanol. The temperature of the mixture immediately rose from 5 to 30° and then fell, at which point about two-thirds of the chloramide had reacted. A mixture of 14 g of $FeSO_4 \cdot 7H_2O$ in 80 ml of methanol was then added, but the reaction proceeded only slowly, being complete in 75 min. The reaction mixture was then acidified with 5 N H_2SO_4, diluted fivefold with water, and extracted with ether; the ether was dried and evaporated to give 6 g of a product mixture which was chromatographed on alumina. Elution with hexane and CH_2Cl_2 gave the chloro ether (eq 6), and elution with methanol gave *t*-butylurea, mp 179–180° (lit.[33] mp 179°).

Anal. Calcd for $C_5H_{12}N_2O$: C, 51.70; H, 10.41; N, 24.12. Found: C, 51.55; H, 10.66; N, 24.29.

Registry No.—**2a**, 16339-82-5; **2b**, 19520-00-4; **4**, 19520-01-5; **5**, 19520-02-6; **6**, 19520-03-7; **7**, 19520-04-8; **8**, 19520-05-9; **9**, 19520-06-0; **10** (*cis*), 19519-95-0; **10** (*trans*), 19519-96-1; **11** (*cis*), 19519-97-2; **11** (*trans*), 19519-98-3; **12**, 19541-51-6; **13**, 19520-07-1; **15**, 19520-08-2; **16**, 19520-09-3; **17**, 19520-10-6; **18**, 19520-11-7; N-chloro-N-methylbutanesulfonamide, 16867-16-6; N-chloro-N-methylmethanesulfonamide, 2350-09-6; N-chloro-N-isopropylcyanamide, 19520-14-0; N-*t*-butyl-N-2-chlorocyclohexylurea, 19520-15-1; N-(2-chloro-2-phenylethyl)-N-*t*-butylcyanamide, 19520-16-2.

(32) F. Zetzsche and H. Lindlar, *Chem. Ber.*, **71**, 2095 (1938).

(33) Infrared Spectrum No. 9751, Sadtler Research Laboratories, Philadelphia, Pa.