cyclooctene. The isomers, 10.62 g (67%), were isolated by distillation: bp 50° (0.85 mm); n^{20}_D 1.4342; d^{25}_4 1.265. The presence of the two isomers in a ratio near 1:1 was established by gas chromatography using a 5-ft Dow Corning silicone 11 on Fluoropak column. The F^{19} nmr spectrum of the mixture showed the typical ABX pattern.

Anal. Calcd for $C_8H_{14}F_4N_2$: C, 44.86; H, 6.54; F, 35.51; N, 13.08. Found: C, 44.20; H, 6.62; F, 35.60; N, 14.42.

Registry No.—Tetrafluorohydrazine, 10036-47-2; fraction A, 16666-28-7; fraction B (*cis*), 16666-34-5; fraction C (*trans*), 16666-35-6; fraction D, 16666-29-8; fraction E (*cis*), 14182-81-1; fraction F (*trans*), 16666-31-2; *cis*-1,2-bis(difluoramino)cyclooctane, 16666-32-3; *trans*-1,2-bis(difluoramino)cyclooctane, 16666-33-4.

Acknowledgment.—Measurement and interpretation of the nmr spectra by Mrs. Carolyn Haney and Dr. F. A. Johnson are greatly appreciated. Technical assistance was rendered by Mr. J. O. Woods.

The Addition of N,N-Dichloro Carbamates to Conjugated Dienes

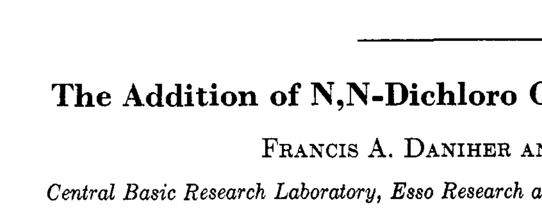
Francis A. Daniher and Peter E. Butler[1]

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036

Received December 14, 1967

The addition of N,N-dichloro carbamates (methyl, isopropyl, and bisethylene glycol) to a series of conjugated dienes (butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, chloroprene, and piperylene) has been found to give high yields of the corresponding N-chloro-ω-chlorocrotyl carbamates. The mode of addition of these pseudohalogens has been shown to be primarily 1,4 with minor amounts of other adducts also being formed. The N-chloro function of the adducts can be reduced in high yield with sodium sulfite to give the corresponding carbamates. Spectral data pertinent to the proof of structures are presented. A possible mechanism for the addition is discussed.

The addition of the pseudo-halogen, N,N-dichlorourethan, to a number of olefins has been reported.[2,3] The reaction is reported to give anti-Markovnikov adducts with terminal olefins.[2] With the isomeric-2-butenes[3c] and *trans*-3-hexene[2] mixtures of the *erythro* and *threo* isomers are formed. The initial adducts

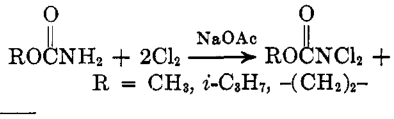


$$RCH{=}CHR' + C_2H_5O\overset{O}{\overset{\|}{C}}NCl_2 \longrightarrow RCH(Cl)CH(R')N(Cl)\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow RCH(Cl)CH(R')NH\overset{O}{\overset{\|}{C}}OC_2H_5$$

β-chloro-N-chloro carbamates were not isolated but were reduced to the β-chloroethyl carbamates with either sodium bisulfite[2] or potassium iodide followed by thiosulfate solution.[3]

As part of a continuing study in this laboratory[4] of the chemistry of unsaturated hydrocarbons, the reaction of N,N-dichloro carbamates with a series of conjugated dienes has been examined.

The particular N,N-dichloro carbamates employed were methyl,[5] isopropyl, and a novel difunctional species, N,N,N′,N′-tetrachloroethylene glycol biscarbamate. These materials were prepared in fair to good yields by chlorination of the corresponding carbamate in aqueous sodium acetate solution.[2]



$$RO\overset{O}{\overset{\|}{C}}NH_2 + 2Cl_2 \xrightarrow{NaOAc} RO\overset{O}{\overset{\|}{C}}NCl_2 + 2HCl$$
$$R = CH_3,\ i\text{-}C_3H_7,\ \text{-}(CH_2)_2\text{-}$$

Results

The addition reactions could be performed in a number of ways. The N,N-dichloro carbamate could be added dropwise to a cooled solution of the diene or vice versa. With gaseous butadiene it was found to be particularly advantageous simply to distil the material, after dilution with nitrogen, into a chilled solution of the N,N-dichloro carbamate. Removal of the solvent afforded near quantitative yields of monoadduct.

The crude products were analyzed by a combination of gas chromatography (gc) and nuclear magnetic resonance spectroscopy (nmr). The products were then further purified by distillation *in vacuo*. The yields of analytically pure product along with pertinent physical data are recorded in the Experimental Section. The nmr parameters of the adducts are tabulated in Table I.

The reduction of the N-chloro group of the adducts could be effected in good yield with sodium sulfite to give the corresponding crotyl carbamates. The nmr parameters of these materials are tabulated in Table I.

An examination of the infrared and nmr spectra of the N-chloro adducts and their corresponding reduction products clearly indicate that the principal mode of addition is 1,4. As an example, the infrared spectrum of the butadiene adduct shows strong absorptions for the *trans*-disubstituted double bond. In the nmr spectra, the chemical shift of the CH_2Cl grouping was essentially the same in the N-chloro adduct and its corresponding reduction product. On the other hand, the chemical shift of the CH_2–N group was very sensitive to changes in chemical environment. Upfield shifts of the magnitude of 0.4–0.5 ppm were observed for this signal upon reduction of the N-chloro group ($-CH_2-NCl- \rightarrow CH_2-NH-$). Further substantiation of this assignment is found in the fact that this signal appears as a doublet (J = 5–7 Hz) in the reduction product due to NH-CH< coupling.[6] Exchange of the amide proton with

---

[1] Analytical Research Division.

[2] T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

[3] (a) K. Schrage, *Tetrahedron Lett.*, 5795 (1966); (b) *Tetrahedron*, **23**, 3033, 3039 (1967).

[4] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966).

[5] P. Charbrier, French Patent 56,285 (1952).

[6] R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, p 67.

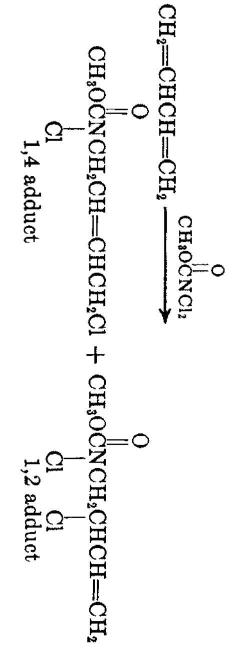
Table I.—Nuclear Magnetic Resonance Parameters of N,N-Dichloro Carbamate–Unsaturate Adducts Group Assignments[a]

		$ROC(=O)N(X)-$	Structure					Chemical shift, ppm: R^b										
Unsaturate	Registry no.	X	1	2	3	4	5	CH_3	$(CH_3)_2$	CH	NX	1	2	3	4	5	Coupling constant,[a] J, cps
Butadiene	16487-86-8	Cl	$-CH_2$	$-CH$	$=CH$	$-CH_2Cl$		3.78 s	...	...	...	4.15 m	......5.88 m......		4.15 m		
	16487-79-9	H	$-CH_2$	$-CH$	$=CH$	$-CH_2Cl$		3.61 s	...	...	5.85 b	3.76 m	......5.78 m......		4.05 m		
	16487-72-2	H	$-CH_2$	$-CH(Cl)$	$-CH$	$=CH_2$		3.63 s	...	...	5.90 b	3.45 m	4.47 q	5.93 ddd	5.32 dd 5.19 dd		$J_{2,3} = 7.2$; $J_{3,4} = 16.5$ (t); 9.5 (c); $J_{4g} = 2.0$
	16487-87-9	Cl	$-CH_2$	$-CH$	$=CH$	$-CH_2Cl$		...	1.27 d	4.92 hp	...	4.14 m	......5.87 m......		4.14 m		$J_R = 6.5$
	16487-80-2	H	$-CH_2$	$-CH$	$=CH$	$-CH_2Cl$		...	1.20 d	4.85 hp	5.52 b	3.75 m	......5.77 m......		4.02 m		$J_R = 6.3$
Isoprene	16487-88-0	Cl	$-CH_2$	$-C(CH_3)$	$=CH$	$-CH_2Cl$		3.78 s	...	...	...	4.17 s	1.73 s	5.66 t	4.11 d		$J_{3,4} = 7.5$; $J_{2,3} = 1.2$; $J_{1,3} = 1.4$
	16487-81-3	H	$-CH_2$	$-C(CH_3)$	$=CH$	$-CH_2Cl$		3.62 s	...	...	5.90 t	3.68 d	1.73 s	5.57 t	4.07 d		$J_{3,4} = 7.9$
	16487-89-1	Cl	$-CH_2$	$-C(CH_3)$	$=CH$	$-CH_2Cl$		...	1.27 d	4.93 hp	...	4.15 s	1.73 bs	5.63 t	4.12 d		$J_R = 6.3$
	16487-82-4	H	$-CH_2$	$-C(CH_3)$	$=CH$	$-CH_2Cl$		...	1.24 d	4.94 hp	5.1	3.76 d	1.73 bs	5.61 t	4.09 d		$J_R = 6.3$; $J_{3,4} = 7.8$; $J_{NH-1} = 6.5$
	16487-93-7	Cl	$-CH_2$	$-C(Cl)$	$=CH$	$-CH_2Cl$		3.77 s	...	...	...	4.29 s	1.77 s	1.85 s	4.11 s		
2,3-Dimethyl-1,3-butadiene	16487-43-7	H	$-CH_2$	$-C(CH_3)$	$=C(CH_3)$	$-CH_2Cl$		3.62 s	...	...	5.35 b	3.78 d	1.82 bs	1.82 bs	4.04 s		
	16487-90-4	Cl	$-CH_2$	$-(CH_3)$	$-C(CH_3)$	$-CH_2Cl$		...	1.33 d	5.02 hp	...	4.34 s	1.82 bs	1.82 bs	4.16 s		
	16487-83-5	H	$-CH_2$	$-(CH_3)$	$-C(CH_3)$	$-CH_2Cl$		...	1.23 d	4.92 hp	4.55 b	3.82 d	1.82 bs	1.82 bs	4.08 s		
Piperylene	16487-92-6	Cl	$-CH_2$	$-CH$	$=CH$	$-CH(Cl)$	$-CH_3$	3.77 s	...	...	...	4.15 m	.....*ca.* 5.6 m.....		4.55 m	1.58 d	$J_{4,5} = 6.6$
	16487-74-4	Cl	$-CH$	$-(CH_3)$	$-CH$	$=CH$	$-CH_2Cl$	3.77 s	...	...	...	5.06 m	1.33 d	......*ca.* 5.8......		4.05 m	$J_{1,2} = 6.3$
	16487-75-5	Cl	$-CH_2$	$-CH(Cl)$	$-CH$	$=CH$	$-CH_3$	3.77 s	...	...	...	...	4.45 m	.....5.75 m.....		1.73 d	$J_{4,5} = 5.5$
	16487-85-7	H	$-CH_2$	$-CH$	$=CH$	$-CH(Cl)$	$-CH_3$	3.63 s	...	...	6.10 b	3.75 m	.....*ca.* 5.7 m.....		4.55 m	1.55 d	$J_{4,5} = 6.5$
	16487-76-6	H	$-CH$	$-(CH_3)$	$-CH$	$=CH$	$-CH_2Cl$	3.63 s	...	...	6.10 b	4.26 m	1.23 d	.......5.74.......		4.03 m	$J_{1,2} = 7.0$
	16487-77-7	H	$-CH_2$	$-CH(Cl)$	$-CH$	$=CH$	$-CH_3$	3.63 s	...	...	6.10 b	~3.4 m	~4.4 m	.......5.78.......		1.72 d	$J_{4,5} = 5.5$
Chloroprene	16487-93-7	Cl	$-CH_2$	$-C(Cl)$	$-CH$	$-CH_2Cl$		3.81 s	...	...	...	4.43 s	...	6.06 t	4.27 d		$J_{1,3} = 1.0$; $J_{1,4} = 0.7$; $J_{3,4} = 7.3$
	16487-44-8	H	$-CH_2$	$-C(Cl)$	$=CH$	$-CH_2Cl$		3.71 s	...	...	5.79 b	4.02 d	...	6.03 t	4.22 d		
									$(R = -CH_2)$								
	16487-94-8	Cl	$-CH_2$	$-C(Cl)$	$=CH$	$-CH_2Cl$		...	4.43 s	...	...	4.43 s	...	6.06 t	4.23 d		$J_{3,4} = 7.2$
	16487-84-6	H	$-CH_2$	$-C(Cl)$	$=CH$	$-CH_2Cl$		...	4.21 s	...	~4.1 b	3.93 d	...	6.05 t	4.25 d		$J_{NH-1} = 6.0$

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, hp = heptet, b = broad, g = geminal, (c) = *cis*, (t) = *trans*. [b] R = methyl, isopropyl, or $(CH_2)_2$.

deuterium oxide caused the doublet to coalesce to a singlet. These data are compatible only with the 1,4 assignment for the adducts.

N,N-Dichloromethyl Carbamate Additions. Butadiene.—The reaction of N,N-dichloromethyl carbamate (DMC) proceeded smoothly to afford a nearly quantitative yield (>98%) of 86% of 1,4 adduct and 14% of the 1,2 adduct. The nmr spectrum of the crude product shows peaks due to both isomers. Integration of the relative amounts of protons of the respective —CH═CH— and ═CH_2 groups allowed a calculation of the isomer ratio. Analysis of the crude product by gc indicated a 90:10 ratio of 1,4 to 1,2 adduct, the 1,2 adduct being eluted first.



$$CH_2{=}CHCH{=}CH_2 \xrightarrow{CH_3O\overset{O}{\overset{\|}{C}}NCl_2} CH_3O\overset{O}{\overset{\|}{C}}\underset{Cl}{N}CH_2CH{=}CHCH_2Cl + CH_3O\overset{O}{\overset{\|}{C}}\underset{Cl}{N}CH_2\underset{Cl}{C}HCH{=}CH_2$$

1,4 adduct 1,2 adduct

In the 1,4 adduct, the olefin protons and the allylic methylene groups form a tightly coupled ABC_2D_2 system. The olefinic protons of the internal double bond appear as a complex two-proton multiplet at 5.88 ppm while the methylene groups which have nearly the same chemical shift appear as a four-proton multiplet at 4.15 ppm. Strong double irradiation of the olefin region collapses the methylene multiplet into a broad singlet. *trans* stereochemistry of the double bond in the major isomer is shown by characteristic bands at 3000 [═C—H stretching (str)] and 963 cm^{-1} [═C—H out of plane deformation (def)].[7a] Other bands due to the carbamate group were found at 1715 cm^{-1} (C═O str).[7b]

The minor isomer, the 1,2 adduct, was characterized by the typical resonance pattern of a terminal vinyl group which appears between 5.1 and 6.1 ppm. Signals due to other protons were coincident with those of the major isomer.

The ratio of isomers was independent of the solvent employed in the reaction. A 90:10 mixture of 1,4 and 1,2 adducts (determined by gc analysis) was obtained whether the reaction was run in pentane, benzene, methylene chloride, carbon tetrachloride, ether, or neat. In ether some chlorination of the solvent occurred; however, the ratio of the adducts formed was still 90:10. Furthermore, the same ratio of adducts was obtained when the reaction was performed in the dark under a nitrogen atmosphere. However, when the reaction was conducted in the dark under an oxygen atmosphere, addition was not observed and only starting material was recovered.

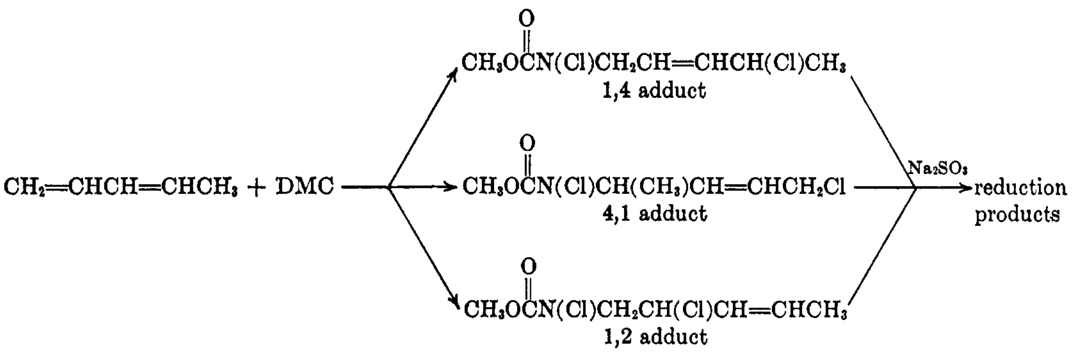
A number of reagents were examined for the reduction of the N-chloro group. The use of aqueous sodium bisulfite solution[2] afforded a 66% yield of reduced product. The ratio of 1,4 and 1,2 adducts in the crude reduction product remained at 90:10 so that no allylic rearrangement occurred during reduction.

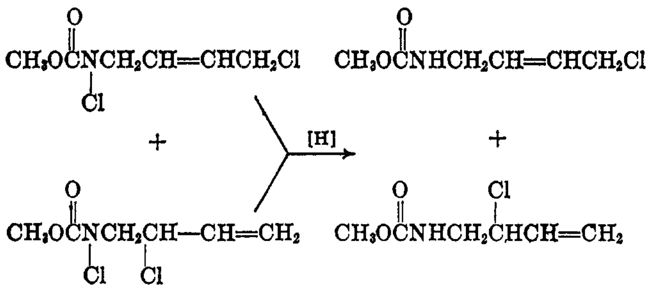
The reduction of the N-chloro group by an exchange reaction with methyl carbamate was also attempted. It has been reported[8] that the reaction of equimolar

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959: (a) p 34; (b) p 222; (c) p 219.

[8] R. L. Datta and D. Gupta, *J. Amer. Chem. Soc.*, **37**, 569 (1915).

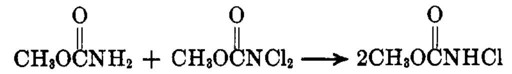
SCHEME I





$$CH_3O\overset{O}{\overset{\|}{C}}\underset{\underset{Cl}{|}}{N}CH_2CH{=}CHCH_2Cl + CH_3O\overset{O}{\overset{\|}{C}}\underset{\underset{Cl}{|}}{N}CH_2\underset{\underset{Cl}{|}}{C}H{-}CH{=}CH_2 \xrightarrow{[H]} CH_3O\overset{O}{\overset{\|}{C}}NHCH_2CH{=}CHCH_2Cl + CH_3O\overset{O}{\overset{\|}{C}}NHCH_2\overset{Cl}{\overset{|}{C}}HCH{=}CH_2$$

amounts of methyl carbamate and N,N-dichloromethyl carbamate results in the formation of N-chloromethyl carbamate.

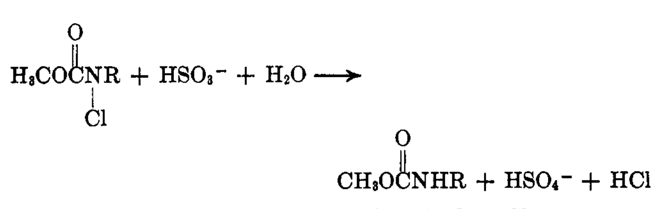


$$CH_3O\overset{O}{\overset{\|}{C}}NH_2 + CH_3O\overset{O}{\overset{\|}{C}}NCl_2 \longrightarrow 2CH_3O\overset{O}{\overset{\|}{C}}NHCl$$

The reaction of equimolar amounts of methyl carbamate and the isomeric mixture of N-chloro adducts was examined by nmr spectroscopy. No detectable amount of reduction product was observed after 125 hr at room temperature or after subsequent heating at 60° for 4 hr.

The reagent of choice for the reduction of the N-chloro group was found to be sodium sulfite. Stirring a methylene chloride solution of adduct with a 3 M excess of aqueous sodium sulfite solution at room temperature for 0.5 hr resulted in an 89% yield of reduction product.

The superiority of the sulfite method probably resides in the ability of the sulfite to buffer the acid generated in the reduction reaction. When bisulfite is used as a reducing agent, the pH of the aqueous solution at the end of the reaction is about 3 as monitored by pH paper. In addition, sulfur dioxide is liberated. The acid generated may then hydrolyze part of the product lowering the yield. On the other hand, with sulfite qualitatively less sulfur dioxide is liberated. Also, the pH of the aqueous solution remains near neutral indicating a more effective buffering action.



$$H_3CO\overset{O}{\overset{\|}{C}}\underset{\underset{Cl}{|}}{N}R + HSO_3^- + H_2O \longrightarrow CH_3O\overset{O}{\overset{\|}{C}}NHR + HSO_4^- + HCl$$

$$HCl + HSO_3^- \longrightarrow SO_2\uparrow + H_2O + Cl^-$$

$$HCl + SO_3^- \longrightarrow HSO_3^- + Cl^-$$

In one experiment, the mixture of reduction products was distilled to effect a partial separation of the isomers.

The infrared spectrum of the 1,4 isomer has a prominent band at 960 cm^{-1} (=CH— out of plane def)[7a] that strongly supports the proposed *trans*-disubstituted olefin structure. The nmr data are in agreement with this infrared assignment. Conversion into the N—H group results in a shielding of the adjacent methylene group. It now is chemically shifted from the methylene group next to chlorine and is a multiplet at 3.76 ppm. The —CH_2Cl protons of the reduced adduct show up as a multiplet at 4.05 ppm while the olefin protons are a multiplet at 5.78 ppm. The interaction of these three groups was confirmed by a field sweep double resonance experiment. Irradiation at the center of the olefin multiplet collapsed either multiplet to a singlet.

Infrared and nmr analysis of the reduced 1,2 isomer confirms the structure of the original product. Prominent infrared bands at 1000 and 925 cm^{-1} [7a] (=C—H, =CH_2 out of plane def) are characteristic for the terminal vinyl group. Bands due to the carbamate group are at 1245 (C—O str), 1705 (C=O str[7b]), and 1525 cm^{-1} [7c] (N—H + C—N combination band). The nmr data support the infrared assignments. The vinylic methine proton is a doublet of a double doublet at 5.93 ppm. It is coupled to the nonequivalent terminal methylene protons at 5.19 and 5.32 ppm and to the allylic methine proton at 3.45 ppm. This proton is a quartet due to nearly equivalent coupling with both the vinyl proton and the methylene group adjacent to nitrogen. In the reduced product, the methoxy protons are slightly upfield at 3.63 ppm while the N—H proton (removable by deuterium oxide) shows a broad resonance peak at 5.90 ppm.

Other Dienes.—The addition of DMC to isoprene, chloroprene, and 2,3-dimethyl-1,3-butadiene was also examined. The nmr spectrum of the isoprene adduct indicated at least an 85% selectivity for the 1,4-addition product. The remainder of the material presumably resulted from 4,1 addition as evidenced by the presence of a broad singlet at 1.84 ppm for the vinylic methyl group (=C—CH_3) of this adduct and the lack of terminal olefin (=CH_2) absorption (4,3 adduct) or a signal for a tertiary methyl group adjacent to chlorine (1,2 adduct). The latter signal would be expected to be in the 1.5–1.65-ppm region. These isomers could not be separated by gc under a variety of conditions. The reaction of DMC with the latter two dienes led exclusively to the formation of 1,4 adducts (see Table I, p 2638).

Piperylene.—The reaction of piperylene with DMC results in a 95% yield of the three isomeric adducts formed by 1,2 (26%) and 1,4 (44% 1,4 and 30% 4,1) addition to the conjugated system (Scheme I).

The structure of each isomer was established by a detailed study of the nmr spectrum of the crude reaction mixture. These data were supported by infrared and nmr double irradiation studies. The results of the latter technique were invaluable in assigning chemical shifts to overlapping protons and confirming tentative assignments.

Each isomer was characterized by the nmr signal for its methyl group in the piperylene moiety. These groups have well known[9,10] shifts being adjacent to chlorine (1.58 ppm), nitrogen (1.33 ppm), or the double bond (1.73 ppm), respectively. Integration of these signals on an expanded scale allowed quantitative determination of each isomer.

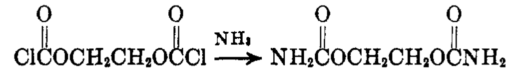
Irradiation of the chloromethine area at 4.55 ppm collapsed the methyl group doublet (J = 6.6 Hz) adjacent to chlorine of the 1,4 adduct to a singlet confirming that this group was coupled to an allylic methine proton (α to chlorine) rather than to an olefinic proton. Likewise strong irradiation in the olefin region collapsed the two-proton methylene signal at 4.15 ppm to a singlet. Reduction of the N-chloro group resulted in a diamagnetic shift of the adjacent methylene group 0.40 ppm upfield establishing its position α to nitrogen. In the reduced product, the position of the methyl group and methine proton adjacent to chlorine did not shift significantly. The doublet could be decoupled easily by irradiation again at 4.55 ppm.

In regard to the 4,1 adduct, irradiation of the olefinic area collapsed the methylene group adjacent to chlorine at 4.05 ppm (the position of this group did not change on reduction of the N-chloro group) to a singlet. Also, irradiation at 5.06 ppm, the position of the allylic methine proton adjacent to nitrogen, collapsed the methyl doublet (J = 6.3 Hz) to a singlet. On reduction, the position of this methine proton moved upfield 0.80 ppm (confirmed by double resonance) as expected. The structure of the 1,2 adduct was shown in a similar manner, although its low concentration in the isomer mixture hindered our decoupling experiments.

The vinylic nature of the methyl group (1.73 ppm) of the 1,2 adduct was shown by strong irradiation of the olefinic area at 5.75 ppm and the resulting collapse of the doublet (J = 5.5 Hz) to a singlet. This confirmed the partial structure, $-CH=CH-CH_3$. The position of the methyl group did not change in the reduced product. The signal for the methine proton on the carbon bearing the chlorine was found overlapped with several other signals at about 4.45 ppm while the adjacent methylene group's absorption was completely buried. On reduction the signal for the methine group remained constant whereas the multiplet for the methylene group next to nitrogen moved upfield to about 4.4 ppm.

N,N-Dichloroisopropyl Carbamate Additions.—The reaction of isopropyl carbamate with chlorine in aqueous sodium acetate solution afforded a 75% yield of product. The addition of this reagent to three dienes, butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene, was examined. The yields of adducts and the isomer ratios are very similar to those obtained with the methyl analog. The reduction of the N-chloro adducts with sulfite proceeded smoothly to afford high yields of crystalline reduction products.

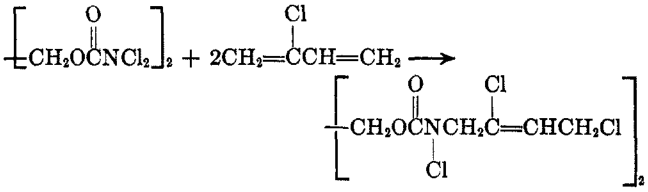
N,N,N′,N′-Tetrachloroethylene Glycol Biscarbamate.—The reaction of ethylene glycol bischloroformate with ammonia gave the biscarbamate[11] in 93% yield.



$$ClC(=O)OCH_2CH_2OC(=O)Cl \xrightarrow{NH_3} NH_2C(=O)OCH_2CH_2OC(=O)NH_2$$

This material was then converted by the standard procedure to the crystalline N,N,N′,N′-tetrachloro carbamate. The crude product was obtained in about 50% yield and was used directly without further purification. The nmr spectrum of the crude product exhibited a single resonance at 4.57 ppm. An acceptable chlorine analysis was also obtained on the crude product.

A quantitative yield of 1,4 adduct was obtained when this material was treated with 2 equiv of chloroprene. The adduct was obtained as a syrup and resisted all attempts at crystallization. The crude product was homogeneous on thin-layer chromatograms. The nmr spectrum of the material supports the proposed structure (see Table I). Treatment of the diadduct with sodium sulfite gave a 71% yield of crystalline bisreduction product.



$$\left[-CH_2OC(=O)NCl_2\right]_2 + 2CH_2=C(Cl)CH=CH_2 \longrightarrow \left[-CH_2OC(=O)N(Cl)CH_2C(Cl)=CHCH_2Cl\right]_2$$

Discussion

The data obtained indicate that the addition reaction proceeds by a radical-chain mechanism. The high preference for 1,4 addition has been observed in the radical addition of a number of reagents to conjugated dienes.[12,13] For example, a 90% or better selectivity for 1,4 addition has been reported for the addition of aliphatic and aromatic thiols to conjugated dienes.[14] The same order of selectivity has also been reported for the addition of protonated N-chlorodialkylamines to butadiene.[15] The ratio of 1,4 and 1,2 adducts resulting from the radical addition of chlorine to butadiene has been reported to be 78:22 while the ratio arising from purely ionic addition is 45:55.[16] Further support for

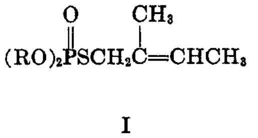
---

[9] W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).

[10] W. H. Mueller, R. M. Rubin, and P. E. Butler, *J. Org. Chem.*, **31**, 3537 (1966).

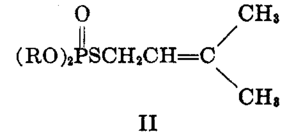
[11] W. Baird, P. Gaubert, and A. Lowe, British Patent 614,295 (1948).

[12] When a reagent may add by either an ionic or radical mechanism to a conjugated diene the position of attack of what would be the chain-carrying species in a radical reaction determines whether the addition is 1,4, 1,2, 4,1, etc. For example, thiophosphoric acids may add to conjugated dienes by either a radical or ionic mechanism.[13] With an unsymmetrical diene such as isoprene the adducts are not the same. The radical product is the 1,4 adduct, I, while the ionic product is the 4,1 adduct, II.



$$(RO)_2P(=O)SCH_2C(CH_3)=CHCH_3$$

I



$$(RO)_2P(=O)SCH_2CH=C(CH_3)_2$$

II

[13] A. A. Oswald, W. H. Mueller, and F. A. Daniher, Abstracts 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, p A055.

[14] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Amer. Chem. Soc.*, **84**, 3897 (1962).

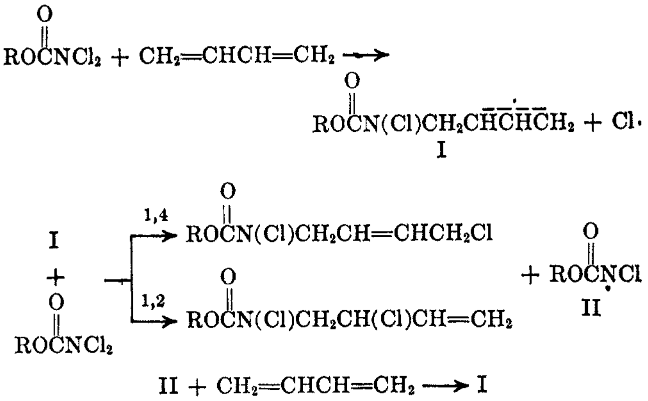
[15] R. S. Neale and R. L. Hinman, *ibid.*, **85**, 2666 (1963).

[16] M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1967).

the radical nature of the reaction is the inhibition of addition by oxygen.

The spontaneity and exothermicity displayed by the reaction coupled with the mild conditions and lack of initiators required for the addition are characteristic of a spontaneous initiated radical–chain reaction. The phenomenon of spontaneous initiation with active halogen reagents has been observed by Walling[17] in the reaction of *t*-butyl hypochlorite and bromite with styrene and 2-butyne and also by Poutsma in the addition of chlorine to cyclohexene[18] and butadiene.[16]

The probable steps for the chain reaction are shown below using butadiene as an example.



$$RO\overset{O}{\overset{\|}{C}}NCl_2 + CH_2{=}CHCH{=}CH_2 \longrightarrow RO\overset{O}{\overset{\|}{C}}N(Cl)CH_2\overline{CH}\dot{\overline{CH}}\overline{CH_2} + Cl\cdot$$

I

$$\text{I} + RO\overset{O}{\overset{\|}{C}}NCl_2 \xrightarrow{1,4} RO\overset{O}{\overset{\|}{C}}N(Cl)CH_2CH{=}CHCH_2Cl; \quad \xrightarrow{1,2} RO\overset{O}{\overset{\|}{C}}N(Cl)CH_2CH(Cl)CH{=}CH_2 \quad + RO\overset{O}{\overset{\|}{C}}\underset{\bullet}{N}Cl$$

II

$$\text{II} + CH_2{=}CHCH{=}CH_2 \longrightarrow \text{I}$$

In the initiation step, N,N-dichloro carbamate and diene combine to give the allylic radical (I) and a chlorine atom. In the propagation steps radical I reacts with another molecule of N,N-dichloro carbamate to give product and the N-chloro carbamate radical, II. Radical II can then react with another molecule of diene to regenerate I.

The abstraction of a chlorine atom from the N,N-dichloro carbamate by the allylic radical occurs preferentially at the least substituted carbon to yield the more thermodynamically stable product.[14] In the case of piperylene, little selectivity is noted since all of the adducts formed apparently are of equal stability, all being substituted 2-pentenes.

Experimental Section

The crude products were analyzed by gas chromatography using an Aerograph Model 1520B gas chromatograph. The column of choice was a 5-ft, 0.25-in.-o.d. column packed with 5% SE30 on 60–80 Chromosorb W. Nuclear magnetic resonance spectra were run on a Varian A-60 spectrometer as *ca.* 50% solutions in carbon tetrachloride with tetramethylsilane as an internal standard unless otherwise noted. Infrared spectra were recorded on a Beckman Model IR-10 infrared spectrophotometer.

Starting Dienes.—The dienes used in this study were commercial samples of the highest purity available. The butadiene (99+% purity) was obtained from the Matheson Co. The isoprene and piperylene were from Matheson Coleman and Bell. The 2,3-dimethyl-1,3-butadiene was obtained from the Borden Co. All of the above dienes were distilled prior to use with the exception of butadiene which was used without further purification. The chloroprene was obtained as a 50% solution in xylene from the E. I. du Pont de Nemours and Co., Inc., Elastomer Chemicals Department, Wilmington, Del. It was separated from the xylene by fractional distillation and then used immediately.

Alkyl Carbamates.—The methyl and isopropyl carbamates were obtained from commercial sources. The ethylene glycol biscarbamate was prepared by a modification of a patent procedure.[11] Ammonia was bubbled into an ice-cold, stirred solution of 60 g of ethylene glycol bischloroformate in 550 ml of dry toluene at such a rate so as to maintain the internal temperature between 5 and 10°. After the absorption of ammonia ceased, the addition was stopped and the reaction mixture allowed to stand at room temperature overnight. The reaction mixture was filtered and the cake washed with pentane and air dried. The residue was slurried with 500 ml of water and filtered, and the residue was dried under high vacuum to give 43 g (93%) of product, mp 163–165°.

N,N-Dichloro Carbamates.—The N,N-dichloro carbamates were prepared by reacting the corresponding carbamates with chlorine in aqueous sodium acetate according to the method of Swern.[2] With this procedure the following N,N-dichloro carbamates were prepared: $CH_3O_2CNCl_2$,[5] bp 47–48° (14 mm), $n^{25}D$ 1.4670, 70%; *i*-$C_3H_7O_2CNCl_2$, bp 58–59° (25 mm), $n^{25}D$ 1.4509, 79% (*Anal.* Calcd for $C_4H_7Cl_2NO_2$: Cl, 41.22. Found: Cl, 40.95); $(-CH_2O\overset{O}{\overset{\|}{C}}NCl_2)_2$, mp 40–43° (*Anal.* Calcd for $C_4H_4Cl_4N_2O_4$: Cl, 49.60. Found: Cl, 49.18).

General Procedure for the Reaction of N,N-Dichloro Carbamates with Conjugated Dienes.—The N,N-dichloro carbamate (0.1 mol) was added dropwise to a stirred, nitrogen-purged solution of conjugated diene (0.1 mol) in 25 ml of methylene chloride cooled to between –10 and –20° by means of a Dry Ice–isopropyl alcohol bath. The rate of addition was such that the internal temperature was maintained between −5 and 5°. After addition was complete, the reaction mixture was allowed to warm slowly to room temperature. The solvent was then removed at water aspirator pressure at ambient temperature. The residue was then analyzed for its isomer content by a combination of gc and nmr. The adducts were then vacuum distilled. The structure, yield of isolated analytically pure material, isomer ratio of adducts (nmr), boiling point, $n^{23}D$, and analytical data for the products are given below: $CH_3OCON(Cl)CH_2CH{=}CHCH_2Cl$, 91%, 86:14, bp 52–56° (0.005 mm), $n^{23}D$ 1.4930 (*Anal.* Calcd for $C_6H_9Cl_2NO_2$: C, 36.28; H, 4.58; N, 7.07. Found: C, 36.27; H, 4.73; N, 6.98); *i*-$C_3H_7OCON(Cl)CH_2CH{=}CHCH_2Cl$, 85%, 85:15, bp 75–77° (0.006 mm), $n^{23}D$ 1.4762 (*Anal.* Calcd for $C_8H_{13}Cl_2NO_2$: C, 42.49; H, 5.80; N, 6.20. Found: C, 42.53; H, 5.85; N, 6.32); $CH_3OCON(Cl)CH_2C(CH_3){=}CHCH_2Cl$, 82%, 85:15, bp 72–74° (0.065 mm), $n^{23}D$ 1.4964 (*Anal.* Calcd for $C_7H_{11}Cl_2NO_2$: C, 39.64; H, 5.23; N, 6.60. Found: C, 39.55; H, 5.35; N, 6.63); *i*-$C_3H_7OCON(Cl)CH_2C(CH_3){=}CHCH_2Cl$, 94%, 85:15, 87° (0.007 mm), $n^{23}D$ 1.4814 (*Anal.* Calcd for $C_9H_{15}Cl_2NO_2$: C, 52.55; H, 7.84; N, 6.81. Found: C, 55.32; H, 8.16; N, 6.81); $CH_3OCON(Cl)CH_2C(CH_3){=}C(CH_3)CH_2Cl$, 80%, 100, bp 83° (0.006 mm), $n^{23}D$ 1.4996 (*Anal.* Calcd for $C_8H_{13}Cl_2NO_2$: C, 42.49; H, 5.80; N, 6.19. Found: C, 42.41; H, 5.99; N, 6.12); *i*-$C_3H_7OCON(Cl)CH_2C(CH_3){=}C(CH_3)CH_2Cl$, 82%, 100, bp 83° (0.003 mm), $n^{23}D$ 1.4850 (*Anal.* Calcd for $C_{10}H_{17}Cl_2NO_2$: C, 47.25; H, 6.75; N, 5.51. Found: C, 47.30; H, 7.06; N, 5.30); $CH_3OCON(Cl)C_5H_8Cl$, 84%, 40:33:27, bp 65° (0.01 mm), $n^{23}D$ 1.4852 (*Anal.* Calcd for $C_7H_{11}Cl_2NO_2$: C, 39.64; H, 5.23; N, 6.60. Found: C, 39.28; H, 5.23; N, 6.23); $CH_3OCON(Cl)CH_2C(Cl){=}CHCH_2Cl$, 82%, 100, bp 78° (0.003 mm), $n^{23}D$ 1.5095 (*Anal.* Calcd for $C_6H_8Cl_3NO_2$: C, 30.99; H, 3.47; N, 6.02. Found: C, 31.06; H, 3.90; N, 6.05); $[CH_2OCON(Cl)CH_2C(Cl){=}CHCH_2Cl]_2$, 100%, 100, oil (*Anal.* Calcd for $C_{12}H_{14}Cl_6N_2O_4$: C, 31.12; H, 3.05; N, 6.05. Found: C, 30.74; H, 3.25; N, 6.08).

The order of addition may be reversed so that the diene is added to a chilled solution of the N,N-dichloro carbamate.

A number of other solvents, which were mentioned in the text have also proved satisfactory for this reaction.

General Procedure for the Reaction of Butadiene with N,N-Dichloro Carbamates.—Butadiene (0.1 mol) was condensed into a Pyrex pressure tube fitted with a Teflon needle valve. The tube was then connected by way of a T-joint to a nitrogen source. The butadiene container was opened and distilled with nitrogen dilution into a stirred, cooled solution of N,N-dichloro carbamate at such a rate so as to maintain the internal temperature at 0–5°. After addition of the butadiene was complete, the reaction was treated as described above.

General Procedure for the Reduction of N,N-Dichloro Carbamate–Conjugated Diene Addicts.—A solution of 0.1 mol of adduct in 100 ml of methylene chloride was vigorously stirred at

---

[17] C. Walling, L. Heaton, and D. D. Tanner, *J. Amer. Chem. Soc.*, **87**, 1715 (1965).

[18] M. L. Poutsma, *ibid.*, **87**, 2161, 2172 (1965), and references cited therein.

ambient temperature with a solution of 0.3 mol of sodium sulfite in 150 ml of water for about 30 min, until the organic layer failed to give a positve test with potassium iodide–starch paper. The layers were separated and the aqueous layer extracted with methylene chloride. The organic extracts were combined, washed with water, and dried over sodium sulfate. The methylene chloride was evaporated at aspirator pressure at ambient temperature to give the reduced carbamate which was then purified by distillation or recrystallization. The following carbamates were prepared: $CH_3OCONHCH_2CH=CHCH_2Cl$, 89%, bp 84–88° (0.009 mm) (*Anal.* Calcd for $C_6H_{10}ClNO_2$: C, 44.38; H, 6.16; N, 8.56. Found: C, 44.05; H, 6.20; N, 8.44); i-$C_3H_7OCONHCH_2CH=CHCH_2Cl$, 78%, mp 61–62° (*Anal.* Calcd for $C_8H_{14}ClNO_2$: C, 50.13; H, 7.36; N, 7.31. Found: C, 49.99; H, 7.45; N, 7.45); $CH_3OCONHCH_2C(CH_3)=CHCH_2Cl$, 76%, mp 31–32° (*Anal.* Calcd for $C_7H_{12}ClNO_2$: C, 47.33; H, 6.81; N, 7.88. Found: C, 47.29; H, 7.04; N, 7.89); i-$C_3H_7OCONHCH_2C(CH_3)=CHCH_2Cl$, 81%, mp 51–52° (*Anal.* Calcd for $C_9H_{16}ClNO_2$: C, 52.55; H, 7.84; N, 6.81. Found: C, 52.32; H, 8.16; N, 6.81); $CH_3OCONHCH_2C(CH_3)=C(CH_3)CH_2Cl$, 84%, mp 52–53° (*Anal.* Calcd for $C_8H_{14}ClNO_2$: C, 50.13; H, 7.36; N, 7.31. Found: C, 50.01; H, 7.30; N, 7.17); i-$C_3H_7OCONHCH_2C(CH_3)=C(CH_3)CH_2Cl$, 86%, mp 59–61° (*Anal.* Calcd for $C_{10}H_{18}ClNO_2$: C, 54.66; H, 8.34; N, 6.38. Found: 54.43; H, 8.26; N, 6.50); $CH_3OCONHCH_2C(Cl)=CHCH_2Cl$, 78%, mp 58–59° (*Anal.* Calcd for $C_6H_9Cl_2NO_2$: C, 36.38; H, 4.58; N, 7.07. Found: C, 36.32; H, 4.55; N, 7.18); $[CH_2OCONHCH_2C(Cl)=CHCH_2Cl]_2$, 71%, mp 98–100° (*Anal.* Calcd for $C_{12}H_{16}Cl_4N_2O_4$: C, 36.57; H, 4.09; N, 7.11. Found: C, 36.19; H, 4.09; N, 7.20); $CH_3OCONHC_5H_8Cl$, 82%, bp 84–86° (0.004 mm) (*Anal.* Calcd for $C_7H_{12}ClNO_2$: C, 47.33; H, 6.81; N, 7.88. Found: C, 46.84; H, 6.20; N, 7.95).

Registry No.—i-$C_3H_7OCON(Cl)CH_2C(CH_3)=C(CH_3)CH_2Cl$, 16487-91-5; $CH_3O_2CNCl_2$, 16487-46-0; i-$C_3H_6O_2CNCl_2$, 16487-47-1; $(-CH_2OCONCl_2)_2$, 16487-45-9.

Acknowledgment.—The authors wish to thank Joseph J. Clemens and Dominick S. DeCaro for their competent technical assistance. The assistance of Peter Paterson in the decoupling work is also appreciated. The elemental analyses were performed by Mr. T. J. Kielty, Jr., and his staff.

Monoadducts of Sulfenyl Chlorides and Conjugated Diolefins[1]

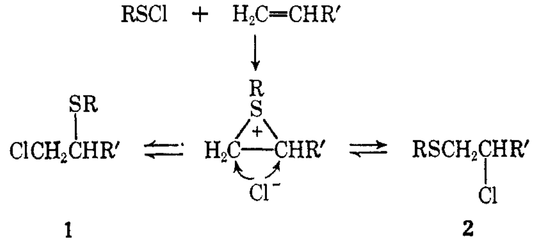
W. H. Mueller[2] and P. E. Butler[3]

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036

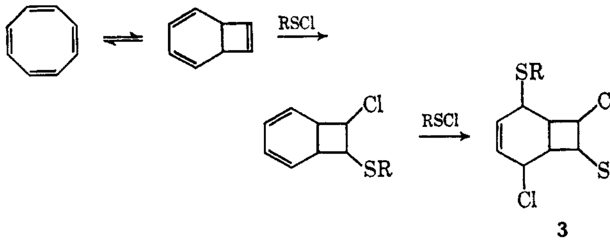
Received March 13, 1968

Methane- or benzenesulfenyl chloride afforded predominantly Markovnikov oriented 1,2 adducts with conjugated dienes under kinetic control. Strong preference for attack on the terminal double bond, *i.e.*, unsubstituted double bond, was found with chloroprene, piperylene, and 4-methyl-1,3-pentadiene. The reaction with isoprene, however, showed little selectivity, the substituted double bond being the slightly more favored reaction site. The kinetically controlled major adducts from methanesulfenyl chloride and piperylene, 4-methyl-1,4-pentadiene, or isoprene isomerized to their corresponding thermodynamically more stable 1,4 products. None of the benzenesulfenyl chloride adducts was found to isomerize. The mechanism of such additions and, in particular, the factors influencing the transition states most likely involved in the addition and subsequent rearrangement are discussed.

A mechanism involving an episulfonium ion intermediate to explain the Markovnikov[4] oriented *trans* addition of 2,4-dinitrobenzenesulfenyl chloride to olefins was first postulated by Kharasch and Buess.[5] More recently episulfonium ion intermediates have been proposed to account for the *trans* stereochemistry and *anti*-Markovnikov orientation of adducts obtained from methane- or benzenesulfenyl chloride and terminal olefins.[6] It has been found that, with these sulfenyl chlorides, ring opening of the cyclic intermediate by the chloride ion is strongly dependent on the nature of R′. When R′ is an alkyl substituent, the kinetically controlled ring opening occurs predominantly at the less sterically hindered terminal carbon giving the anti-Markovnikov products (**1**). These adducts then rearrange to the thermodynamically more stable Markovnikov products (**2**). When R′ is phenyl, however, the Markovnikov adduct (**2**) is the kinetically and thermodynamically favored isomer. Thus steric factors appeared to be quite important for the ring opening of episulfonium ions from nonconjugated olefins while the results from phenyl-substituted olefins suggested strong electronic effects in the case of conjugated olefins.



Earlier workers had tentatively proposed 1,4 addition of sulfenyl chlorides to cyclopentadiene and cyclooctatetraene.[7] The formation of diadduct **3** from cyclooctatetraene has been postulated.



---

[1] A preliminary account of part of this work has appeared: W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966).

[2] To whom inquiries should be directed.

[3] Analytical and Information Division.

[4] Structures which have the chlorine on the most substituted carbon (the least hydrogen containing carbon) have been designated "Markovnikov" oriented while the opposite isomers, the "anti-Markovnikov" adducts, bear the chlorine on the least substituted (greatest number of hydrogens) carbon atom.

[5] N. Kharasch and C. M. Buess, *J. Amer. Chem. Soc.*, **71**, 2724 (1949).

[6] W. H. Mueller and P. E. Butler, *ibid.*, **88**, 2866 (1966); **90**, 2075 1968.

[7] H. Brintzinger and H. Ellwanger, *Chem. Ber.*, **87**, 300 (1954).