to date are indicative of its potential synthetic utility for the preparation of vicinal difluorides.

Work is continuing to assess the conditions necessary for control of the stereochemistry as well as to provide additional data on vicinal F–F coupling constants in other cycloalkene adducts. The latter are quite necessary to establish empirical correlations of fluorine coupling constants to dihedral angles.

Low-temperature fluorination coupled with F^{19} nmr may prove to be a useful diagnostic tool for structure determination.

Acknowledgment.—We are grateful to Mr. Morris Howard for technical assistance, Mrs. Carolyn Haney for nmr spectra, and Mr. Robert Watkins for infrared spectra.

Nucleophilic Substitution on a Hexachloronorbornadiene

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Received August 16, 1965

Sodium methylmercaptide effects stepwise displacement of two chlorine atoms in 5-phenyl-1,2,3,4,7,7-hexachloronorbornadiene (1). Treatment of the bis-substitution product with aged Raney nickel results in selective removal of only one methylthio group. These experiments are discussed briefly in relation to the problem of nucleophilic substitutions on vinyl halides, especially in dipolar aprotic solvents.

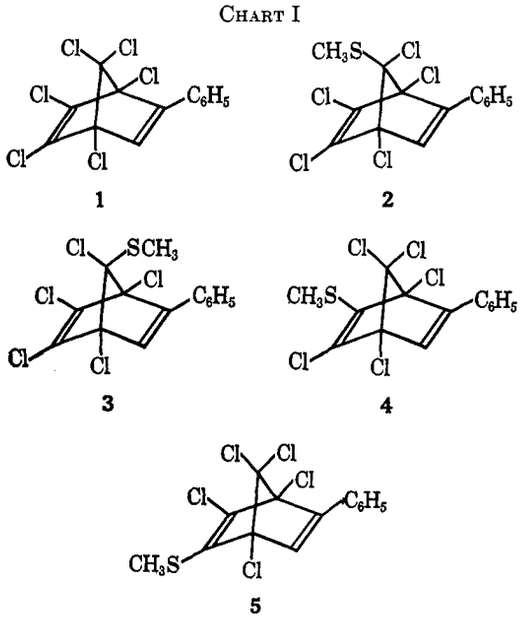
The reactions of vinyl halides with nucleophiles have been the object of considerable recent interest.[2] Truce[2a] has found that nucleophilic substitutions on *cis*-1,2-dichloroethylene by thiolates occur by an elimination-addition sequence involving chloroacetylene as an intermediate. On the other hand, an addition–elimination sequence was implicated in the transformation of vinylidene chloride into *cis*-di-*p*-tolylmercaptoethylene by *p*-toluenethiolate.[2b] We have been interested in the synthesis of norbornadienone thioketals as possible precursors of dithiocarbenes.[3] In attempts to prepare such species, we have observed facile substitution by the addition–elimination process in a *cis*-1,2-dichloroethylene which cannot undergo prior dehydrohalogenation to an acetylene.

5-phenyl-1,2,3,4,7,7-hexachloronorbornadiene (1) has been prepared by McBee[4] in 21% yield from the reaction between hexachlorocyclopentadiene and phenyl acetylene, in the absence of solvent. By operating with toluene as diluent, we have obtained 1 in 42% yield (63% based upon recovered hexachlorocyclopentadiene). Although we initially obtained this material as a viscous liquid, as did McBee,[4] it later crystallized, mp 96–98°. Its nmr spectrum consisted of singlets at τ 2.65 and 3.45, relative areas 5:1. When 1 was allowed to react with 2 equiv of sodium methylmercaptide for 8 hr at 0–25° in dimethylformamide, a new compound was isolated in good yield. Its nmr spectrum (singlets at τ 2.68, 3.53, and 7.53, relative areas 5:1:3, respectively) and microanalysis indicated substitution by a single S-methyl group.

It was clear from spectral evidence that no gross skeletal change had occurred during this substitution. The compound exhibited infrared absorption for the trisubstituted double bond at 12.38 μ and vinylic resonance in the nmr at τ 3.53; for 1 the corresponding values are 12.38 μ and τ 3.45. In a number of 7,7-dialkoxy-5-phenyl-1,2,3,4-tetrachloronorbornadienes prepared by Lemal and coworkers[3f] the trisubstituted double bond is observed in the narrow range of 12.35–12.45 μ, and vinylic resonance in the nmr region occurs between τ 3.45 and 3.65. Further evidence for retention of the 2-phenylnorbornadiene skeleton in the substitution product was provided by ultraviolet spectral data. Maxima are exhibited by 1 at 285, 254, and 223 mμ (ϵ 3300, 8920, and 11,500, respectively). 7,7-Dimethoxy-1,2,3,4-tetrachloro-5-phenylnorbornadiene[3f] has maxima at 275, 247, and 218 mμ (ϵ 2940, 9100, and 10,300, respectively). The monomethylthio-substituted product exhibits ultraviolet absorption maxima at 268 and 228 mμ (ϵ 8070 and 11,620).

Analogy with the reaction of sodium methoxide with 1[4,3a–c] would suggest substitution at the bridge to afford 2 or 3 (Chart I). In view of Truce's observations[2b] on the reaction of vinylidene chloride with

CHART I



(1) Hall Laboratory of Chemistry, Wesleyan University, Middletown, Conn. 06457.

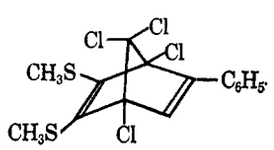
(2) (a) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Am. Chem. Soc.*, **78**, 2743 (1956); (b) W. E. Truce and M. M. Boudakian, *ibid.*, **78**, 2748 (1956); (c) W. E. Truce and R. Kassinger, *ibid.*, **80**, 1916 (1958); (d) L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *ibid.*, **87**, 1917 (1965).

(3) (a) D. M. Lemal, E. P. Gosselink, and A. Ault, *Tetrahedron Letters*, 579 (1964); (b) R. W. Hoffmann and H. Hauser, *ibid.*, 197g (1964); (c) R. W. Hoffman and H. Hauser, *Tetrahedron*, **21**, 891 (1965); (d) U. Schöllkopf and E. Wiskott, *Angew. Chem.*, **75**, 725 (1963); (e) D. M. Lemal and E. H. Banitt, *Tetrahecron Letters*, 245 (1964); (f) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, submitted for publication.

(4) E. T. McBee, J. Idol, and C. Roberts, *ibid.*, **77**, 6674 (1955).

thiolates, however, structures **4** and **5** were considered likely alternatives to **2** and **3**. The possibility that the material is a mixture of monosubstituted compounds cannot be excluded, but we consider this unlikely in view of its sharp melting behavior.

In order to effect bis substitution, **1** was treated with 5 equiv of sodium methylmercaptide for 32 hr at steam-bath temperature in dimethylformamide. After chromatography on alumina, a bis(methylthio) substitution product (but *no* mono) was isolated in fair yield. Its nmr spectrum consisted of three sharp singlets at τ 2.67, 3.59, and 7.53, relative areas 5:1:6, respectively. This material apparently also retained the phenylnorbornadiene skeleton, evidenced by characteristic absorption for the trisubstituted double bond at 12.36 μ, ultraviolet absorption at 257 and 220 mμ (ϵ 9,200 and 10,950, respectively), and close agreement of the positions of its aromatic and vinyl resonances with those of the starting material **1** and of Lemal's bicycloheptadienone ketals.[3f] Since the nmr spectrum indicated the methylthio groups to be magnetically equivalent, attention was focused on symmetrial structures **6** and **7**. (The possibility of asymmetric disubstitution will be discussed below.)



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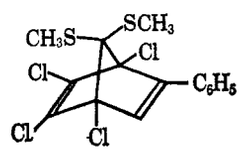

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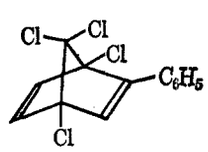
Raney nickel desulfurization was selected as the means of distinguishing between **6** and **7**. Desulfurization of **6** should yield a compound **8** exhibiting only aromatic and vinyl protons by nmr, while desulfurization of thioketal **7** should afford a product **9** showing



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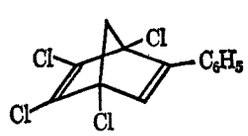

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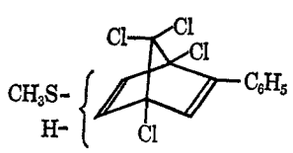
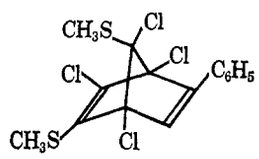


10

methylene resonance. The bis(methylthio) compound was refluxed 4 hr with Raney nickel in acetone. Chromatography on alumina afforded a new substance in good yield. This material had, even after chromatography, a wide melting range, 111–132°, but repeated recrystallization afforded a homogeneous substance, mp 135.8–137.2°, melting point unchanged by further recrystallization. Surprisingly, this substance proved to be neither **8** nor **9**. Its nmr spectrum consisted of singlets at τ 2.70, 3.47, 4.08, and 7.77, with relative areas 5:1:1:3. This corresponds to removal of one methylthio group and appearance of a new vinyl proton. Infrared absorption at 12.36 μ, the nmr absorption at τ 3.47, and the ultraviolet spectrum of this material, consisting of maxima at 257 and 214 mμ (ϵ 5010 and 6760, respectively), evidenced once again the fact that skeletal rearrangement had not occurred during the desulfurization.

This rather uncommon and surprising selective hydrogenolysis can be explained after the fact. The nickel used in the reaction was old, and had been further deactivated by several hours of reflux in acetone, in order to forestall reduction of the olefinic linkages. On this account its reactivity was probably sufficiently marginal that it could differentiate between the two S-methyl groups. We suspect that hydrogenolysis is not completely selective because of the wide melting range of the crude material. On the strength of the assumption that both methylthio groups were initially equivalent, structure **10** for the desulfurization product should be indicated, and structure **6** for the bis-substitution product confirmed, but in fact there is reason to question this assumption.

The possibility remains that the sharp S-methyl singlet in the nmr spectrum of the disubstituted product is due to accidental coincidence of S-methyl protons in an asymmetric adduct such as **11** or one of its three



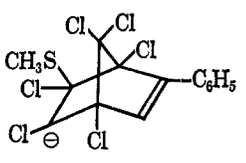
11

position isomers. This explanation would be compatible with the apparently different ease of reduction of the two methylthio groups by Raney nickel. It is difficult to see why a vinyl methylthio group should be reduced more easily than one at the bridge but, since previous hydrogenolyses of polythio compounds have generally resulted in complete reduction,[5] no information is available on this point. We cannot specify the position of the second S-methyl group in the bis-substituted compound, but the desulfurization experiment does clearly indicate that at least one S-methyl group was introduced at a vinylic position. Because of a transient red-brown color observed during the addition of $NaSCH_3$ to **1**, we believe that the first S-methyl group was introduced at the double bond, since this color would be consistent with the intermediate formation of a carbanion such as **12** or **13** in the addition–elimination process.

It is clear from our findings that sodium methylmercaptide can effect substitution of the chlorine atoms in a *cis*-dichloroethylene by the addition–elimination mechanism, when acetylene formation is not allowed. This is not completely surprising; we can make a few additional observations on these reactions, however, which may be of interest with respect to the problem of nucleophilic substitutions at the double bond carried out in a dipolar aprotic solvent such as dimethylformamide. The introduction of a methylthio group at room temperature or below in contrast with much more vigorous conditions necessary for substitutions on vinylidene chloride in ethanol[2b] would appear to attest to the superior nucleophilicity of thiolate anion in dimethylformamide. This is presumably due to absence

(5) G. R. Pettit and E. E. vanTamelen, *Org. Reactions*, **12**, 356 (1962).

of hydrogen bonding to the solvent, which greatly diminishes the reactivity of the anion. The phenomenon of enhanced nucleophilicity in dipolar aprotic solvents has been well substantiated in recent years.[6] It is also interesting to note that we have not isolated any product corresponding to 1,2 addition of thiol to the double bond. The initially formed carbanion, *i.e.*, **12** or **13**, cannot be protonated, and hence must quickly undergo β elimination of chloride.



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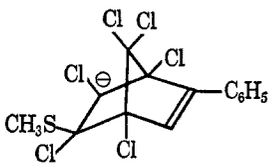

13

We are unable at this time to decide between structures **4** and **5** for the monosubstitution product. Steric hindrance between chlorine and phenyl in carbanion **12** might be great enough to render this mode of addition, leading to **4**, unlikely, but it is difficult to assess the importance of this effect.

Experimental Section[7,8]

5-Phenyl-1,2,3,4,7,7-hexachloronorbornadiene (1).—Phenylacetylene (51.06 g, 0.50 mole) and hexachlorocyclopentadiene (136.40 g, 0.50 mole) were dissolved in 200 ml of toluene, and the solution refluxed for 72 hr. After the toluene had been removed at the rotary evaporator, the dark brown residue was distilled at reduced pressure. The first fraction was unreacted hexachlorocyclopentadiene, 28.7 g, bp 100–102° (1.5 mm). The second fraction was the desired adduct (1), 78.7 g (42% yield, or 63% based upon recovered hexachlorocyclopentadiene), bp 144–147 (1.5 mm) as a colorless viscous oil (lit.[4] bp 150–152° at 2 mm, 21% yield). A small portion of this oil was triturated with pentane at −78°, whereupon it crystallized. When the remainder of the adduct was seeded with these crystals, it set to a solid mass, mp 88–92° (Hershberg). After one recrystallization from heptane, the adduct was obtained as rods, mp 96–98°, sufficiently pure for further work. The nmr spectrum (CCl_4) consisted of singlets at τ 2.65 and 3.45, relative areas 5:1, respectively. The ultraviolet spectrum was measured in 95% ethanol: λ_{max} 285 mμ (ϵ 3300), 254 mμ (ϵ 8920), and 223 mμ (ϵ 11,500).

5-Phenyl-2- (or 3-) methylthio-1,3,4,7,7- (or 1,2,4,7,7-) pentachloronorbornadiene (4 or 5).—The hexachloride (1) (4.00 g, 0.0107 mole) was dissolved in 150 ml of dimethylformamide and chilled to 0°. Sodium methylmercaptide (1.55 g, 0.0221 mole), dissolved in 125 ml of dimethylformamide, was added over a 10-min interval as the solution was stirred magnetically. After 4 days, the light brown solution was poured into 1200 ml of water and extracted with carbon tetrachloride. The carbon tetrachloride extracts were washed with water and dried over sodium sulfate. The solvent was taken off at the rotary evaporator, leaving a brown oil. This was chromatographed on alumina. Elution with pentane afforded a colorless oil which crystallized upon trituration with pentane at −78° to afford the mono(methylthio)-substituted compound (**4** or **5**), 2.61 g (61%), mp 62–64° (block). An analytical sample, mp 63–64°, was obtained after seven recrystallizations from heptane.

Anal. Calcd for $C_{14}H_9Cl_5S$: C, 43.50; H, 2.35; Cl, 45.86; S, 8.29. Found: C, 43.42; H, 2.07; Cl, 45.94; S, 8.44.

The nmr spectrum (CCl_4) consisted of singlets at τ 2.68, 3.53, and 7.53, relative areas 5:1:3, respectively. The ultraviolet spectrum was measured in 95% ethanol: λ_{max} 268 mμ (ϵ 8070) and 228 mμ (ϵ 11,620).

5-Phenyl-2,3?-bis(methylthio)-1,4,7,7-tetrachloronorbornadiene.—The hexachloride (1) (4.00 g, 0.0107 mole) was dissolved in 125 ml of dimethylformamide at room temperature. Sodium methylmercaptide (4.00 g, 0.0570 mole) was dissolved in 125 ml of dimethylformamide and added over a 15-min interval to the first solution. The dark brown solution was heated on the steam bath for 32 hr, with occasional swirling. At the end of this time it was diluted with 1400 ml of water and extracted with chloroform. The chloroform extracts were washed with water and dried over sodium sulfate. Evaporation of the chloroform left a black oil; this was taken up in a small amount of benzene and chromatographed on alumina. Elution with pentane afforded a colorless oil, the bis(methylthio)-substituted compound, which crystallized upon trituration with pentane at −78° [1.19 g, 28%; mp 58–60° (block)]. An analytical sample, mp 60.5–61.0°, was obtained after five recrystallizations from heptane.

Anal. Calcd for $C_{15}H_{12}Cl_4S_2$: C, 45.24; H, 3.04; Cl, 35.62; S, 16.10. Found: C, 45.23; H, 3.02; Cl, 35.80; S, 16.20.

The ultraviolet spectrum was measured in 95% ethanol: λ_{max} 257 mμ (ϵ 9200) and 220 mμ (ϵ 10,950). For nmr spectrum, see discussion.

5-Phenyl-2- (or 7-) methylthio-1,4,7,7-tetrachloronorbornadiene (10).—Raney nickel, W-2 grade, 5 months old, 4.0 g, was washed several times with acetone and then deactivated for 2 hr in 20 ml of refluxing acetone. The bis(methylthio) compound (0.196 g, 0.000493 mole) was dissolved in 10 ml of acetone and added to the Raney nickel suspension. The mixture was refluxed 4 hr, allowed to cool, and filtered through a Filter-Cel pad. The pad was then washed with 30 ml of acetone. The filtrate was evaporated, the residual oil was taken up in ether, and the ether was dried over sodium sulfate. Distillation of the ether left a colorless oil, the half-desulfurized compound (**10**) which crystallized upon trituration with pentane at −78°, mp 81–111°. This was taken up in benzene and chromatographed over alumina. Elution with 4:1 pentane–benzene afforded the compound in a purer state, 0.125 g (72%), mp 111–132°. An analytical sample, mp 135.8–137.2°, was obtained after four recrystallizations from heptane.

Anal. Calcd for $C_{14}H_{10}Cl_4S$: C, 47.75; H, 2.86; S, 9.11. Found: C, 48.09; H, 3.11; S, 9.15.

The ultraviolet spectrum (95% ethanol) exhibited these features: λ_{max} 257 mμ (ϵ 5010) and 214 mμ (ϵ 6760). For nmr spectrum, see discussion.

Acknowledgment.—The author is deeply grateful to Professor David M. Lemal for advice and encouragement and for the use of experimental facilities, and to the Research Corporation for financial support.

(6) (a) J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961); (b) R. Fuchs and A. Nisbet, *ibid.*, **81**, 2371 (1959); (c) D. J. Cram, B. Rickborn, and G. R. Knox, *ibid.*, **82**, 6412 (1960).

(7) Except where noted, melting points were determined on a Kofler micro hot stage and are corrected. Nmr spectra were measured at 60 Mc/sec on a Varian Associates A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane as internal standard. Microanalyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(8) Sodium methylmercaptide was prepared from sodium methoxide and methanethiol in methanol. It was dried in a desiccator and washed with ether before use.