not be obtained for these materials even when they were heated 200° in the inlet system of the mass spectrometer.

Registry No.—**4**, 7688-03-1; **5**, 28861-05-4; **6**, 28861-04-3; **8**, 751-37-1; **14**, 2762-95-0; diphenylacetylene, 501-65-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; benzyne, 462-80-6.

Acknowledgment.—We thank P. Maruca and L. Roseman for assistance in the laboratory and Drs. J. Grunwell and R. Schaeffer for valuable discussions. We also gratefully acknowledge The Research Corporation for partial financial support of this research.

Steric Deshielding in Nonrigid Systems. II.[1] The Preparation and Nuclear Magnetic Resonance Spectra of the Hexachlorocyclopentadiene Adducts of 1,3-Alkadienes

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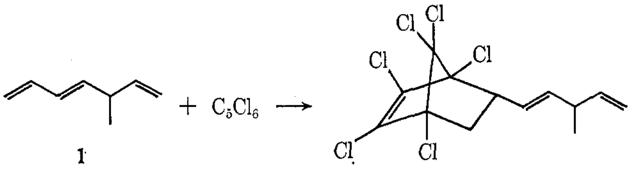
Hexachlorocyclopentadiene is remarkably regiospecific in its reaction with olefins, reacting more readily with terminal than with internal olefins and more readily with conjugated than with isolated olefins. A steric deshielding mechanism is invoked to account for the difference in the nmr spectra of the adducts of *cis*- and *trans*-1,3-alkadienes. The mechanism is extended to include the deshielding of allylic protons by *cis*-alkyl substituents in rigid and nonrigid systems.

Hexachlorocyclopentadiene (C_5Cl_6) is a well-known and very reactive diene in Diels–Alder chemistry. Its reactions have been well studied and have led to the synthesis of many interesting and useful hexachlorobicyclo[2.2.1]heptenes.[3] It reacts readily under mild conditions even with "unactivated" olefins but differs from the typical Diels–Alder diene in that it has been shown to have an "inverse electron demand;" that is, it reacts preferentially with electron-rich dienes and not at all with tetracyanoethylene.[4] This characteristic may be associated with the concept of "spiroconjugation" as described by Simmons and Fukunaga.[5]

We have studied the reaction of C_5Cl_6 with various 1,3-alkadienes and have found that the reaction is remarkably regiospecific. Hexachlorocyclopentadiene reacts more readily with a conjugated than with an isolated olefin and more readily with a terminal than with an internal olefin giving good yields of single products. Moreover, we have found that a diene capable of assuming a cisoid geometry is more reactive than one for which this conformation is disfavored.[6] In addition, the nmr spectra of the products have proven interesting and very useful in determining the geometry of the double bond adjacent to the bicyclic moiety.

Regiospecificity.—Reaction of 5-methyl-1-*trans*-3,6-heptatriene (**1**) with C_5Cl_6 for 6 hr at 90° gives a single product (**13**) in 84% yield. The ultraviolet spectrum of **13** shows no absorption characteristic of a conjugated diene [for **1**, λ_{max} 227 nm (log ϵ 4.40)].[7] Thus, the reaction occurs at one of the conjugated double bonds. The appearance of five olefinic protons in the nmr spectrum shows that it is the terminal, conjugated double bond that reacts. Examination of the spectra of the products derived from 1,3,7-octatriene (**2**) and 1,3,6-octatriene (**3**) showed that here, also, reaction occurs exclusively at the terminal, conjugated double bond. The generality of this regiospecificity was shown by examination of a series of 1,3-alkadienes (see Table I). With only one exception, the reaction occurs exclusively at the terminal position. In the case of *cis*-1,3-pentadiene, about 7% of the alternate product is apparent from the presence of a doublet (J = 7.0 Hz) at τ 9.04 in the nmr spectrum.



1

13

Specificity in the reaction of C_5Cl_6 with monoolefins was also demonstrated by treating *trans*-1,4,9-decatriene with an excess of the halocarbon. The only product isolated (~60% yield of recrystallized material) exhibits a 1.8-proton multiplet at τ 4.5–4.8 and analyzes correctly for the 2:1 product. Therefore, reaction occurs specifically to give the terminal diadduct. A brief study of *cis*-1,5,9-decatriene indicated that here, also, reaction occurs exclusively at the terminal sites.

Considering the "inverse electron demand" of C_5Cl_6, one would expect conjugation to decrease reactivity and, furthermore, one would expect alkyl substitution to increase reactivity. In both instances, the reverse has been found to be true. Although electronic effects are undoubtedly important in this reaction, they are handily outweighted by steric factors.[8] In the case of conjugation, the decrease in electron density caused

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[1] Part I: C. G. Cárdenas, *Tetrahedron Lett.*, 4013 (1969).

[2] Address correspondence to author at Glidden-Durkee.

[3] H. E. Ungnade and E. T. McBee, *Chem. Rev.*, **58**, 249 (1958).

[4] J. Sauer and H. Wiest, *Angew. Chem. Int. Ed. Engl.*, **1**, 269 (1962).

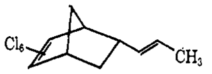
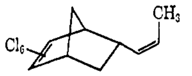
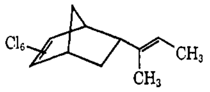
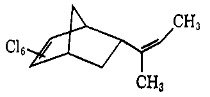
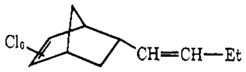
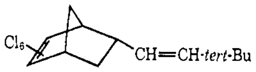
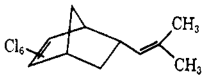
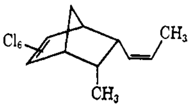
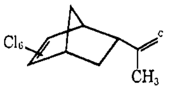
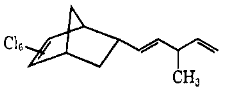
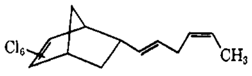
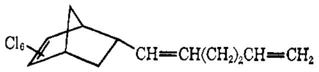
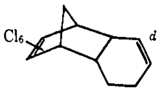
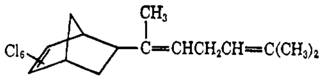
[5] H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

[6] The role of secondary orbital interactions when reaction occurs adjacent to an unsaturated site has been discussed previously: C. G. Cárdenas, *Chem. Commun.*, 134 (1970).

[7] S. Tanaka, K. Mabuchi, and N. Shimazaki, *J. Org. Chem.*, **29**, 1626 (1964).

[8] (a) W.-H. Chang, *J. Chem. Soc.*, 2305 (1965); (b) K. L. Williamson, Y.-F. Li Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969).

TABLE I
STRUCTURE AND PROPERTIES OF C_5Cl_6 ADDUCTS

Starting material	Product	Compd	Yield, %	Bp, °C (mm)
trans-1,3-Pentadiene		**4**	88	87 (0.05)
cis-1,3-Pentadiene		**5**	80	94 (0.09)
trans-3-Methyl-1,3-pentadiene		**6**	80	94 (0.03)
cis-3-Methyl-1,3-pentadiene		**7**	80	93 (0.03)
1,3-Hexadiene[a]		**8**	80	97 (0.03)
5,5-Dimethyl-1,3-hexadiene[b]		**9**	82	97–99 (0.03)
4-Methyl-1,3-pentadiene		**10**	83	98 (0.09)
cis,*cis*-2,4-Hexadiene		**11**	62	92 (0.04)
Isoprene		**12**	74	84 (0.03)
5-Methyl-1-*trans*-3,6-heptatriene		**13**	84	104 (0.09)
1-*trans*-3-*cis*-6-Octatriene		**14**	46	111 (0.04)
1,3,7-Octatriene		**15**	69	104 (0.02)
1,3-Cyclohexadiene		**16**	74	*e*
β-Ocimene[f]		**17**	78	

[a] Consisting of 96.4% trans and 3.6% cis. [b] Consisting of 94.4% trans and 5.6% cis. [c] Velsicol Corp., British Patent 614,931 (1948); *Chem. Abstr.*, **43**, 4693*e* (1949). [d] R. Reimenschneider and B. E. Grabity, *Monatsh. Chem.*, **91**, 22 (1960); *Chem. Abstr.*, **54**, 22527*h* (1960). [e] Solid, mp 113–115°. [f] Consisting of 85.9% trans and 14.1% cis.

by an adjacent double bond is outweighed by the increased polarizability of the system which can better stabilize[8b] a polar transition state.[6,9]

Nmr Spectra.—Table II contains data describing the nmr spectra of some of the C_5Cl_6 adducts prepared in this study. The data for the adducts of *cis*-1,3-hexadiene, *cis*-5,5-dimethyl-1,3-hexadiene, and *cis*-β-ocimene are not complete since the measurements were made on mixtures enriched in the trans isomer. The chemical shifts and coupling constants were obtained by inspection of spectra obtained either on a Varian A-60 or a Hitachi R-20 spectrometer.

It is well known that in C_5Cl_6 derivatives as well as other bicyclo [2.2.1] systems exo protons appear at slightly lower field than their endo counterparts. The geminal coupling constant ($J_{n_1\text{-}x_1}$) should be of the order of 13 Hz[10–16] and the vicinal coupling con-

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(9) After this paper was submitted for publication, a report appeared describing analogous but much less pronounced selectivity for the addition of dichlorocarbene, a less bulky electrophile, to similar systems. E. W. Duck, J. M. Locke, and S. R. Wallis, *J. Chem. Soc. C*, 2000 (1970).

(10) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963).

(11) K. L. Williamson, N. C. Jacobus, and K. T. Soucy, *ibid.*, **86**, 4021 (1964).

(12) D. F. O'Brian and J. W. Gates, Jr., *J. Org. Chem.*, **30**, 2593 (1965).

(13) M. M. Martin and R. A. Koster, *ibid.*, **33**, 3428 (1968).

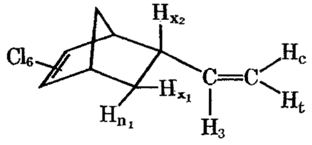
(14) R. H. Cox and S. L. Smith, *J. Phys. Chem.*, **71**, 1809 (1967).

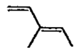
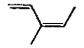
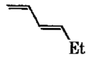
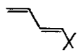
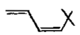
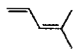
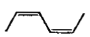
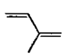
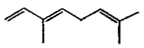
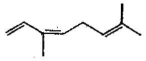
(15) R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967).

(16) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967.

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF C_5Cl_6 ADDUCTS



		Chemical shifts, τ						Coupling constants, Hz						
Starting material	Product	H_{n1}	H_{x1}	H_{x2}	H_3	H_c	H_t	H_{n1}–H_{x1}	H_{n1}–H_{x2}	H_{x1}–H_{x2}	H_{x2}–H_3	H_3–H_t	H_3–H_c	H_c–H_t
	4	8.15	7.33	6.71	5.00	4.33	–CH_3 (8.31)	12.5	4.0	8.5	8.5		15.5	H_c–CH_3 6.0
	5	8.25	7.23	6.22	5.10	–CH_3 (8.27)	4.27	12.5	4.0	8.5	~9	~9	H_3–CH_3 1.5	H_t–CH_3 7.0
	6	7.87	7.40	6.64	–CH_3 (8.33)	4.5–4.9	–CH_3 (8.38)	12.5	5.0	8.5				H_c–CH_3 6.0
	7	7.84	7.41	5.95	–CH_3 (8.47)	–CH_3 (8.26)	4.38	13.0	5.0	8.5				H_t–CH_3 7
	*trans*-**8**	8.11	7.21	6.68	5.00	4.30	–Et (7.7–8.3, 9.02)	12.0	4.0	8.5	8.5		15.5	H_c–CH_2 6.0 CH_2–CH_3 7.0
	*cis*-**8**			~6.1										
	*trans*-**9**	8.06	7.32	6.70	5.10	4.30	*tert*-Bu (9.00)	12.0	4.0	8.0	8.0		15.5	
	*cis*-**9**			~5.9										
	10	8.2	7.27	6.35	5.35	–CH_3 (8.2)	–CH_3 (8.2)	12.0	4.0	9.5	9.5			
	11	–CH_3 (9.08)	7.00	6.22	5.02	–CH_3 (8.29)	4.23	H_{x1}–CH_3 7.0		10.0	10.0	10.0	H_3–CH_3 1.5	H_t–CH_3 7.0
	12	7.87	7.36	6.72	–CH_3 8.15	4.9–5.4	4.9–5.4	13.0	4.5	9.0				
	*trans*-**17**	7.86	7.40	6.63[a]	–CH_3 8.1–8.6	4.7–5.2 (H_4, H_6)	–CH_2– 7.3	12.5	4.5	8.3				H_c–CH_2 ~7
	*cis*-**17**			5.94[a]										

[a] See Figure 1.

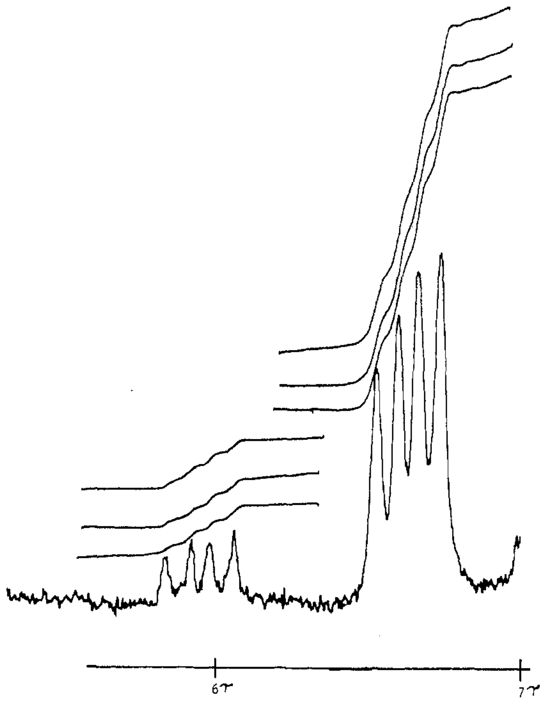
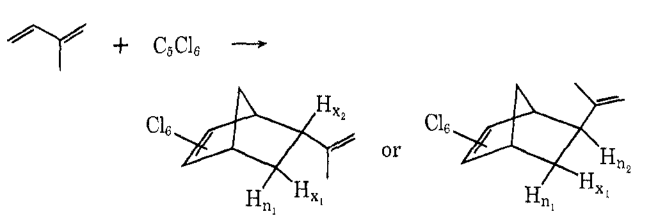


Figure 1.—The 60-MHz nmr signals assigned to H_{x_2} in the mixture of C_5Cl_6 adducts (**17**) of *β*-ocimene.

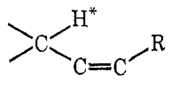
stants my be estimated from the Karplus curve[17] as $J_{x_1\text{-}x_2} \approx 8$ Hz and $J_{n_1\text{-}x_2} \approx 3$ Hz for an endo adduct and $J_{x_1\text{-}n_2} \approx 3$ Hz and $J_{n_1\text{-}n_2} \approx 8$ Hz for an exo isomer. Thus, for the isoprene adduct (*endo*-**12** or *exo*-**12**), for example, we have an ABC system and can assign the chemical shifts and coupling constants by comparison with the predicted values. Examination of the spectrum provides the chemical shifts as given in Table II and $J_{n_1\text{-}x_1} = 13.0$, $J_{n_1\text{-vic}} = 4.5$, and $J_{x_1\text{-vic}} = 9.0$ Hz, in agreement with the expected endo structure of the adduct *endo*-**12**. Similar arguments were used to assign analogous structure to the other adducts.



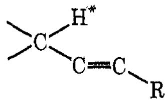
endo-**12** *exo*-**12**

The proton labeled as H_{x_2} (Table II) appears as a pair of doublets in cases such as **12** where H_3 = alkyl. When H_3 = H, however, $J_{x_2\text{-}H_3} \approx J_{x_1\text{-}x_2} \approx 9$ Hz and H_{x_2} appears as a pair of triplets. Of importance is the dependence of the chemical shift of H_{x_2} on the presence of an alkyl group in place of H_{cis}. *Thus, when adjacent to a trans or terminal olefin, H_{x_2} appears at τ ~6.7, whereas it is shifted to τ ~6.1 when adjacent to a cis or geminally disubstituted olefin.*

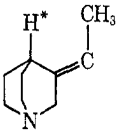
Analogous shifts have been reported for allylic methines in general (**18**, $\Delta\tau \approx 0.5$ ppm)[18-20] for the 3-ethylidene-1-azabicyclo[2.2.2]octanes (**19**, $\Delta\tau = 0.42$ ppm)[21] and for conjugated dienes (**20**, $\Delta\tau \approx 0.5$ ppm).[1] In seeking an explanation for this effect we have considered various factors.



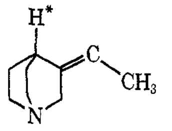
cis-**18**



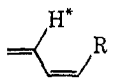
trans-**18**



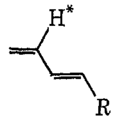
cis-**19**



trans-**19**

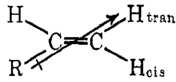


cis-**20**



trans-**20**

Group Dipole Effect.—The observation that in 1-alkenes H_{trans} is shielded with respect to H_{cis} (see **21**) has been attributed to the presence of a permanent dipole as drawn.[22] The effect is small, however, causing a chemical shift difference of <0.1 ppm for R = Me, Et, or *n*Bu in **21**. Accordingly H* in *trans*-**18** should experience a similar but diminished shielding effect with respect to H* in *cis*-**18**. The observed magnitude of the chemical shift difference, therefore, cannot be accounted for by this factor. In addition, it has been pointed out that allylic methylenes are affected much less ($\Delta\tau \approx 0.1$ ppm) and allylic methyls essentially not at all.[18,23] A group dipole effect would be expected to cause similar, if not greater, shifts as alkyl substitution on the carbon bearing H* is decreased.



21

Carbon–Carbon Double Bond Anisotropy.—The anisotropic effect of a carbon–carbon double bond has been the subject of some discussion.[25] Its applicability to the point in question[20] may be ruled out by a consideration of isomer pairs in which the position of the affected proton relative to the double bond remains unchanged. For example, in 3,5-cholestadiene introduction of a methyl group at C-6 serves to change the chemical shift of H-4 from τ 4.22 to 3.58.[1] Here H-4 retains

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[17] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968), and references cited therein; and A. P. Marchand, N. W. Marchand, and A. L. Segre, *Tetrahedron Lett.*, 5207 (1970).

[18] F. C. Stehling and K. W. Bartz, *Anal. Chem.*, **38**, 1467 (1966).

[19] D. J. Frost and J. P. Ward, *Tetrahedron Lett.*, 3779 (1968).

[20] R. B. Bates, A. D. Brewer, B. R. Knights, and J. W. Rowe, *ibid.*, 6163 (1968).

[21] J. C. Nouls, G. Van Binst, and R. H. Martin, *ibid.*, 4065 (1967).

[22] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, **83**, 231 (1961).

[23] In fact, the chemical shift difference for allylic methyls is reversed, a methyl cis to an alkyl group appearing at higher field than its counterpart.[18,24]

[24] R. Zurfluh, E. N. Wall, J. B. Siddall, and J. A. Edwards, *J. Amer. Chem. Soc.*, **90**, 6224 (1968); W. S. Johnson, A. van der Gen, and J. J. Swoboda, *ibid.*, **89**, 170 (1967); and R. B. Bates and D. M. Gale, *ibid.*, **82**, 5749 (1960).

[25] A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 54 (1965); J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**, 2357 (1967).

the same position with respect to the double bonds but is still deshielded τ 0.64. Further examples of analogous conjugated systems have been cited.[1] A monoolefinic isomer pair which may also be considered is the 3-ethylidene-1-azabicyclo[2.2.2]octane pair (**19**). These isomers have been characterized by means of the nuclear Overhauser effect.[21,26] The bridgehead proton (H*) maintains its position in space and is shifted downfield τ 0.42 in the cis isomer.

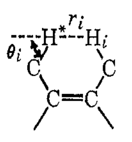
Carbon–Carbon Single Bond Anisotropy.—Having shown that the observed effect is not caused by the double bond, we may conclude that the deshielding effect is caused directly by the *cis*-alkyl group. For a proton in a rigid system as in **19**, the effect of the carbon–methyl single bond may be calculated using McConnell's relationship[27] along with the anisotropy terms provided by ApSimon, *et al.*[28] The net effect predicted is one of *shielding* in the cis isomer relative to the trans. Thus, it is unlikely that bond anisotropy is a cause of the observed effect.

Steric Deshielding.—An elegant discussion of the magnetic deshielding experienced by a spatially crowded hydrogen in a rigid system has been presented recently by Cheney.[29] Examples of systems experiencing this effect have been reviewed[29,30] and include various cage compounds and aromatics. Cheney has provided the empirical relation

$$\delta_s^{H^*} = -105 \sum_i \cos\theta \exp(-2.671 r_i)$$

wherein the steric shift ($\delta_s^{H^*}$) of the proton in question (H*) is related to the proximity (r_i) of the interacting nucleus (H_i) and the angel (θ_i) between the extension of the H_i–H* internuclear line and the H*–C bond.[29]

Although the nonrigidity of the compounds reported herein prevents the facile calculation of the expected steric shift, an estimate of a maximum shift of 0.5–0.6 ppm for $R_{cis} = CH_3$ can be made by considering only the most affected rotamer, *i.e.*, the rotamer having H* and H_i in the same plane and in closest proximity (see **22**). The magnitude of the observed shift will be affected by various factors, the more pertinent of which bear mentioning.



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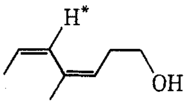
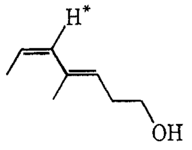
The size and nature of the *cis*-alkyl group will obviously affect the degree of deshielding. For example, a *cis-tert*-butyl group compared to a methyl group will provide significantly different values of both r_i and θ_i. Thus, the C_5Cl_6 adducts of the 5,5-dimethyl-1,3-hexadienes (Table II) show a larger deshielding effect on H* (H_{x_2}) than those of the 1,3-pentadienes (∼0.8 *vs.* 0.49 ppm).

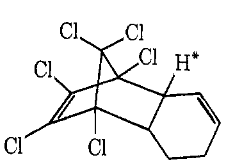
The importance of the distribution of rotamers should not be minimized. In a previous communication[1] we discussed a *cis*-alkyl steric shift in conjugated dienes (see **20**). The observed chemical shift difference for the isomer pairs considered ranges from 0.33 to 0.66 ppm. The one exception found was compound **23** which shows no effect. Examination of the uv spectrum of *cis*-**23**, however, showed that no deshielding effect should be expected, since the low extinction coefficient (5850 *vs.* >17,000 for other similar dienes)[1] indicated a low concentration of planar rotamers. The C_5Cl_6 adduct **16** of 1,3-cyclohexadiene provides another example of a proton adjacent to a cis double bond which is not deshielded (τ_{H^*} = 6.5–7.0). Here, the *cis*-alkyl group, being part of a semirigid ring, cannot assume a deshielding position and no effect should be anticipated. In nonrigid molecules, the presence of alkyl groups on the carbon bearing H* (see **22**) serves to increase the H*–H_i interaction. Thus, the decrease in deshielding (*vide supra*) observed by Stehling and Bartz[18] for the series methine, methylene, and methyl is to be expected.



cis-**23**



trans-**23**



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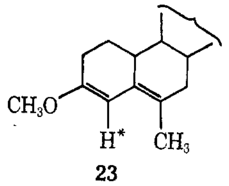
Since the mechanism of steric deshielding involves a van der Waals repulsion and a decrease in electron density at the deshielded site, substituents which can affect the charge distribution will be expected to alter the degree of observed deshielding. Thus, one finds that H* in **23** is deshielded by only 0.15 ppm when compared to H* in **24**.[1] The electron-donating effect of the methoxy substituent effectively reduces the expected electron drainage in H*. An analogous set of compounds without the methoxy substituent exhibit a deshielding effect of 0.64 ppm.[1]



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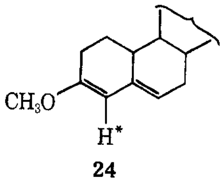

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Thus, we believe that the above cases represent examples of nonrigid molecules in which a spatially crowded proton is deshielded. The reliability of this effect is such that it may be employed as a tool in the determination of stereoisomerism. A family of compounds which exemplify its utility is the acyclic dimers of butadiene.

5-Methyl-1,3,6-heptatriene (1).—Infrared methods are often found to be unreliable for the determination of stereoisomerism in 1,3-alkadienes.[31] In the present case the carbon–hydrogen out-of-plane deformation

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[26] F. A. L. Anet and A. J. R. Brown, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

[27] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

[28] J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**, 2339 (1967).

[29] B. V. Cheney, *J. Amer. Chem. Soc.*, **90**, 5386 (1968).

[30] J. G. Lindberg and A. G. Pinkus, *J. Magn. Resonance*, **1**, 652 (1969).

[31] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., p 46.

band for the trans olefin is shifted to higher frequency and is masked by the 990-cm^{-1} vinyl band. However, examination of the nmr spectrum of its C_5Cl_6 adduct **13** readily classifies **1** (as obtained from Monomer-Polymer Laboratories) as the trans isomer.

1,3,7-Octatriene (**2**).—Metal-catalyzed syntheses of 1,3,7-octatriene have been reported recently by Smutny[32] and by Takahashi.[33] These authors do not comment on the stereoisomerism of the triene although Butler and Brooks have reported syntheses of both isomers.[34] Examination of the spectrum of 1,3,7-octatriene provided by Smutny and Chung[32b] permits one to estimate an approximately equimolar distribution of cis and trans isomers.[1] Verification is obtained by treatment of the mixture with C_5Cl_6. The nmr spectrum of the crude product mixture exhibits six-line multiplets centered at τ 6.22 (H_{x_2} in the cis isomer) and at τ 6.63 (H_{x_2} in the trans isomer) in a ratio of 4:6.

1,3,6-Octatriene (**3**).—Various isomers of **3** are obtainable from butadiene depending upon the catalyst employed.[35] However, the nature of the internal double bond has never been rigorously defined and the possibility of 1,4,6-octatriene as an alternate structure has not been excluded. Reaction with C_5Cl_6 shows that the material provided by the Aldrich Chemical Co. consists solely of 1-*trans*-3-*cis*-6-octatriene (H_{x_2} = τ 6.67). On the other hand, dimerization of butadiene in the presence of a zero valent nickel complex in a hydroxylic solvent provides a mixture where the 1,3,6-octatriene fraction consists of two isomers different from the one described above. Preparation of the C_5Cl_6 adducts shows that the mixture consists of 1-*trans*-3-*trans*-6-octatriene and 1-*cis*-3,6-octatriene (H_{x_2} = τ 6.68 and 6.26, respectively).[36]

Experimental Section

All boiling points and melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer. Molecular weight determinations were made by vapor phase osmometry. Nmr measurements were made on a Varian A-60 or a Hitachi R-20 spectrometer.

The C_5Cl_6 adducts were prepared by stirring a solution (1:1) of the olefin and C_5Cl_6 under nitrogen in a glass-walled pressure vessel. Reactions were carried out at ~90° for 3-20 hr. The pure adduct was obtained by distillation or, in the case of **16**, recrystallization from CH_2Cl_2–EtOH. Molecular weight and elemental analyses of the adducts are listed in Table III. All C_5Cl_6 adducts studied exhibit a very strong single infrared band at ~6.20 μ in contrast to the bands at 6.24 and 6.36 μ[3] of pure C_5Cl_6. Descriptions of the nmr spectra not found in Table II are listed below and in Tables IV and V.

1,3-Cyclohexadiene Adduct (**16**).—The nmr spectrum consists of broad multiplets at τ 3.6–4.4, 6.5–7.2, and 7.7–8.8 in a ratio of 1.0:1.0:2.0.

***trans*-1,4,9-Decatriene Adduct.**—Reaction of an equimolar solution of the triene and C_5Cl_6 for 21 hr at 90° provided an 81% conversion to a mixture of mono- and diadducts in 95% yield. The nmr spectrum of the crude product after removal of starting materials showed 3.9 olefinic protons, which, coupled with a molecular weight determination of 500 (calculated for monoadduct = 409, for diadduct = 682), suggests a 2:1 mixture of the monoadduct and the diadduct with all addition taking place at the terminal sites.

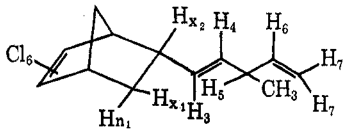
Table III

Analytical Data on C_5Cl_6 Adducts

Compd	Mol wt Calcd	Mol wt Found	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
4	341	340	35.2	34.9	2.4	2.5
5	341	360	35.2	35.1	2.4	2.3
6	355	357	37.2	37.2	2.8	2.8
7	355	350	37.2	37.1	2.8	2.8
8	355	351	37.2	37.1	2.8	2.9
9	383	382	40.8	40.7	3.7	3.6
10	355	358	37.2	36.6	2.8	2.8
11	355	357	37.2	36.9	2.8	2.9
13	381	390	41.0	41.0	3.2	3.2
14	381	381	41.0	41.3	3.2	3.3
15	381	382	41.0	40.7	3.2	3.3
16	353	356	37.4	37.7	2.3	2.3
17	409	411	44.0	44.2	3.9	3.9

Table IV

Nmr Data on the C_5Cl_6 Adduct of 5-Methyl-1-*trans*-3,6-heptatriene



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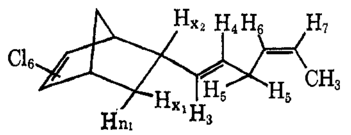
τ	Protons	Multiplicity[a]	Assignment	Coupling constants, Hz
4.0–4.6	2.1	m	H_4,H_6	H_{n_1}–H_{x_1} 12.5
4.8–5.3	2.9	m	H_3,H_7	H_{n_1}–H_{x_2}, 4.0
6.67	1.0	dt	H_{x_2}	H_{x_1}–H_{x_2}, 9.0
7.31	2.1	dd	H_{x_1}	H_{x_2}–H_3 9.0
7.2		s	H_5	H_4–H_5, ~7
8.08	1.0	dd	H_{n_1}	H_5–CH_3, 7.0
8.92	2.9	d	$-CH_3$	H_5–H_6, ~7

[a] d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, s = sextet.

Table V

Nmr Data on the C_5Cl_6 Adduct of 1-*trans*-3-*cis*-6-Octatriene[a]



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τ	Protons	Multiplicity[b]	Assignment	Coupling constants, Hz
4.1–5.3	4.1	m	H_3,H_4,H_6,H_7	H_{n_1}–H_{x_2}, 12.0
6.69	1.1	dt	H_{x_2}	H_{n_1}–H_{x_2}, 4.0
7.31	3.0	dd	H_{x_1}	H_{x_1}–H_{x_2}, 8.5
7.1–7.6		m	H_5	H_{x_2}–H_3, 8.5
8.12	1.0	dd	H_{n_1}	H_7–CH_3, 6
8.41	2.8	d	$-CH_3$	

[a] The C_5Cl_6 adduct of the 1,3,6-octatriene mixture obtained from the dimerization of butadiene gave a similar spectrum wherein H_{x_2} appears at τ 6.26 and 6.68 in a ratio of ~3:7. These two doublets of triplets correspond to H_{x_2} adjacent to a cis and to a trans double bond, respectively. [b] See Table IV.

Anal. Calcd for a 2:1 mixture of $C_{15}H_{16}Cl_6$ and $C_{20}H_{16}Cl_{12}$: C, 40.05; H, 3.22. Found: C, 40.34; H, 3.12.

Treatment of 28.1 g of the above mixture with an additional 27.3 g (0.10 mol) of C_5Cl_6 for 15 hr at 100° provided the pure diadduct after recrystallization from pentane, mp 128–130°, mol wt 674. The nmr spectrum showed 1.8 olefinic protons in a

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(32) (a) E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1967); (b) E. J. Smutny and H. Chung, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**, No. 2, B112 (1969).

(33) S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, 2451 (1967).

(34) G. B. Butler and T. W. Brooks, *J. Org. Chem.*, **28**, 2699 (1963).

(35) H. Takahasi, S. Tai, and M. Yamaguchi, *ibid.*, **30**, 1661 (1965), and references cited therein.

(36) P. Heimbach, *Angew. Chem. Int. Ed. Engl.*, **7**, 882 (1968).

multiplet between τ 4.5 and 4.8, thus verifying that reaction had occurred exclusively at the terminal sites.

Anal. Calcd for $C_{20}H_{16}Cl_{12}$: C, 35.23; H, 2.37. Found: C, 35.4; H, 2.4.

Registry No.—**4**, 28861-35-0; **5**, 28861-36-1; **6**, 28861-37-2; **7**, 28861-38-3; *cis*-**8**, 28861-39-4; *trans*-**8**, 28861-40-7; *cis*-**9**, 28861-41-8; *trans*-**9**, 28861-42-9; **10**, 28861-43-0; **11**, 28861-44-1; **12**, 28861-45-2; **13**, 28861-46-3; **14**, 28861-47-4; **15**, 28861-48-5; **16**, 28861-49-6; *cis*-**17**, 28861-50-9; *trans*-**17**, 28861-51-0; *trans*-1,4,9-decatriene diadduct with hexachlorocyclopentadiene, 28861-52-1.

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Halogenated Ketenes. XXI. Cycloadditions with Carbonyl Compounds[1,2]

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The cycloaddition of methyl-, chloro-, isopropyl-, and phenoxyketenes with chloral has been accomplished. Both *cis*- and *trans*-2-oxetanones were obtained in approximately equal amounts. The generation of dichloroketene by the dehalogenation of trichloroacetyl chloride in the presence of acetone and cyclohexanone, respectively, afforded these cycloadducts. Zinc appears to activate the carbonyl group, thus increasing the reactivity with dichloroketene. However, chloroketene forms only α,β-dichlorovinyl dichloroacetate under these conditions.

The cycloaddition of ketenes and carbonyl compounds to produce 2-oxetanones (β actones) dates back to the early investigations of Staudinger.[3] Most of the early work was with diphenylketene, and it was found that the addition of simple carbonyl compounds to diphenylketene did not normally proceed unless elevated temperatures were employed. Since the high temperatures required for cycloadditions polymerized aldoketenes and lower ketoketenes, early investigation were mostly limited to diphenylketene.[4]

Later the cycloaddition of ketene to aldehydes was found to proceed smoothly in ether in the presence of mild Friedel–Crafts type catalysts.[5] Ketones, however, required much stronger catalysts and more vigorous conditions to react with ketene.[6]

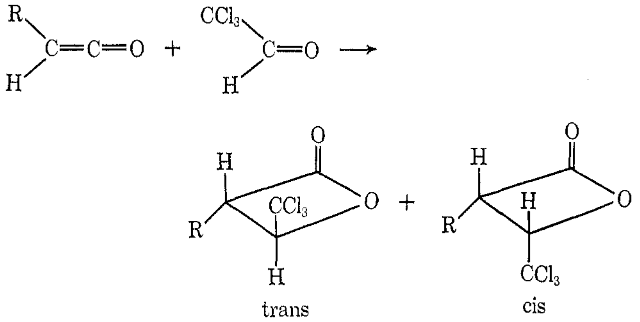
Borrmann and Wegler have recently reported that the cycloaddition of simple ketoketenes and carbonyl compounds is possible when the carbonyl compound is activated by electronegative substituents on the α carbon.[7] Thus, the cycloaddition of several ketenes to chloral were accomplished. The cycloadduct of dichloroketene and chloral was prepared by the *in situ* preparation of dichloroketene and subsequent trapping of this elusive ketene with chloral.[8] However, under these conditions it was found that dichloroketene would not react with simple ketones such as acetone, cyclohexanone, and acetophenone.

In the few literature reports where ketene–carbonyl cycloadditions could produce geometrical isomers, the stereochemical course of the cycloadditions has not been reported.[7,9,10] Borrmann and Wegler, in the only report of aldoketene–carbonyl cycloadditions, described the cycloaddition of phenoxy- and ring-substituted phenoxyketenes to chloral but did not describe the stereochemistry of the products.[5]

We wish now to describe the cycloaddition of several aldoketenes with chloral and report the stereochemistry of these cycloadditions.[11] Also, we describe a method for the cycloaddition of dichloroketene with some simple ketones.

Results

The cycloaddition of aldoketenes to chloral produces *cis*- and *trans*-4-trichloromethyl-2-oxetanones.



The aldoketenes were generated *in situ* by the dehydrochlorination of the appropriately substituted acyl chlorides and/or by dehalogenation of appropriately substituted α-haloacyl halides with zinc.

As England and Krespan found in the generation of difluoroketene by *in situ* dehalogenation, the α-bromoacyl chloride is the preferred acid halide.[12] 2-Bromopropanoyl chloride consistently dehalogenated with greater ease, as evidenced by the amount of zinc consumed, than did the bromo bromide, the chloro bromide, or the chloro chloride.

The isomeric β lactones were isolated and separated by fractional distillation, preparative vpc, or column chromatography and identified by ir and nmr spectra.

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[1] Support of this investigation by the Robert A. Welch Foundation, the National Science Foundation, and a North Texas State University Faculty Research Grant is gratefully acknowledged.

[2] Paper XX: W. T. Brady and J. P. Hieble, *J. Org. Chem.*, submitted for publication.

[3] H. Staudinger, *Chem. Ber.*, **41**, 1493 (1908).

[4] R. N. Lacey in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1968.

[5] F. E. Kung, U. S. Patent 2,356,459 (1944); *Chem. Abstr.*, **39**, 88 (1945).

[6] H. E. Zaugg, *Org. React.*, **8**, 314 (1954).

[7] D. Borrmann and R. Wegler, *Chem. Ber.*, **99**, 1245 (1966).

[8] D. Borrmann and R. Wegler, *ibid.*, **102**, 64 (1969).

[9] D. Borrmann and R. Wegler, *ibid.*, **100**, 1575 (1967).

[10] R. H. Hasek and E. U. Elam, U. S. Patent 3,004,989 (1961); *Chem. Abstr.*, **56**, 4623 (1962).

[11] A preliminary report of a portion of this work has appeared: W. T. Brady and L. Smith, *Tetrahedron Lett.*, 2963 (1970).

[12] D. C. England and C. G. Krespan, *J. Org. Chem.*, **33**, 816 (1968).