Steric Control in the Free-Radical Addition of Carbon Tetrachloride to Norbornenes

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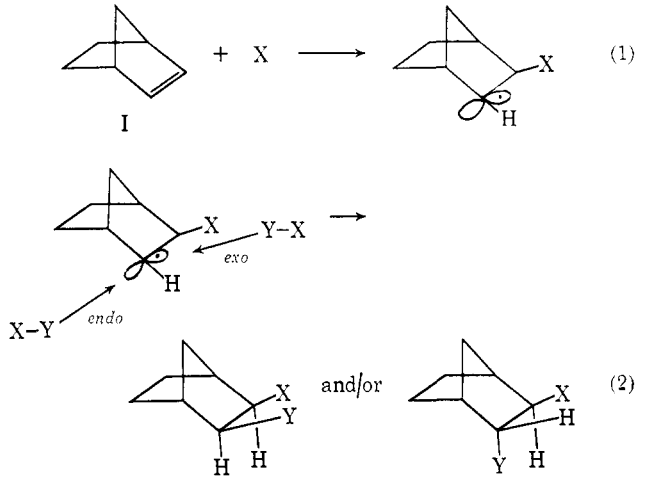
Abstract: The free-radical addition of carbon tetrachloride to norbornene (I) gave a high yield of *trans* (III) and *cis* (IV) adducts in an 18.2:1 ratio. Similar reaction with 5,5-dimethyl-2-norbornene (II) provided *cis* (V) and *trans* (VI) adducts in a 1.2:1 ratio, along with a substantial amount of higher telomer. These results suggest that the stereochemistry of the reaction is directed not only by the *exo* presence of the CCl_3 group but by the steric bulk of the *endo*-5 substituent. Steric inhibition of chain transfer led to competing telomerization reactions. No evidence was found for the reversible addition of the CCl_3 radical. The relative first-order rates of disappearance of I/II were determined to be 1.09/1.00.

The factors governing the stereochemistry of free-radical additions to norbornene derivatives have been the subject of considerable study.[1] In general, it has been found that when small addenda, *e.g.*, HBr or DBr, are employed, both *cis* and *trans* addition occurs, giving rise to products resulting in part from initial *endo* attack.[2,3] In these cases, strong steric barriers appear to be absent.

When larger addenda are involved, however, steric factors come more prominently into play. In the case of bulky attacking groups, initial addition occurs without exception from the less hindered *exo* side.[1,4] The direction of chain transfer, however, varies sharply, depending on the addenda employed. The variance in *cis–exo vs. trans* addition is summarized in Table I.



Inspection of Table I shows that no real correlation is possible between either size of the entering group or ease of chain transfer and the resulting stereochemistry. Hence, the attractive generalization that the entering radical attacks from the *exo* side and the propagating species transfers from the *endo* direction does not hold in all instances. In those anomalous cases the implication is that the propagating species encounters more steric repulsion from the 5- and 6-*endo* hydrogens than from the 2-*exo* substituent.

Table I. Compilation of Radical Additions of Large Addenda to Norbornene

X	Y	% *trans*[a]	% *cis–exo*[a]	Ref
p-$MeArSO_2$	Cl	100	...	*d*
ArS	D	Minor	Major	*e*
Cl_3C	Cl	100	...	*f*
Cl_3C	Br	100	...	*f*
EtO_2C	COCl	100	...	*g*
EtO_2CNH	Cl	34[b] (29[c])	66[b] (71[c])	*h*
EtO_2CCH_2	Br	...	100	*i*
C_3F_7	I	100	...	*j*

[a] Based on total 1:1 adducts. [b] Ultraviolet light induced. [c] AIBN initiated. [d] S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961). [e] S. J. Cristol and T. W. Russell (unpublished work) and D. I. Davies and J. A. Claisse (unpublished work) reported in ref 1, pp 161–162. [f] E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964). [g] C. Pac and S. Tsutsumi, *Tetrahedron Lett.*, 2341 (1965). [h] K. Schrage, *Tetrahedron*, **23**, 3033 (1967). [i] J. Weinstock, Abstracts of Papers, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept 1955, p O-19. [j] N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962).

Further obscuring a consistent mechanistic explanation are the reported free radical additions to 5,6-fused norbornenes.[5–7] For example, the reaction of *p*-thiocresol with 6-chloroaldrin was reported[7] to give the same product as the reaction of *p*-toluenesulfonyl chloride with aldrin.[8] Hence, the first addition would be required to occur in a *cis–exo* fashion, while the second would have to proceed exclusively *trans*. Similarly, the reaction of chloroform with 6-bromoaldrin and the reaction of bromotrichloromethane with aldrin were reported[5] to give the same product. An explanation of these apparent anomalies has been offered.[9]

To gain further insight into this general problem, we undertook a detailed comparative study of the radical addition of carbon tetrachloride to norbornene

(1) For a recent review of the subject, see D. I. Davies and S. J. Cristol in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press Ltd., London, 1965, Chapter 5.
(2) N. A. LeBel, *J. Amer. Chem. Soc.*, **82**, 623 (1960); N. A. LeBel, J. E. Huber, and L. H. Zalkow, *ibid.*, **84**, 2226 (1962); N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).
(3) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).
(4) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).
(5) D. I. Davies, *J. Chem. Soc.*, 3669 (1960).
(6) J. A. Berson and R. Swidler, *J. Amer. Chem. Soc.*, **75**, 4366 (1953); **76**, 4060 (1954); J. A. Berson, *ibid.*, **76**, 5748 (1954).
(7) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957).
(8) See Table I, footnote *d*.
(9) Reference 1, pp 161–163.

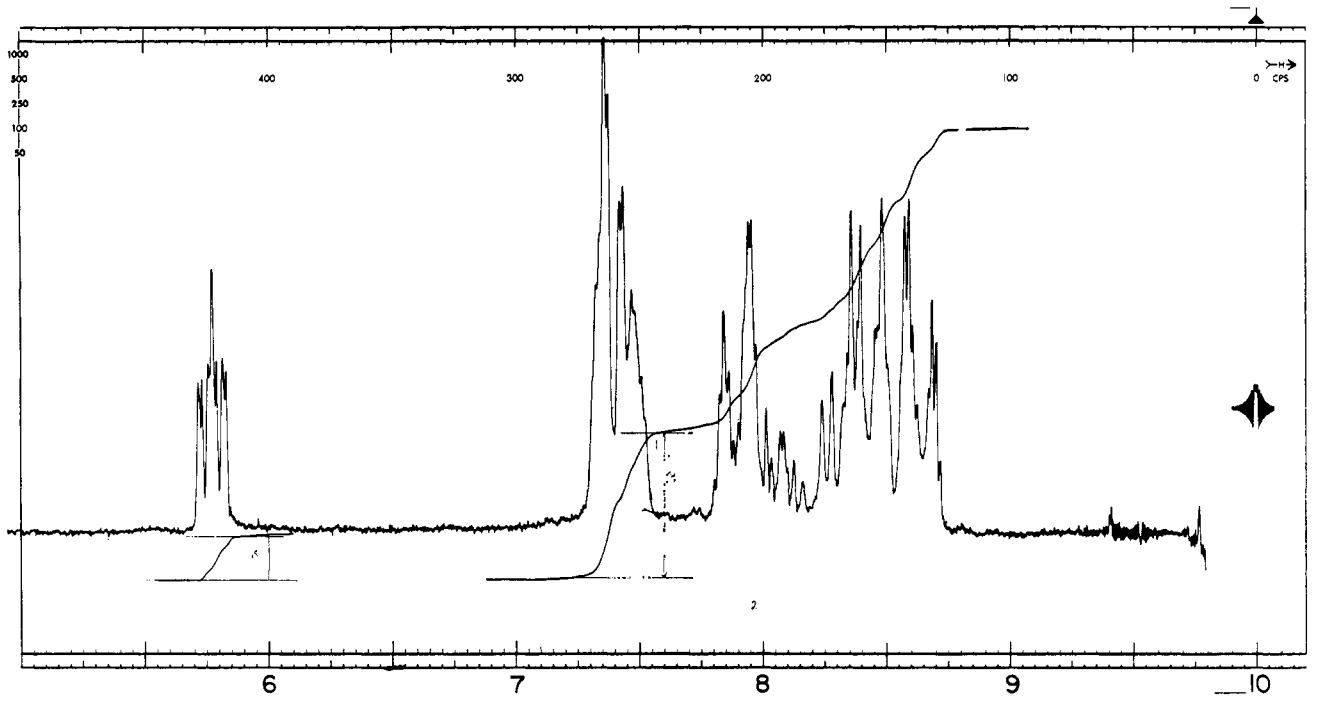
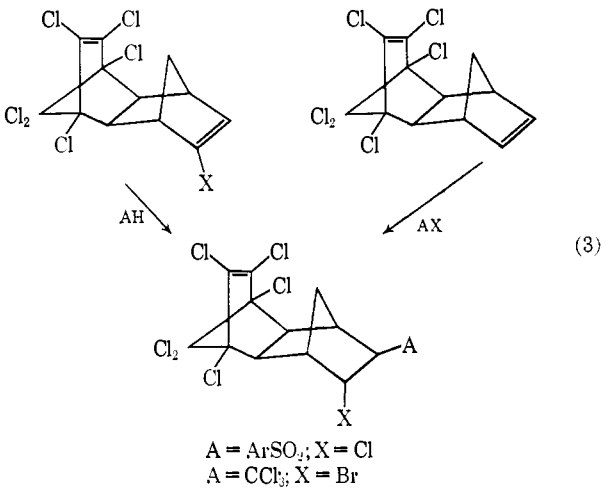


Figure 1. Nmr spectrum (100 MHz) of *endo*-2-chloro-*exo*-3-trichloromethylnorbornane (III).

(I) and 5,5-dimethyl-2-norbornene (II). Our specific objectives were to determine the influence of a 5-*endo* substituent on the initial point of radical attack (C-2 *vs.* C-3) and the direction and ease of chain transfer of the



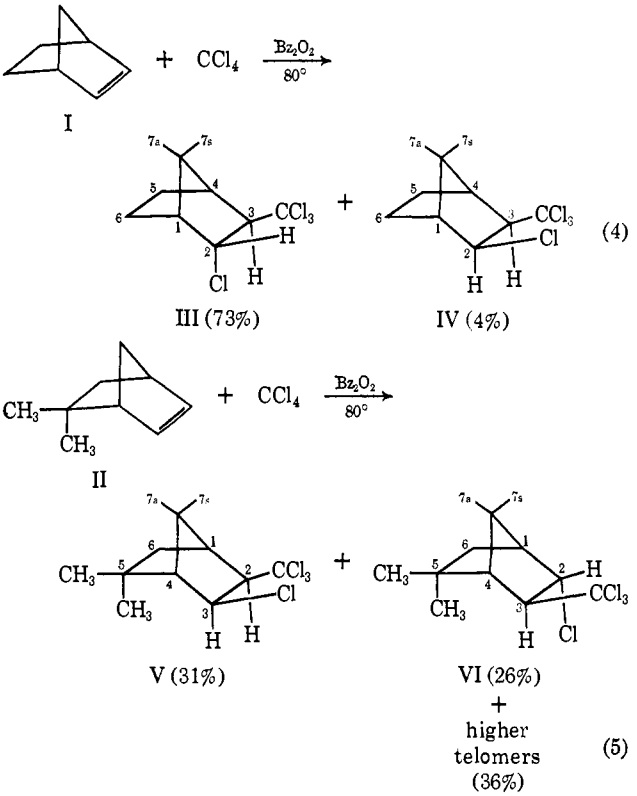
(3)

A = $ArSO_2$; X = Cl
A = CCl_3; X = Br

intermediate radical. We were further concerned about the possibility that steric inhibition to chain transfer might be responsible for the chronic low yields observed in many radical additions to 5-*endo*-substituted norbornenes.[10]

Results

The benzoyl peroxide initiated reaction of carbon tetrachloride with norbornene (I) at 80° afforded the *trans* (III) and *cis* (IV) adducts in 73 and 4% yields, respectively. Similar reaction with 5,5-dimethyl-2-norbornene (II) gave rise to *cis* adduct V and *trans* adduct VI in 31 and 26% yields, as well as a substantial amount of telomeric residue.[11] Control experiments showed that there was no interconversion between products under either reaction or analytical (vpc) conditions.



The 100-MHz nmr spectra of compounds III–VI are shown in Figures 1–4. Chemical shifts and coupling constants are tabulated in Tables II and III, respectively. These assignments were obtained by inspection of the spectra and by appropriate spin-decoupling experiments.

The nmr spectrum of compound VI (Figure 4) was analyzed in the following manner. The lowest field

(10) D. J. Trecker, unpublished results.
(11) Both reactions afforded traces of unidentified products, totaling less than 3%, which were detected by vpc.

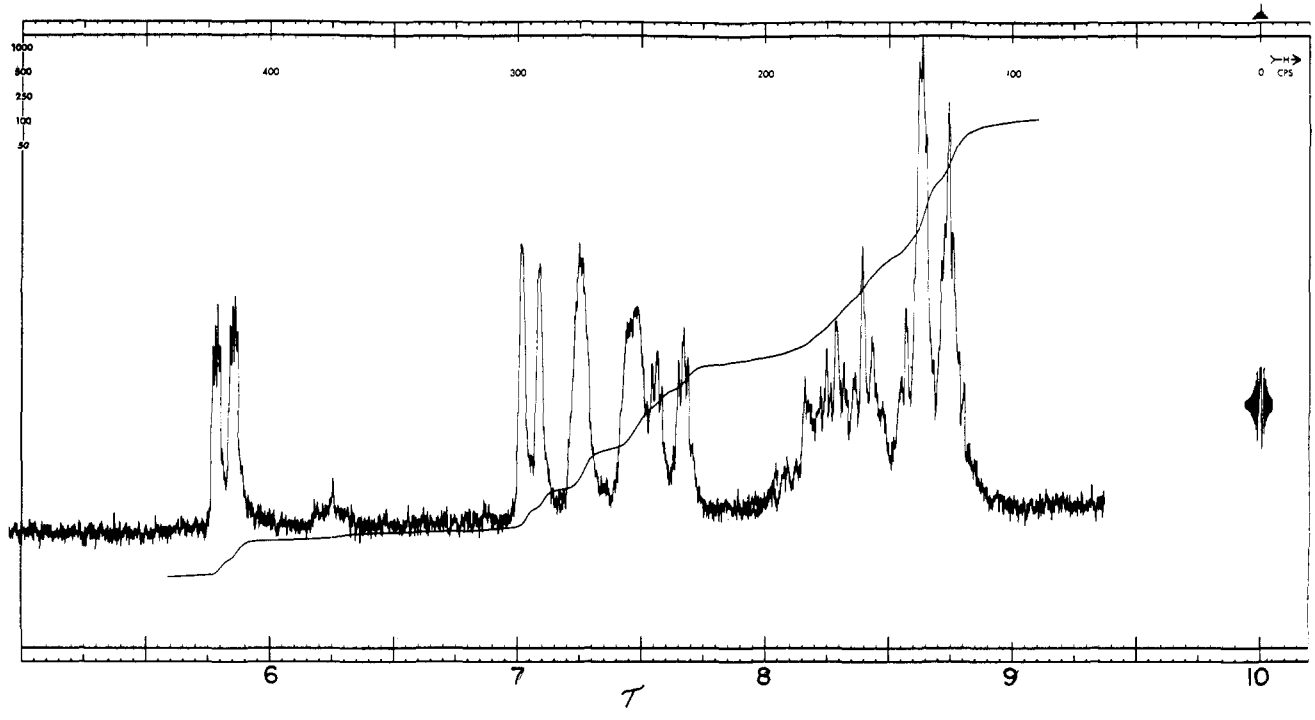


Figure 2. Nmr spectrum (100 MHz) of *exo*-2-chloro-*exo*-3-trichloromethylnorbornane (IV).

signal (τ 5.75) was assigned to the proton geminal to chlorine, and the next lowest field resonance (τ 6.80) was assigned to the proton adjacent to the trichloromethyl group. Inspection of these signals showed that the proton geminal to chlorine was coupled to three different protons by values of 5.4, 4.9, and 1.6 Hz. The proton adjacent to the trichloromethyl group is coupled to two different protons with values of 5.4 and 2.0 Hz. Irradiation at τ 5.75 (Figure 4a) decoupled this proton and indicated that the 5.4-Hz coupling constant is common to the proton adjacent to chlorine and the proton geminal to the trichloromethyl group. A coupling constant of this value indicates that the two protons are situated *trans* to one another.[12] The 4.1-Hz splitting is due to the bridgehead proton at C-1 (which gives rise to the broad signal at τ 7.53). The presence and magnitude of this coupling indicates that the proton next to chlorine is oriented *exo*.[12] The 1.6-Hz splitting observed in the resonance of the 2x proton is associated with the eight-line signal at τ 8.65. This signal is assigned to the 6x proton, because it exhibits coupling constants of 13.0 and 1.6 Hz. Irradiation on the broad signal at τ 7.53 (due to the bridgehead proton at C-1, Figure 4b) removed the 4.9-Hz splitting from the resonance due to the 6x proton. The 1.6-Hz coupling between the 2x and 6x protons results from the "W" configuration of the bonds between them.[13] This and the evaluation of the coupling between the 3n and 7a protons (2.0 Hz) confirmed the configuration assigned.

The nmr spectrum of compound V (Figure 3) was analyzed in a similar fashion. The lowest field signal

Table II. Chemical Shifts (τ)

	Compound			
H	III	IV	V	VI
1	7.4[a]	7.46	7.32	7.53
2x	5.77	...	...	5.75
2n	...	5.82	7.01	...
3x	...	...	...	...
3n	7.4[a]	7.06	5.44	6.80
4	7.4[a]	7.26	7.89	7.83
5x	8.35			
5n				
6x			8.50	8.65
6n			8.79	8.19
7s	7.90	7.62	7.62	7.90
7a	8.62		8.29	8.16

[a] Could not be determined accurately due to interferences.

Table III. Coupling Constants (Hz)

	Compound			
J	III	IV	V	VI
$J_{1,2x}$	5.8			
$J_{1,2n}$		1.0	0.9	...
$J_{2x,3n}$	3.9	...	...	5.4
$J_{2n,3n}$	...	7.0	7.0	...
$J_{2n,7a}$		2.0	2.1	...
$J_{2x,6x}$	1.5			1.6
$J_{3x,4}$				...
$J_{3n,7a}$				2.0
$J_{3n,4}$				...
$J_{4,5x}$	4.0			...
$J_{6x,6n}$			12.3	13.0
$J_{6x,1}$			4.0	4.9
$J_{6n,7s}$		1.9	3.0	2.0
$J_{7s,7a}$	11.0		11.0	11.0
$J_{5x,5n}$	11.6		...	...

(12) F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967); S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 5885 (1967); J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(13) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964); A. Rassat, C. W. Jefford, J. M. Lehn, and B. Walgell, *Tetrahedron Lett.*, 233 (1964).

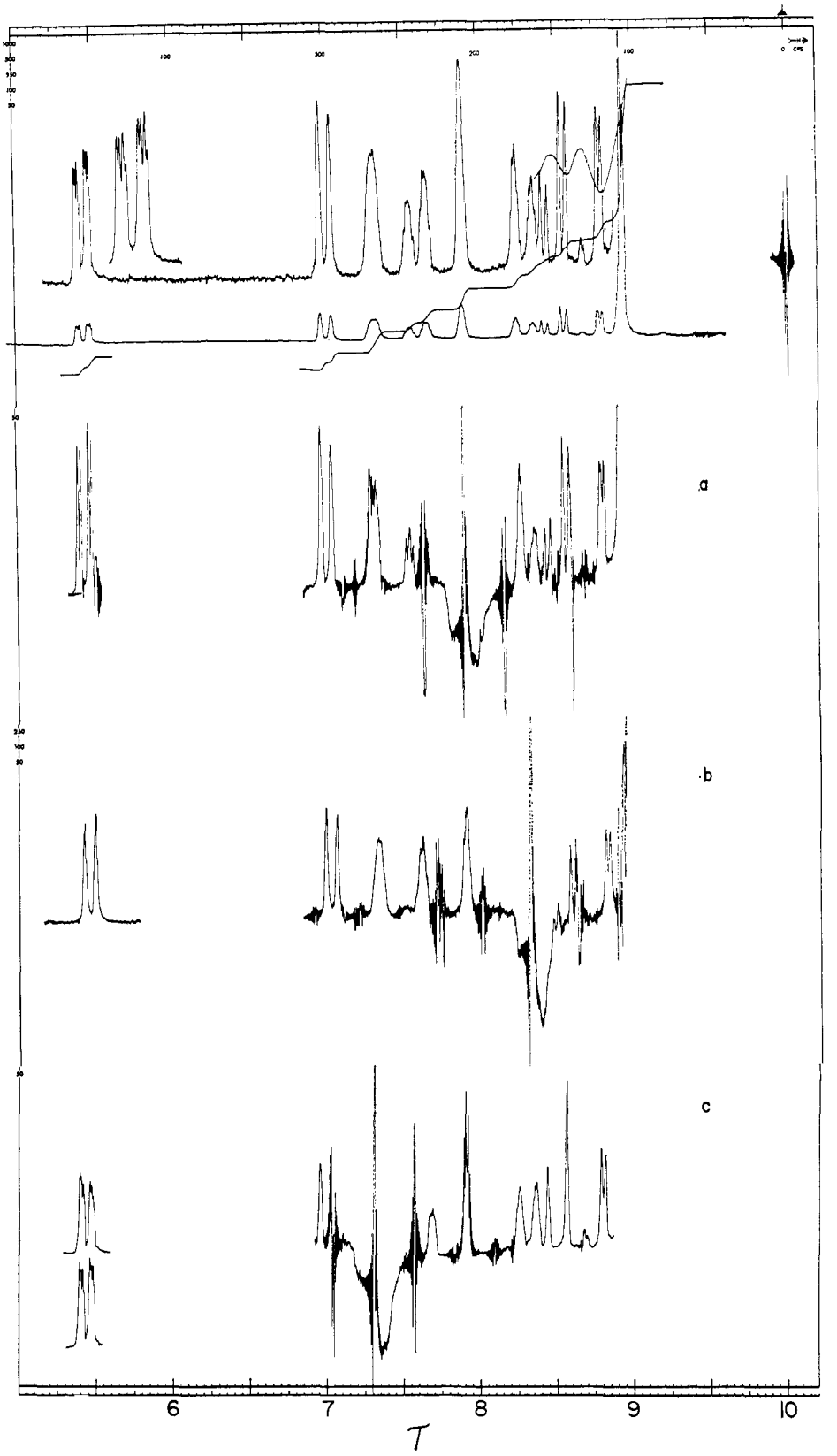


Figure 3. Nmr spectrum (100 MHz) of *exo*-2-trichloromethyl-*exo*-3-chloro-5,5-dimethylnorbornane (V): a, double irradiation on the 4 proton; b, double irradiation on the 7a proton; c, double irradiation on the 1 proton.

(τ 5.44) was assigned to the proton adjacent to the chlorine, and the next lowest field resonance (τ 7.01) was assigned to the proton geminal to the trichloromethyl group. The latter signal appears as a doublet with a splitting of 7.0 Hz. This is also the value of the major coupling in the downfield signal, a doublet with additional fine splitting. Double irradiation experiments confirmed that these two signals were coupled. The magnitude of coupling (7.0 Hz) indicated[12] a *cis* orientation of the two protons. In addition, decoupling

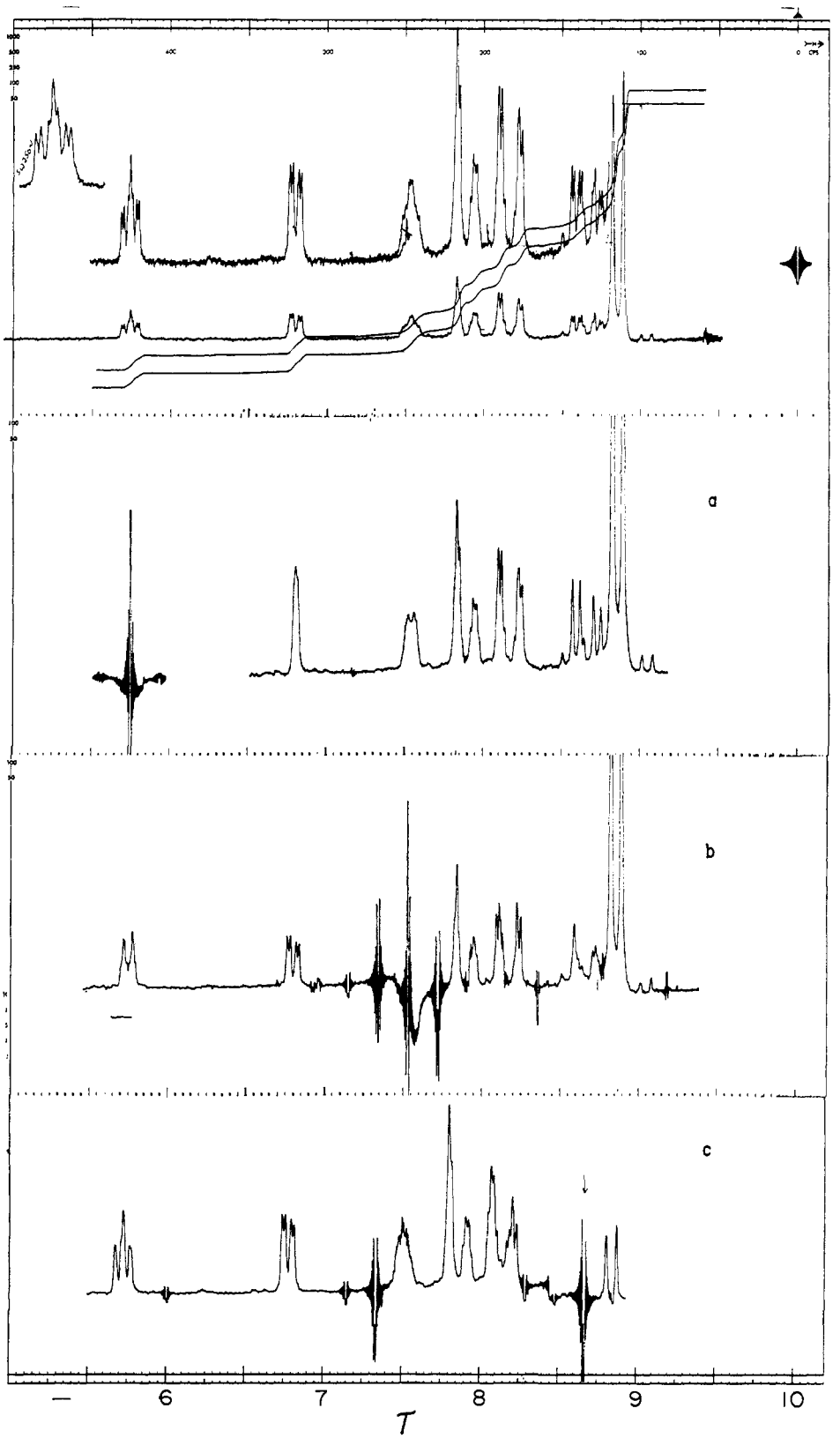


Figure 4. Nmr spectrum (100 MHz) of *endo*-2-chloro-*exo*-3-trichloromethyl-5,5-dimethylnorbornane (VI): a, double irradiation on the 2x proton; b, double irradiation on the 1 proton; c, double irradiation on the 6x proton.

(Figures 3a and 3b) showed that the fine structures in the downfield signal (τ 5.44) is due to splitting (2.1 Hz) by the 7a proton (τ 8.29) and splitting (0.9 Hz) by the 4 proton. Since neither the proton adjacent to chlorine nor the proton geminal to the trichloromethyl group is coupled to a bridgehead proton by the expected value (4.0 Hz), and since the proton adjacent to chlorine is split by the 7a proton, the chloro- and trichloromethyl groups must be oriented *cis–exo*.

The observation of a small coupling constant between

an *endo* proton and a bridgehead proton in a substituted norbornane is quite unusual.[12] In this case, distortion of the molecule resulting from steric interaction of the chloro- and trichloromethyl groups apparently changes the angle between projections of the C-3–H bond and the C-4–H bond. A change in this dihedral angle would account for the observed splitting.[14] If this is the case, then the *endo* proton adjacent to chlorine must be coupled to the nearest bridgehead proton. Since it is coupled to the 1 proton, and not to the 4 proton (Figure 3c), the chlorine must be attached to C-2. On this basis the configuration of the compound must be that of structure V.

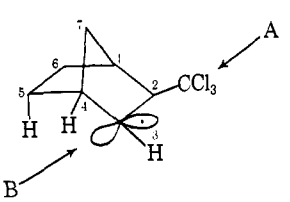
The pattern due to the proton adjacent to chlorine in the spectra of compounds III and IV (Figures 1 and 2) are similar to those observed for adducts V and VI (Figures 3 and 4). The lines appearing below τ 8 in the spectrum of adduct IV were assigned on the basis of decoupling experiments and by analogy to similar signals in the spectrum of *cis–exo* adduct V. The critical coupling constants ($J_{1,2n}$) and ($J_{2n,3n}$) which appeared in the spectrum of adduct IV have approximately the same values as the corresponding coupling constants in *cis–exo* adduct V. On this basis, compound IV was assigned a *cis–exo* structure.

The structure of adduct III was previously assigned a *trans* configuration.[15] The nmr data reported here corroborate this assignment. The splitting pattern of the proton geminal to chlorine is similar to that observed in the spectrum of *trans* adduct VI. Double irradiation of the spectrum of adduct III was not as informative as with compounds IV–VI, due to the unfortunate overlap of the signals of protons 1, 3n, and 4.

Rate studies indicated that both I and II followed the expected[16] first-order rates of disappearance, after brief induction periods. The kinetic plots are shown in Figure 5. Under the reaction conditions employed, $k_I \simeq 8.7 \times 10^{-4}$ sec^{-1} and $k_{II} \simeq 8.0 \times 10^{-4}$ sec^{-1}, giving relative rates of disappearance of I/II $\simeq$ 1.09.

Discussion

The overwhelming preference for attack of the trichloromethyl radical from the *exo* side of norbornene and transfer of chloride from carbon tetrachloride to the *endo* side of radical VII (path B) was noted earlier by



VII

Tobler and Foster.[15] Our studies confirm their results. The detection of some *cis–exo* adduct (IV) suggests that chlorine transfer along path A is not entirely inhibited.[17] This may be partially due to the fact that torsional strain[18] between C-3–H and C-4–H

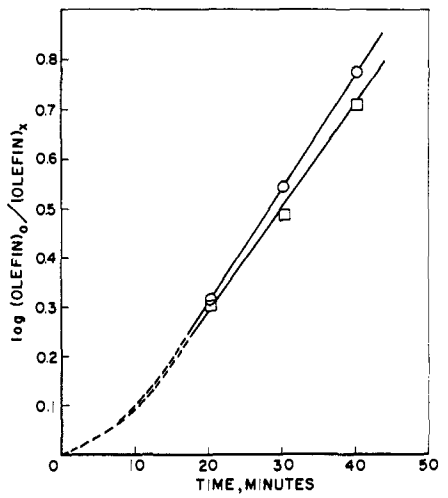
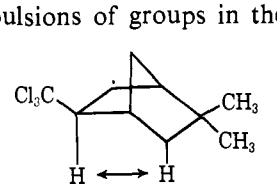


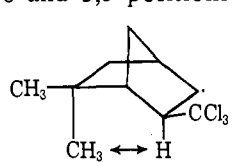
Figure 5. First-order plots of norbornene (○) and 5,5-dimethyl-2-norbornene (□) disappearance at 80 ± 1°.

bonds develops in the *endo* abstraction step. As transfer of a chlorine occurs to the *endo* side of VII, the hybridization of C-3 changes from sp^2 to sp^3. As this occurs, the C-3–H and C-4–H bonds must sweep through an eclipsed conformation having maximum torsional strain. When chlorine is transferred to the *exo* side (path A), the C-3–H and C-4–H bonds do not pass through an eclipsed conformation. The contribution of such strain to *endo* chain transfer would not be expected to offset the major nonbonded effect exerted by the *exo*-trichloromethyl group, with the result that the predominant product was still the *trans* adduct III.

The steric control of product formation was most strikingly shown with 5,5-dimethyl-2-norbornene. Several points merit attention here. First, it is apparent that, based on the nearly equivalent amounts of *cis* adduct V and *trans* adduct VI obtained (1.2:1 ratio), the transannular 5-methyl groups exerted little influence on the entering trichloromethyl radical. The small effect observed may be rationalized as follows. Reaction of ·CCl$_3$ with 5,5-dimethyl-2-norbornene (II) should cause sp^3 development at the carbon atom attacked, with consequent movement of the olefinic hydrogen into an *endo* position. The second carbon atom should then accommodate the resulting odd electron in an sp^2 configuration with little resulting change in geometry. The only anticipated steric difference, then, between attack at C$_2$ and C$_3$ lies in the *endo,endo* repulsions of groups in the 2,6 and 3,5 positions[19] of



VIII

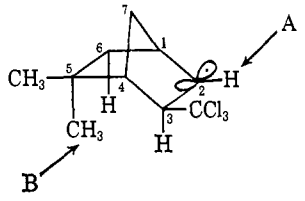


IX

intermediates VIII and IX. Attack at C$_2$ creates a hydrogen–hydrogen repulsion (VIII), while attack at C$_3$ results in a hydrogen–methyl repulsion (IX). Although it is difficult to estimate the relative magnitude to these repulsions, the difference may be sufficient to account for the slight preference for C$_2$ attack.

(14) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(15) See Table I, footnote *f*.
(16) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 243–259.
(17) The formation of IV suggests that the detected (vpc), but unisolated, minor products from reaction 5 may be the *trans* adduct corresponding to V and the *cis* adduct corresponding to VI.
(18) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).
(19) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 87, 375 (1965).

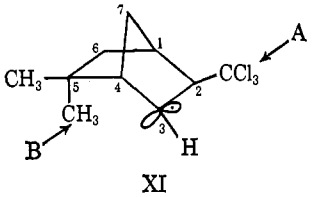
This effect is admittedly small. On the other hand, the steric influence of the *endo*-5-methyl group on chain transfer and, hence, product stereochemistry is quite significant. The results are best explained by again considering a model in which the intermediate radical has essentially planar sp^2 character at the 2-carbon. In such an intermediate (X), attack along the line of the p orbital of the odd electron involves a choice between



X

the hindrance of the *endo*-6-hydrogen (path B) and the *exo*-3-trichloromethyl group (path A). As with norbornene itself, the less hindered path was found to be from the *endo* direction (B), and the product formed was the *trans* adduct VI. Again the opposing torsional effect, which favors *exo* attack, was apparently insufficient to overcome the steric factor.

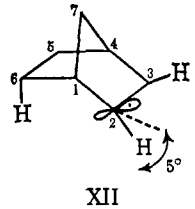
In the case of intermediate XI, the choice is less clear *a priori*. The approaching carbon tetrachloride molecule is, in this instance, confronted with bulky



XI

substituents along both of its possible paths of approach. Experimentally, path A was found to be favored, and the sole isolable product from this intermediate was the *cis–exo* adduct (V). Hence, the presence of an *endo*-5-substituent was sufficient to reverse completely the normal mode of *trans* addition.

It is interesting to consider these facts in light of reported chlorine atom abstractions by the 2-norbornyl radical. Kooyman and Vegter[20] demonstrated that the ratio of *exo*/*endo* chlorination of norbornane was a function of the size of the chlorinating agent. Molecular chlorine gave about 70% *exo*- and 25% *endo*-chloride, whereas SO_2Cl_2, CCl_4, and PCl_5 gave 95% of the *exo*-halide. This delicate balance of stereoselection was discussed by Fujimoto and Fukui[21] in terms of the theoretical direction of orbital extension in the 2-norbornyl radical. These authors suggested that the most stable configuration of this intermediate, albeit



XII

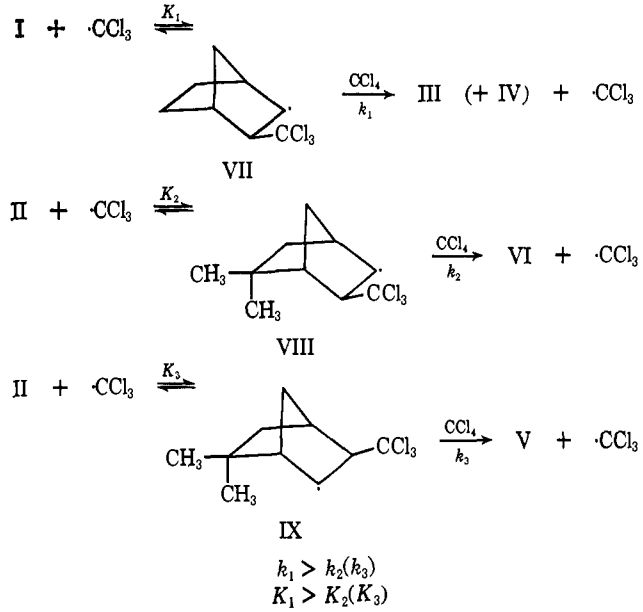
by a small margin, is a slightly deformed sp^2 configuration in which the half-occupied orbital has maximum extension is the *exo* direction with attendant displacement of the 2-hydrogen (XII). This allegedly results in a favorable disposition for *exo* attack.

Regardless of the theoretical treatment, it seems apparent that whenever the *exo*-3 group and the *endo*-6 group (or *exo*-2 group and *endo*-5 group) are of similar steric magnitude, chain transfer from a bulky reagent takes place from the *exo* direction. This is in agreement with observed stereoselection of intermediate XI and the consequent formation of V.

Schleyer's torsional strain argument[18] may again be invoked to explain these results. The development of torsional strain between C_3–H and C_4–H will only be possible in the transition state of *endo* abstraction; *exo* chain transfer will result in no such eclipsing. The real significance of this effect is difficult to assess here. In fact, the occurrence of *exo* abstraction (path A) may be entirely due to the *endo*-5-methyl lying more nearly along the line of impending bond formation than the *exo*-2-trichloromethyl group. This simple steric argument is entirely supported by molecular models.[22]

There remains for consideration the reason why 5,5-dimethyl-2-norbornene (II) affords lower yields of carbon tetrachloride adducts than does norbornene. Two possible explanations present themselves. One is that the addition of the trichloromethyl radical to the norbornene double bonds is reversible, as has been amply demonstrated for alkane thiyl radicals.[23] If this were the case, the equilibrium might be expected to lie considerably farther to the right for I than for II ($K_1 > K_2, K_3$), with steric inhibition to chain transfer more pronounced in VIII and IX than from VII ($k_1 > k_2, k_3$), due to the presence of the *endo*-5-methyl group. This sequence is shown in Scheme I.

Scheme I



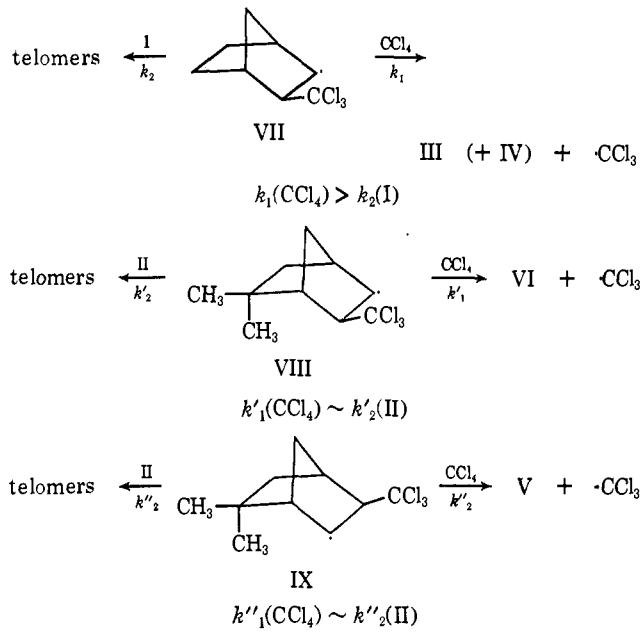
$k_1 > k_2(k_3)$
$K_1 > K_2(K_3)$

Alternatively, the addition of $\cdot CCl_3$ might be irreversible, as advocated by Huyser and Kellogg,[24] with the hindrance to chain transfer in VIII and IX leading instead to the lower activation process of addition to a

(20) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, 4, 382 (1958).
(21) H. Fujimoto and K. Fukui, *Tetrahedron Lett.*, 5551 (1966).
(22) Similar directive effects were noted in the lithium aluminum hydride ring opening of 2,3-*exo*-epoxy-5,5-dimethylnorbornane exclusively to 6,6-dimethyl-2-*exo*-norbornanol (footnote 5 in ref 19).
(23) C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 81, 1144 (1959); E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, 28, 1676 (1963).
(24) E. S. Huyser and R. M. Kellogg, *ibid.*, 30, 3003 (1965).

second norbornene molecule. Thus, using the notations of Scheme II, $k_1(CCl_4) > k_2(I)$, with chain transfer and, hence, 1:1 addition predominating. In contrast, with compound II, $k_1'(CCl_4) \approx k_2'(II)$ and $k_1'(CCl_4) \approx k_2''(II)$, with the result that higher telomerization competes with chain transfer.

Scheme II



Distinction between these two possibilities is based on the kinetic response of the two norbornene compounds. Reversible addition of ·CCl_3 to I and II followed by a more favorable rate of abstraction from VII than from VIII and IX ($k_1 > k_2, k_3$; $K_1 > K_2, K_3$) would result in a markedly lower rate of disappearance of II. Experimentally, this was not the case (Figure 5). The relative rates of disappearance of I and II were very nearly equivalent. Moreover, substantial telomeric residues resulted from reaction of II, but not from reaction of I.

These facts are in better accord with Scheme II and favor the explanation that steric inhibition of chain transfer in VIII and IX allows telomerization to compete favorably with abstraction.

Experimental Section

Free-Radical Addition of Carbon Tetrachloride to Norbornene. In the manner previously described,[15] carbon tetrachloride was treated with norbornene to yield, upon distillation, pure 2-*endo*-chloro-3-*exo*-trichloromethylnorbornane (III)[15] and a fraction (bp 74° (0.1 mm)) enriched in IV. Isolation of 2-*exo*-chloro-3-*exo*-trichloromethylnorbornane (IV) was achieved by preparative-scale vpc (20 ft × 3/8 in. column of 10% SE-30 on Chromosorb W, 185°).

Anal. Calcd for $C_8H_{10}Cl_4$: C, 38.74; H, 4.06; Cl, 57.20. Found: C, 38.46; H, 3.74; Cl, 57.10.

To obtain exact yield data, vpc analysis (12 ft × 1/8 in. column of 10% W-98 on Chromosorb G, 185°) was conducted on a reaction mixture of carbon tetrachloride (154 g, 1.0 mol), norbornene (18.8 g, 0.2 mol), and benzoyl peroxide (2.4 g, 0.01 mol). 1-Chloronaphthalene served as the internal standard. Work-up afforded 5.9 g (16% yield, based on 2:1 telomer) of residue.

Free-Radical Addition of Carbon Tetrachloride to 5,5-Dimethyl-2-norbornene (II). A solution of carbon tetrachloride (154 g, 1.0 mol), II (24.4 g, 0.2 mol), and benzoyl peroxide (2.4 g, 0.01 mol) was held under reflux for 16 hr. Distillation gave four fractions (31.8 g, 0.115 mol, bp 88–91° (1.5 mm)) consisting of mixtures of 2-*exo*-trichloromethyl-3-*exo*-chloro-5,5-dimethylnorbornane (V) and 2-*endo*-chloro-3-*exo*-trichloromethyl-5,5-dimethylnorbornane (VI), and left a dark, viscous residue (14.4 g). The last two distillation fractions solidified upon standing to give crystals which were washed repeatedly with *n*-heptane, filtered, and dried. The crystals (V) melted at 83–84°.

Anal. Calcd for $C_{10}H_{14}Cl_4$: C, 43.51; H, 5.11; Cl, 51.38; mol wt, 276. Found: C, 43.96; H, 5.21; Cl, 51.53; mol wt, 274.

Compound VI, a clear liquid which crystallized upon standing, was isolated from the first distillation fraction *via* preparative-scale vpc (20 ft × 3/8 in. column of 20% neopentylglycol adipate on Chromosorb W, 185°. The crystals melted at 35–36°.

Anal. Calcd for $C_{10}H_{14}Cl_4$: C, 43.51; H, 5.11; Cl, 51.38. Found: C, 43.80; H, 5.09; Cl, 51.36.

Quantitative analysis of V and VI in subsequent runs was accomplished by vpc (12 ft × 1/8 in. column of 10% W-98 on Chromosorb G, 185°), employing 1-bromonaphthalene as an internal standard.

Kinetic Determinations. A solution of I (0.895 g, 9.52×10^{-3} mol), II (0.959 g, 7.86×10^{-3} mol), carbon tetrachloride (12.1 g, 7.88×10^{-2} mol), and benzoyl peroxide (0.382 g, 1.58×10^{-3} mol) was heated at 80 ± 1° in an oil bath. Samples were withdrawn at 10-min intervals and analyzed by vpc (12 ft × 1/8 in. column of 10% W-98 on Chromosorb G, 75°). Toluene was used as an internal standard. The data resulting from these determinations are shown in graph form in Figure 5.

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