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Bromine Addition to Cyanonorbornene Derivatives[1]

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The addition reactions of *endo*-5-cyanonorbornene, *trans-endo,exo*-5,6-dicyanonorbornene, *cis-endo*-5,6-dicyanonorbornene, and *cis-exo*-5,6-dicyanonorbornene with bromine have been studied. The assignments of the configurations of bromine adducts were determined mainly on the basis of the NMR spectra. As to *trans-endo,exo*-5,6-dicyanonorbornene, reaction mixtures have been found to contain *trans* and *exo-cis* adducts. The reaction conditions involving the proportions of these isomers and a rationale for the formation of the *exo-cis* adduct are discussed. *cis-endo*-5,6-Dicyanonorbornene and *cis-exo*-5,6-dicyanonorbornene gave the *exo-cis* adduct and the *trans* adduct respectively. The stereochemistry of bromine atoms may be explained in terms of a steric factor. A kinetic study showed that these addition reactions in solution in acetic acid obey the second-order rate law and that the magnitudes of the rate constants are in the order; *cis-exo*-5,6-dicyanonorbornene>*trans-endo,exo*-5,6-dicyanonorbornene>*cis-endo*-5,6-dicyanonorbornene.

Recently Traylor[2] noted that *cis*-electrophilic additions to a wide variety of bicycloheptene structures have been established and that several explanation have been proffered for the observation of *exo-cis* additions to norbornenes—the twist-strain theory, molecular electrophilic addition, torsional effects, and so on.

However, concerning halogen additions to norbornene derivatives bearing electronegative substituents, much attention has been paid only to the bromination of the cyclopentadiene–maleic anhydride adduct.[3-5] Kwart and Kaplan[5] explained the *exo-cis* addition of bromine to the *endo*-adduct on the basis of steric hindrance or *endo*-carbonyl participation.

As part of a study of the electronic and steric effects in the stereochemistry of halogen additions to norbornene derivatives, we have investigated the halogenation of four cyanonorbornenes, *endo*-5-cyanonorbornene, *trans-endo, exo*-5,6-dicyanonorbornene, *cis-endo*-5,6-dicyanonorbornene, and *cis-exo*-5,6-dicyanonorbornene. First, the confirmation of the halogen adduct and the structural assignment have been studied; secondly, in order to study the reactivity of bromine to four substrates, the kinetics of bromination in dry acetic acid have been investigated and the magnitudes of the rate constants have been deduced by the second-order approximate treatment of the resulting kinetic data.

Experimental[6]

Reagents. *a)* endo-*5-Cyanonorbornene (Substrate I)*: The procedure of Alder, Heimbach, and Reubke[7] was followed, using 1 mol of freshly-distilled cyclopentadiene (67 g) and 1 mol of acrylonitrile (53 g). The resulting reaction mixture was separated into the *exo*-adduct (bp 81—84°C/10.5 mmHg, 18 g; lit,[7] 80—85°C/12 mmHg) and the *endo*-adduct (bp 99°C/26 mmHg, 37 g; lit,[7] 88°C/12 mmHg) by fractional distillation. Both adducts were confirmed to be more than 99% pure by glc analysis.

b) trans-endo,exo-*5,6-Dicyanonorbornene (Substrate II)*: The procedure of Blomquist and Winslow[8] was followed. From 0.1 mol (7.8 g) of fumaronitrile prepared in the usual way and 0.11 mol (9 m*l*) of cyclopentadiene in 50 m*l* of ethanol, we obtained 11.5 g (83%) of the substrate II, which showed a mp of 103—104°C (lit,[8] 95.5—96°C) on recrystallization from ethanol. (Found: C, 74.77; H, 5.59; N, 19.08%.)

c) cis-endo-*5,6-Dicyanonorbornene (Substrate III) and* cis-exo-*5,6-Dicyanonorbornene (Substrate IV)*: As the crude malenitrile prepared from maleamide as described by Blomquist[8] contained considerable amounts of fumaronitrile and another component, malenitrile (mp 30—32°C, lit,[8] 30—31°C) was purified by liquid-column chromatography (elute, benzene; silica gel, 100 mesh). Gas chromatography indicated a purity of 99%. The procedure of Blomquist[8] was followed using 0.02 mol (1.56 g) of malenitrile and 0.024 mol (2 m*l*) of cyclopentadiene. The fractional recrystallization of the resulting reaction mixture gave 2.0 g of the *endo* adduct, which was also confirmed to be pure by a comparison with the NMR spectrum of the crude adduct in d_6-DMSO (mp 163—165°C; Found: C, 74.77; H, 5.52; N, 19.33%; lit,[8] 155—156°C) and 0.2 g of the *exo* adduct (mp 108—110°C; lit,[9] 108—110°C).

Bromination of Substrate I with Bromine. A solution of bromine (8.0 g, 0.05 mol) in 25 m*l* of carbon tetrachloride was stirred, drop by drop, into a solution of Substrate I (6.0 g, 0.05 mol) in 50 m*l* of carbon tetrachloride over a 30-min period at 0°C. After the stirring had been continued for an additional 3 hr, a solid separated. This material[10] weighed 10.5 g; it was recrystallized from ethanol (mp 154—156°C) and confirmed to be dibromide by elemental analysis

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[1] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971; Proceedings, Vol. III, p. 1562.

[2] T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

[3] H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **75**, 3356 (1953).

[4] J. A. Berson, *ibid.*, **76**, 4060 (1954).

[5] H. Kwart and L. Kaplan, *ibid.*, **76**, 4078 (1954).

[6] All the melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. The infrared spectra were recorded on a Hitachi EPI-2G apparatus, while the NMR spectra were obtained with a JNM-3H-60 spectrometer, using TMS as the internal standard. The mass spectra were measured with a Hitachi-RMU-6E instrument operating at 70 eV.

[7] K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958).

[8] A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

[9] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964).

[10] Abbreviated as I-*t* hereafter.

and by a study of its mass spectrum. The stereochemistry of the bromine atoms was estimated to be *trans* by studying the NMR spectrum. Found: C, 34.64; H, 2.98; N, 5.20%; Calcd for $C_8H_9NBr_2$: C, 34.45; H, 3.25; N, 5.20%; M^+: 277 (1), 279 (2), 281 (1).[11]

NMR spectrum (in $CDCl_3$): τ: 6.35 [2H, m, W_h (band width at half-height)]=*ca.* 4 Hz, H-*endo* 5 and H-*endo* 6,[12] 7.00 (2H, d,q,. J=4.6, 5.4, and 1.8 Hz, H-*exo* 5 and H-*exo* 6), (in d_6-DMSO): τ: 5.65 (2H, m, W_h=*ca.* 4 Hz) 5.88 (2H, d,t,. J=4.6, 5.4, and 1.8 Hz).

Chlorination of Substrate I with Chlorine. Chlorine gas (3.6 g, 0.05 mol) was passed through a solution of Substrate I (8.0 g, 0.05 mol) in 50 m*l* of carbon tetrachloride with stirring over a period of about one hour at 0°C.

The crystalline product (5.0 g) was separated by filtration on a glass filter, and the filtrate was evaporated to dryness; this afforded a small amount of an oily product (about 1.0 g). The crystalline product purified by means of liquid-column chromatography (elute, chloroform; silica gel, 100 mesh) (mp 141—143°C) was confirmed to be dichloride by elemental analysis and by a study of the mass spectrum. The stereochemistry of chlorine atoms of the dichloride was identified as *trans* on the basis of the similarity of its NMR spectrum with that of the dibromide. Found: C, 50.75; H, 4.70; N, 7.30%; Calcd for $C_8H_9NCl_2$: C, 50.75; H, 4.77; N, 7.36%. M^+: 189 (9), 191 (6), 193 (1).

The oily product when distilled yielded a distillate boiling at 93°C/10^{-3} mmHg (0.6 g). The gas-chromatographic separation of the distillate afforded a colorless liquid which was estimated to consist of *endo*-5-cyano-*anti* or *syn*-7-chloronorbornene (23%) and 5-chloro-2-cyano-nortricyclene (77%) by means of elemental analysis and a study of the mass spectrum and NMR spectrum ($CDCl_3$). Found: C, 62.30; H, 4.75; N, 9.23%. Calcd for C_8H_8NCl: C, 62.56; H, 5.25; N, 9.12%. M^+: 153 (3), 155 (1).

Assignments of the Spectral Data of the Liquid Product. *endo*-5-Cyano-*anti* or *syn*-7-chloronorbornene; H_1, H_2 protons, 3.84 ppm, H_7 proton, 5.85 ppm. $C_5H_5Cl^+$: 110 (3), 112 (1), retro Diels-Alder fraction.[16] 5-Chloro-2-cyano-nortricyclene; H_5 proton, 5.67 ppm. IR, 805 cm^{-1} (800—810 cm^{-1})[17] characteristic absorption of nortricyclene.

Bromination of Substrate II with Bromine. A few milliliters of a bromine solution containing 8.0 g of bromine in 25 m*l* of carbon tetrachloride was stirred into a solution of Substrate II (7.5 g, 0.05 mol) in 50 m*l* of carbon tetrachloride, but the bromine color did not disappear immediately; therefore, the residual bromine solution was added under reflux over a period of 30 min, and the stirring was continued for an additional 4 hr. The separated crystalline compound (10.0 g) was filtered from a hot reaction solution and recrystallized from benzene; mp 205—206°C.[18] The stereochemistry of bromine atoms was estimated to be *exo-cis* on the basis of NMR spectrum in the d_6-DMSO solution. Found: C, 35.64; H, 2.68; N, 9.20%; Calcd for $C_9H_8Br_2N_2$: C, 35.56; H, 2.65; N, 9.22%; M^+: 302 (1), 304 (2), 306 (1).

The above procedure was also followed on the same scale in an acetic acid solution at 30°C. The residue resulting after the evaporation of the acetic acid was recrystallized from benzene; mp 150—180°C (9.7 g). This material (2.0g) was dissolved in 20 m*l* of hot ethanol, and the less soluble material filtered while still hot was recrystallized from toluene (mp 206.5—207.5°C (0.2 g)), corresponding to the *exo-cis* adduct. Then the crystalline compound which separated on standing from the ethanol mother liquor was once more dissolved in about 15 m*l* of hot ethanol. The less soluble material was removed by filtration, whereupon about 0.8 g of crystals separated from the ethanol mother liquor. The resulting solid was recrystallized from ethanol; mp 138—140°C (0.5 g). The stereochemistry of bromine atoms in this adduct[19] was estimated to be *trans* on the basis of the NMR spectrum in the d_6-DMSO solution. [τ: 5.22 (1H, d, d,. J=3.8 and 4.5 Hz, H-*exo* 5 or H-*exo* 6), 5.89 (1H, t, J=$\sim$3.0 Hz, H-*endo* 6 or H-*endo* 5), 6.16 (1H, t, J=4.5 Hz, H-*exo* 2), 6.50 (1H, d, d,. J=2.1 and 5.0 Hz), 7.06 (2H, m, H-1 and 4), 7.81 (1H, forming the one part of the AB system, H-7a), 8.10 (1H, forming the other part of the AB system, H-7b)]. Found: C, 35.75; H, 2.63; N, 9.37%. Calcd for $C_9H_8Br_2N_2$: C, 35.56; H, 2.65; N, 9.22%.

Bromination of Substrate III with Bromine. Substrate III (1.44 g, 0.01 mol) dissolved in 90 m*l* of acetic acid was treated with 1.9 g (0.012 mol) of bromine dissolved in 30 m*l* of acetic acid. After stirring had been continued for three days at room temperature, a crystalline product separated. This material weighed 2.2 g and was identified as a crude *exo-cis* adduct (mp 289—290°C[20] (recrystallized from 1-propanol)). Found: C, 35.83; H, 2.60; N, 9.04%. Calcd for $C_9H_8N_2Br_2$: C, 35.56; H, 2.65; N, 9.22%. The mother liquor was evaporated to dryness, leaving a further quantity (0.2 g) of the *exo-cis* adduct, as was confirmed by the NMR spectrum (see Table 3).

Bromination of Substrate IV with Bromine. A solution of bromine (0.019 g, 0.012 mol) in 5 m*l* of acetic acid was added to a dark brown measured flask containing a solution of Substrate IV (0.145 g, 0.01 mol) in 17 m*l* of acetic acid, and then the mixture was allowed to stand at 30°C for 3 hr. After the end of the reaction, the solvent was evaporated and the resulting product was recrystallized from ethanol; mp 179—182°C[21] (0.15 g). The stereochemistry of bromine atoms was confirmed to be *trans* on the basis of the NMR spectrum of the d_6-DMSO solution (see Table 3). Found: C, 35.63; H, 2.66; N, 9.33%. Calcd for $C_9H_8N_2Br_2$: C, 35.56; H, 2.65; N, 9.22%.

Determination of the Rate of Addition. The rate of addition was determined by the titration method which was similar to that of Buckles and his co-workers.[22]

Solutions of the substrate in about 80 m*l* of acetic acid were warmed to bath temperature in a 100-m*l*, dark brown, measured flask, into which a stock solution of bromine in acetic acid was then pipetted and mixed. The acetic acid was then rapidly added to make a vloume of 100 m*l*. At appropriate intervals, 5.0-m*l* samples were pipetted into a

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[11] The number in brackets shows the ratio of the peak strength.

[12] If the stereochemistry of the two bromine atoms is assumed to be *exo-cis*, the broad absorption (W_h=4 Hz) at 6.35 ppm can not be explained on the basis of the reported magnitude of the *endo-endo* coupling constants (approximately 6—7 Hz);[13–15] therefore, the stereochemistry was suggested to be *trans*.

[13] P. Laszlo and R. Schlever, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

[14] C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

[15] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," ed. by D. H. R. Barton and W. Doering, Pergamon Press, New York, N. Y. (1969), p. 289.

[16] S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966).

[17] J. D. Roberts, E. R. Trumbull, J. W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3116 (1950).

[18] Abbreviated as II-*c* hereafter.

[19] Abbreviated as II-*t* hereafter.

[20] Abbreviated as III-*c* hereafter.

[21] Abbreviated as IV-*t* hereafter.

[22] R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32**, 888 (1967).

flask containing 50 m*l* of a 2.5% KI methanol solution. The flask was swirled 5 times and then allowed to stand for 1 min, after which the iodine was titrated with a standard thiosulfate solution (1/50N) with a starch indicator.

The time for the start of the reaction was taken as the time at which half of the bromine solution was out of the pipet. The time for the stop of the reaction was determined in a manner similar to that used for the start of the reaction.

In the case of Substrate IV, rate-measurements experiments were carried out on the scale of one-fifth, as in the above description.

Assignment of Spectral Lines. In Fig. 1 are shown the decoupled spectra of compound II-*c* (mp 206.5—207.5°C) in the d_6-DMSO solution obtained using the frequency-sweep technique (Hitachi-R 20—60 spectrophotometer).[23] Part A shows the normal spectrum. The absorption at τ 7.05 is readily identified as the result of the bridge-head protons by means of the broad patterns resulting from several coupling interactions. The low-field absorption centered at τ 5.35 (doublet of quartets) is also identified as the result of two hydrogens attached to the brominated carbons on the basis of its chemical shifts[24] and integrated areas. The absorption at τ 8.03 shows the C_7 AB pattern. On the basis of the discussion presented above, the two residual absorptions at τ 6.30 and τ 6.63 are assigned as 2-*endo* or 3-*exo* hydrogens. Part B shows the spectrum obtained upon the irradiation of the C_1, C_4 protons at τ 7.05. First, the appearance of the upfield part of the C_7 AB pattern changes to a triplet of doublets. The coupling constant values (1.8 Hz) are reasonable as a zigzag, long-range coupling. Secondly, the irradiation at τ 7.05 alters the pair of doublets at τ 6.30 to only one doublet in order to remove 4.5 Hz coupling. The value of 4.5 Hz corresponds to the coupling between the bridge proton C_1 or C_4 and the C_2 *exo* or C_3 *endo* proton respectively, since the absorption at τ 6.30 may be assigned to either the 2-*exo* or 3-*endo* proton. The magnitude of the coupling between the C_4 proton and the C_3 *endo* proton was expected to be almost zero because of the unfavorable vicinal dihedral angle,[25] so the resonance at τ 6.30 is confirmed as the 2-*exo* proton. Thus the 4.5 Hz coupling between the C_1 and C_2 *exo* protons is established. The irradiation of the upper-field part of the C_7 AB pattern (Part C in Fig. 1) eliminates the splitting, 1.8 Hz, of C_5, C_6 hydrogens at τ 5.35. By combining the results of Part B and Part C, the 1.8 Hz splitting is established as a zigzag, long-range coupling between C_5 *endo* or C_6 *endo* hydrogen[26] and C_{7b} hydrogen. Thus, $J_{5\text{-}endo,\,6\text{-}endo}$ and $J_{7b,7a}$ are confirmed to be 6.3 Hz and 11.7 Hz respectively. Therefore, the stereochemistry of bromine atoms is established as *exo-cis*.

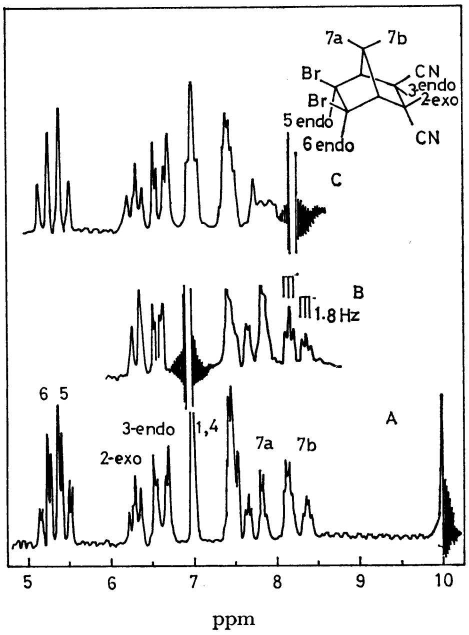
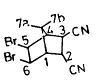
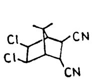
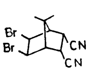
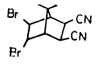


Fig. 1. NMR spectra of compound II-*c* in solution in d_6-DMSO A: normal; B: decoupled from protons 1,4; C: decoupled from proton 7b.

The stereochemistry of compound II-*t* is established as *trans* on the basis of the decoupling experiments involving

Table 1. Chemical shifts[a)] and coupling constants (Hz)

Compound	2	3	1, 4[b)]	5	6	7a	7b
	6.31	6.61	7.05	5.44	5.26	7.80	8.26
	$J_{7a,\,7b}=11.7$, $J_{5\text{-}endo,\,6\text{-}endo}=6.3$, $J_{2\text{-}exo,\,3\text{-}endo}=5.7$, $J_{2\text{-}exo,\,1}=4.5$, $J_{7b,\,5\text{- or }6\text{-}endo}=1.8$.						
	6.25	6.62	7.13	5.50	5.31	7.89	8.29
	$J_{7a,\,7b}=12.0$, $J_{5\text{-}endo,\,6\text{-}endo}=6.3$, $J_{2\text{-}exo,\,3\text{-}endo}=5.4$, $J_{2\text{-}exo,\,1}=5.4$, $J_{7b,\,5\text{- or }6\text{-}enao}=2.1$.						
	6.31	6.31	7.03	5.28	5.28	7.87	8.38
	$J_{7a,\,7b}=10.8$, $J_{7b,\,5\text{- or }6\text{-}endo}=2.4$.						
	6.37	6.37	7.05	5.84	5.30	7.75	8.01
	$J_{7a,\,7b}=11.8$, $J_{7b,\,5\text{-}endo}=2.1$, $J_{5\text{-}endo,\,6\text{-}exo}=3.9$, $J_{6\text{-}exo,\,1}=3.9$.						

a) Values are shifts in τ-units.
b) Chemical shifts represent the positions of band centers.
c) The stereochemistry was estimated on the basis of the similarity of NMR spectrum of the material (small quantity, broad range of mp near 124°C) obtained from chlorination of substrate II in hot CCl_4 solution to that of compound II-*c*.

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[23] Measurements were carried out by Mr. Yoshio Takai of The Institute of Scientific and Industrial Research, Osaka University.

[24] P. M. Subramanian, M. T. Emerson, and N. A. Lebel, *J. Org. Chem.*, **30**, 2624 (1965).

[25] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[26] The low-field peak (τ 5.26) among C_5, C_6 *endo* protons may be assigned to the C_6 *endo* proton since the C_6 *endo* proton is favorably situated for shielding by the C_2 *endo* cyano group;[27] this explanation seems to be in good agreement with the fact that two C_5, C_6 *endo* protons of III-*c* show a signal at τ 5.28 (in d_6-DMSO).

[27] J. M. Jackman and G. Y. Sarkis, This Bulletin, **42**, 1179 (1969).

trans-5-chloro-6-iodo-*trans*-2,3-norbornanedicarbonitrile[28] and the arguments presented in Footnote[12], but the question of whether the C_6 proton is *exo* or *endo* remains unresolved and is now under investigation. Therefore, the absorptions of the appearance of a triplet at τ 5.89 and τ 6.16 (described before) are substantially duplicates of two doublets, so the coupling constants, 5.0, 2.1, 4.5, and 3.8 Hz, can be assigned to $J_{2\text{-}exo,3\text{-}endo}$, $J_{7a,3\text{-}endo}$, $J_{5\text{-}exo,4}$ (or $J_{6\text{-}exo,1}$), and $J_{5\text{-}exo,6\text{-}endo}$ (or $J_{5\text{-}endo,6\text{-}exo}$) respectively.

The stereochemistry of compound III-*c* is confirmed to be *exo-cis* as follows. The doublet (1.8 Hz splitting) at τ 5.28 corresponds to C_5, C_6 hydrogens attached to the carbons bearing bromine atoms, as is shown by the chemical shifts and integrated areas, so it is reasonable to consider that the 1.8 Hz coupling may be attributed to the long-range coupling between C_5 *endo* or C_6 *endo* and C_{7b} hydrogen. The stereochemistry of compound IV-*t* is confirmed *trans* in a way similar to that used for compound II-*t*. The assigned chemical shifts and coupling constants are listed in Table 1.

Discussion

Fortunately, the rates of bromine addition to Substrates II, III, and IV in the measurable region could be obtained by the conventional titration method. The concentrations of bromine against the reaction time are plotted in Fig. 2 for the addition reactions of bromine to Substrates II, III, and IV. The finding on *cis-endo*-5,6-norbornene-carboxylic anhydride (Substrate V) is also plotted for the sake of comparison. Figure 2 shows that the reactivity falls in this sequence; Substrate IV>II>III≃V, indicating that the *endo* orientation of cyano groups retards the addition reactions of bromine. The stereochemical results obtained here would seem to suggest that, in this addition reaction, *exo*-substituents exert such a steric influence on the rate-determining transition state as to reduce the rate of addition; that is, it may be considered that the entering bromide ion in the transition state may be sterically hindered by the *endo*-cyano group so that the *endo* orientation of substituents may produce a much greater rate reduction. This explanation[29] does not contradict the kinetic results to be described below.

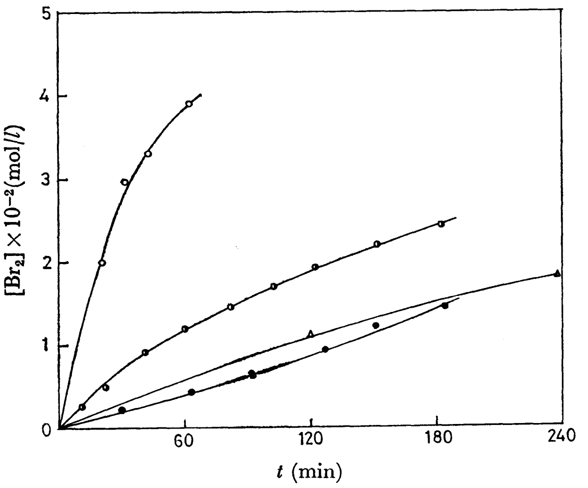

Fig. 2. Plots of consumed bromine against time for bromine addition reactions
○: Substrate IV (29.8°C); △: Substrate III (29.9°C); ◑: Substrate II (30.1°C); ●: Substrate V (30.0°C).

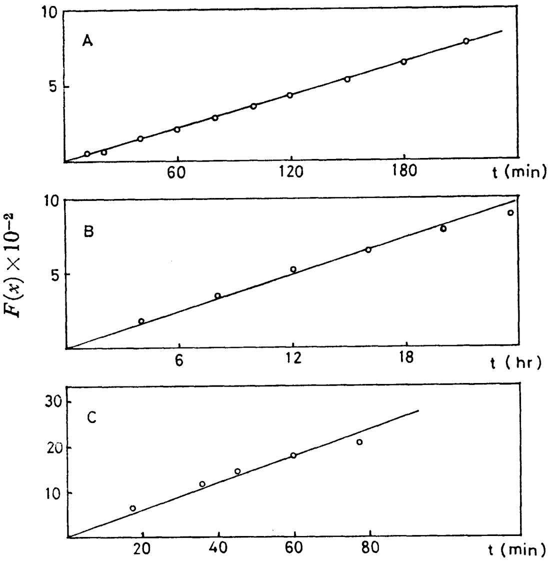

Fig. 3. Typical plots of second-order bromination rates A: Data for substrate II at 30.1°C (*a*: 6.072×10^{-2} mol/*l* *b*: 4.995×10^{-2} mol/*l*) B: Data for substrate III at 29.9°C (*a*: 5.991×10^{-2} mol/*l*, *b*: 4.960×10^{-2} mol/*l*) C: Data for substrate IV at 29.8°C (*a*: 5.994×10^{-2} mol/*l*, *b*: 4.970×10^{-2} mol/*l*) $F(x)=\log[b(a-x)/a(b-x)]$ a=initial bromine concentration, b=initial substrate concentration, x=bromine reacted at time t.

Figure 3 shows the rate data treated by a second-order rate equation $(dx/dt=k\times[\mathrm{Br_2}]\times[\mathrm{Sub}])$.

Table 2. Rate constants for bromination of substrates (II, III, and IV) in acetic acid

Substrate	Temp (°C)	10^4 k (*l*/mol sec)	Concentration (mol/*l*)
II	30.1	12.78 (52.0)[a]	0.05
	29.9	16.90 (52.0)	0.05
	19.9	8.84 (42.7)	0.05
	20.0	17.07 (80.8)	0.1
	30.1	26.32 (89.0)	0.1
III	29.9	6.05 (60.0)	0.05
	19.9	1.59 (32.8)	0.05
IV	29.8	121.5 (79.0)	0.05
	28.9	122.3 (78.1)	0.05
V	30.0	5.17 (27.4)	0.05
	29.9	7.28 (37.9)	0.05

a) Numbers in brackets indicate the percentage of completion where plots of log $[b(a-x)/a(b-x)]$, *versus* time were linear.

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28) The NMR spectrum of this compound will be discussed in detail elsewhere.

29) Kwart and Miller,[30] in a kinetic study of the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis-exo*-5,6-norbornene-carboxylic anhydride and Substrate V in glacial acetic acid, have explained the lower reactivity of the latter in terms of the field effect, by which they suggested that the nucleophilic character of the double bond may be reduced preferably in the case of the *endo*-anhydride. This view corresponds to the situation in which the *exo*-side attacking of a reagent and the formation of the intermediate cation may be the rate-determining steps.

30) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961).

TABLE 3. BROMINATION OF SUBSTRATES (II, III, AND IV)

Substrate	Solvent	Reaction time	Temp (°C)	Yield (%)	*cis* (%)	*trans* (%)
II	CCl_4	2 hr	76.8	89	67	33
	CCl_4	24 hr	30.0	96[a)]	54	46
	AcOH	6 hr	20.0	100[a)]	23	77
	AcOH	2.5 hr	28.9	90[a)]	24	76
	AcOH	5.5 hr	39.5	100[a)]	45	55
III	AcOH	3 days	room temp	80	100	0
IV	AcOH	3 hr	30.0	55	11	89

a) A solution of bromine (1.76 g 0.011 mol) in 90 m*l* acetic acid and substrate II (1.44 g, 0.01 mol) were introduced in a dark brown measured flask immersed in the aquarium provided with a mercury thermoregulator. The crude product obtained after removal of acetic acid was washed with *n*-hexane to remove a trace of acetic acid and submitted to quantitative analysis.

As to Substrate II, the data were best fitted by the second-order rate law, but the plots of the rate data of Substrate III treated by the second-order rate law show a slight downward trend while the plots of the rate data of Substrate IV treated by the second-order rate law also show a downward trend. However, in the present study, it is considered reasonable, in attempting to know the order of magnitude of rate constants, to assume that the rate approxinately fits the second-order rate law.[31)]

The rate constants deduced above are summarized in Table 2. The bromination of Substrate II was also carried out in carbon tetrachloride, but in this solvent no such clean-cut results were obtained. A relatively rapid consumption of bromine was observed after an arbitrary interval from the start of reaction, suggesting that the reaction in this solvent was homolytic. This trend (homolytic) was also observed in the bromination of Substrate II in acetic acid at 39.5°C.

Table 3 summarizes the approximate compositions of the dibromide mixtures obtained under various reaction conditions; they were calculated on the basis of a NMR-spectra analysis in the d_6-DMSO solution.

Table 3 shows that, in a carbon tetrachloride solution, the *exo* adduct of Substrate II predominates over the *trans* adduct of Substrate II, and this reaction in carbon tetrachloride is found to show a partial homolytic character, as was discussed in the part concerning rate study. In acetic acid at 39.5°C, where the bromination was considered to be partially homolytic on the basis of the rate study, the proportion of the *exo-cis* adduct increased. This type of observation of an *exo-cis* adduct increase with an increase in the homolytic character has been reported by Berson and his coworkers[4,32,33)] for the bromination of the maleic anhydride adduct of furan and cyclopentadiene. As to the bromination of the anhydride adduct of furan, only a *trans* adduct was obtained in a polar solvent such as acetic acid.

However, in the present study, the *exo-cis* adduct (23—24%) has been obtained with a residual *trans* adduct in acetic acid at 20 or 30°C.

Judging from the rate data at 20 or 30°C, the reaction in acetic acid may be considered to proceed by the heterolytic mechanism, so the formation of the *exo-cis* adduct may be explained by the steric concept that the attacking reagent bromide ion suffers a repulsive, non-bonded interaction with the *endo* cyano group of Substrate II in the *endo* direction. The stereochemistry of the bromine addition of Substrates III and IV shown in Table 3 may be explained in terms of the steric hindrance described above.

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31) When treated by a third-order rate equation ($dx/dt = k \times [Br_2]^2 \times [Sub]$), the rate data gave less precise results.

32) J. A. Berson and R. Swiuler, *J. Amer. Chem. Soc.*, **75**, 4366 (1953).

33) J. A. Berson, *ibid.*, **76**, 5748 (1954).