Table IV

Values of $\gamma_{c,t}$

Substituents 2	Substituents 3	ρ_{cis}	Ref.[a]	ρ_{trans}	Ref.[a]	$\gamma_{c,t}$
2	3					
H	H or X	−2.34	1b	−2.20	10	1.1
H	Me or X	−3.29	3	−2.90	14	1.1
Me	H or X	−3.48	5b	−2.61	11	1.3
H	H or 2-C_6H_4X	−0.657	12b	−0.389	*b*	1.7
H	H or 3- or 4-C_6H_4X	−0.643	*c*	−0.466	*d*	1.3

[a] Numbers refer to sets in Table II. [b] Ref. 5. [c] R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963). [d] Ref. 1.

Assignment of Configuration to Geometric Isomers.—It has previously been suggested[2] that assignments of configuration might be made by means of a comparison between the calculated value of some property for the *trans* compound and the observed value of the property. Thus, a comparison of the observed ionization constant for a substituted acrylic acid with the value of the ionization constant for the *trans* compound calculated from the Hammett equation would aid in the assignment of configuration. Assignment of configuration to a *cis* compound on this basis would rest on lack of agreement between the observed constant and the constant calculated for the *trans* compound. The correlations obtained above for *cis* olefinic sets make possible the calculation of a property for both *trans* and *cis* isomers (with the exception of those *cis* isomers in which a strong intramolecular hydrogen bond is likely to occur). This should greatly extend the utility of the Hammett equation as a method of assigning configuration.

The Reactions of Some 7-Chloronorbornenes with Sodium Cyanide[1,2]

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The reactions of 7-chloronorbornadiene (1) and *anti*-7-chloronorbornene (2) with sodium cyanide in aqueous ethanol were studied. The former (1) produced β-cyclopentadienylacrylonitrile, whose formation was rationalized by the nucleophilic attack of a cyanide ion at the C-2 of 1 followed by ring cleavage. The latter (2) produced mainly *anti*-7-cyanonorbornene, along with 2-cyanotricyclo[4.1.0.0^{3,7}]heptane as a by-product. The kinetics and the stereochemical results are in accord with the S_N1 mechanism.

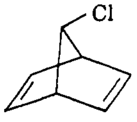
In view of providing a good model for the demonstration of anchimeric assistance for ionization, the solvolysis reactions of norbornyl systems have received much attention in recent years.[3] It seems to us that the position and stereochemistry of an entering nucleophile in the solvolysis of 7-norbornenyl derivatives, in which partial positive charges are developed at the 7-position, throw some light on the precise nature of participation and the precise structure of the carbonium ions produced in the ionization stages.[4]

Initially the purpose of this study was to devise a reaction which results in inversion of configuration of a 7-substituent without skeletal rearrangement. Although a highly nucleophilic reagent such as a sulfur or iodide anion might be more suitable for the purpose, we were afraid we would encounter some difficulties in the determination of stereochemistry of the products formed by these kinds of reagents. Accordingly, we undertook the reactions of 7-norbornenyl halides with sodium cyanide even though it may not be a sufficiently strong nucleophilic reagent.

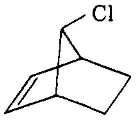
Brown[4a] recently reported the formation of tricyclo[4.1.0.0^{3,7}]hept-4-ene and tricyclo[4.1.0.0^{3,7}]heptane in the solvolyses of 7-chloronorbornadiene and *anti*-7-norbornenyl tosylate in aqueous diglyme containing sodium borohydride, which was suggested by him as a convenient means for trapping carbonium ions formed in solvolysis.[5] Our results obtained here describe the formation of the above kind of product or intermediate and information on their stabilities, although the initial purpose concerning inversion of configuration was not accomplished.

Results

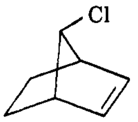
Reactions of the norbornyl chlorides 1–5 with sodium cyanide were carried out in 66% aqueous ethanol under a nitrogen atmosphere. All the reaction mixtures were colorless and homogeneous in the initial stages of the reactions. As expected from the solvolytic behaviors, *syn*-7-chloronorbornene (3), 7-chloronorbornane (4), and 3-chloronortricyclene (5) were so inert that reactions of 3 and 5 at refluxing temperature for 6 hr. and of 4 at 175° for 6 hr. did not show any product formation. However, the reactions of 7-chloronorbornadiene (1) and *anti*-7-chloronorbornene (2) with sodium cyanide proceeded smoothly, resulting in the precipitation of sodium chloride.



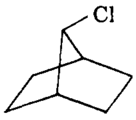
1



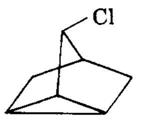
2



3



4



5

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[1] Part VIII of a series on Bicyclic Systems. Part VII: H. Tanida and R. Muneyuki, *Tetrahedron Letters*, **No. 38**, 2787 (1964).

[2] Presented, in part, at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1964.

[3] For a recent review, see J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

[4] With respect to the discussion in this field, refer to (a) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

[5] H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).

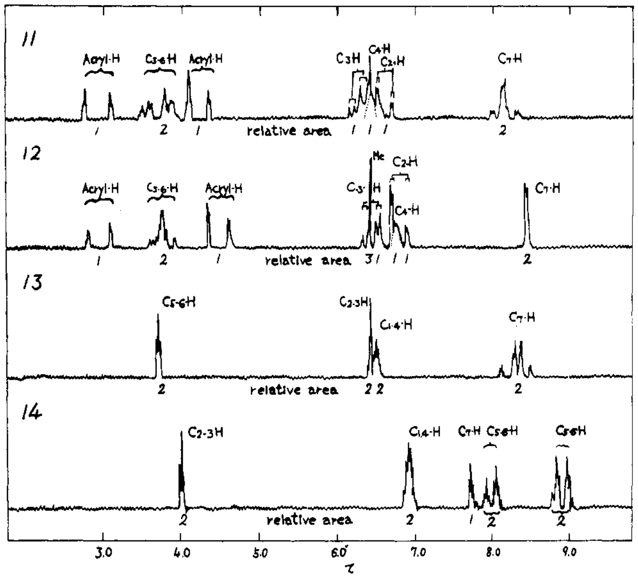


Figure 1.—N.m.r. spectra of compounds 11–14 in deuteriochloroform.

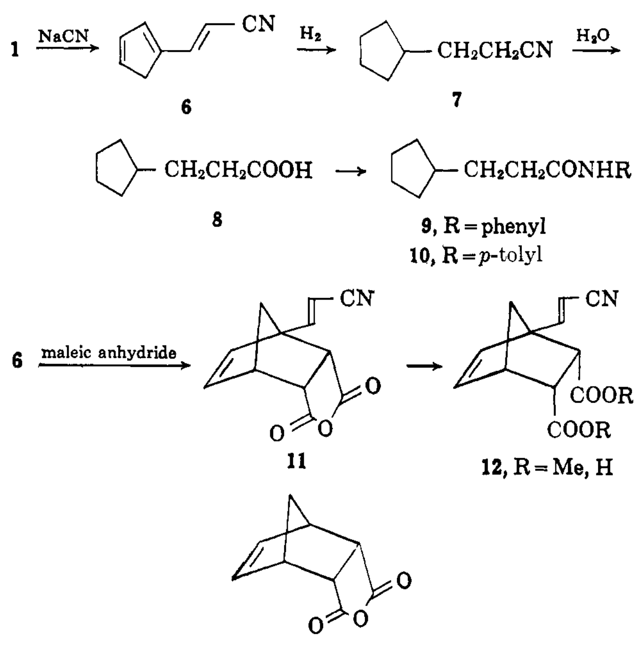
The reaction with **1** was completed within 5 min. at 0° and its rate measurement was accompanied by some technical difficulties. The product **6** obtained from **1** was unstable and could not be isolated in a pure state, but the ultraviolet and infrared spectra of the crude **6** exhibited an intensive absorption band at 318 mμ and a strong peak at 1610 cm.$^{-1}$, respectively, both of which were assigned to a long conjugated carbon–carbon double bond.[6,7]

The catalytic reduction of this crude **6** with the absorption of a little more than 2 moles of hydrogen yielded β-cyclopentylpropionitrile (**7**) in 50% yield from **1** (Chart I).

The infrared spectrum and refractive index of **7** were consistent with those of an authentic sample of β-cyclopentylpropionitrile, which was independently prepared from cyclopentyl bromide.[8–10] Moreover, the hydrolysis product of **7**, β-cyclopentylpropionic acid **8**, and its derivatives **9** and **10** were confirmed by mixture melting points with the corresponding authentic samples.

The structural elucidation of an adduct produced by the reaction of **6** with maleic anhydride yielded a convincing evidence for the structure of **6**. The adduct **11**, $C_{12}H_9NO_3$, was shown to have two double bonds and one cyano group by catalytic reduction and by the infrared spectrum, respectively. The comparison of infrared and n.m.r. spectra of **11** with those of 5-norbornene-*endo*-2,3-dicarboxylic anhydride (**13**) suggested that **11** should have a structure similar to **13**. As shown in Figure 1, the n.m.r. spectrum of the monomethyl ester **12** derived from **11** also gave a strong support for the above suggestion. The signals at τ 8.45, 6.74, 6.53, and 6.73 were assigned to the two protons on the C-7, to a proton on the C-2, to a proton on the C-3, and to the one bridgehead proton, respectively. Accordingly, it turned out that an alkyl group occupied at the other bridgehead. The 10.2- and 3.5-c.p.s. splitting of the signal at τ 6.53 is due to the couplings of the C-3 *exo* proton to the C-2 *exo* proton and the bridgehead proton, respectively, indicating that the carboxyl groups on the C-2 and C-3 have *endo* configuration[11] which was consistent with the prediction based on the well-known Alder rule.[12] The signals at τ 2.93 and 4.46, both of which appeared in doublet peaks having the coupling constants of 16.7 c.p.s., were ascribed to the *trans* olefinic protons of the acryl group. Consequently, the structures of the related compounds were established to be **6**, **11**, and **12**, respectively.

CHART I



The reaction of *anti*-7-chloronorbornene (**2**) with sodium cyanide required a higher temperature than that used for 7-chloronorbornadiene (**1**) and gave a mixture composed of three compounds. Elution chromatography on alumina purely isolated one of them which was identified as *anti*-7-norbornenol and the other two compounds were nitrile derivatives in a ratio of 8:2. The formation of *anti*-7-norbornenol was considered to be due to the hydrolysis of **2**. The nitrile derivatives were hydrogenated over palladium on charcoal yielding a mixture of two saturated nitriles **16** and **17** in the same ratio as that of the original nitriles. The major saturated nitrile was converted by alkaline hydrolysis into a carboxylic amide which was identified as norbornane-7-carboxamide (**18**) by mixture melting point and comparison of infrared spectra with an authentic sample.[13] Lithium aluminum hydride reduction of **18** afforded norbornane-7-methylamine (**20**) in quantitative yield. Accordingly, the structure of the major saturated nitrile was established to be 7-cyanonorbornane (**16**). The minor

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(6) A. E. Gillam and E. S. Stern, "An Introduction of Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Publishers, Ltd., London, 1954, Chapter 6.

(7) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(8) S. Pilat and N. Turkiewicz, *Ber.*, **72B**, 1527 (1939).

(9) E. R. Shepard and J. F. Noth, *J. Org. Chem.*, **19**, 415 (1954).

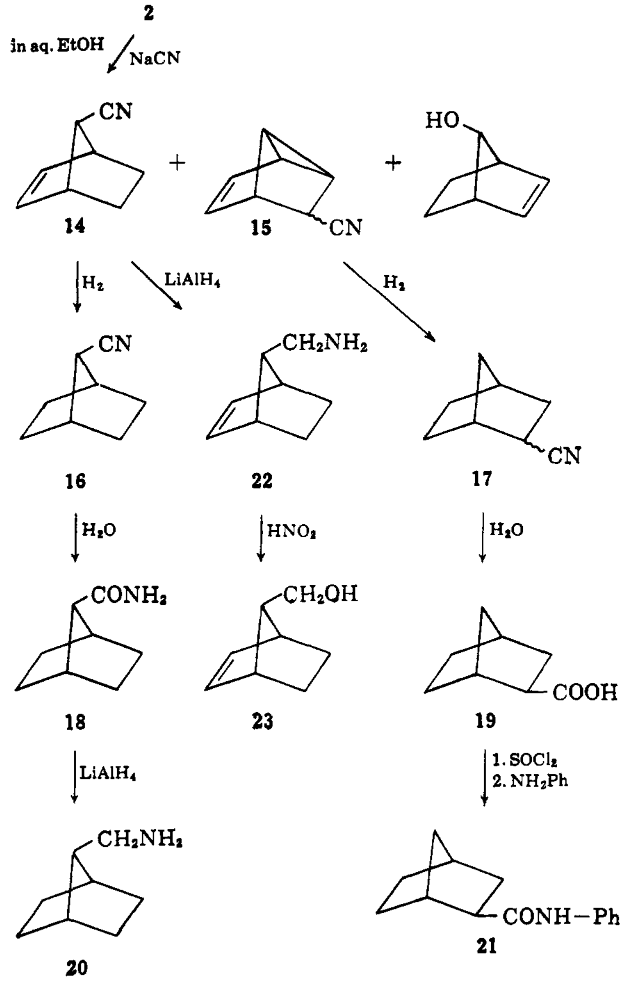
(10) J. W. Barrett, A. H. Cook, and R. P. Linstead, *J. Chem. Soc.*, 1065 (1935).

(11) (a) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (b) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963).

(12) M. C. Kloetzel, *Org. Reactions*, **4**, 10 (1948).

(13) W. R. Boehme, *J. Org. Chem.*, **26**, 2107 (1961).

Chart II



saturated nitrile was transformed by alkaline hydrolysis into a carboxylic acid which was identified as norbornane-*exo*-2-carboxylic acid (**19**) (Chart II) by mixture melting point and comparison of infrared spectra of the acid itself and the derived anilide **21** with the corresponding authentic samples.[14] On the basis of the above results, the original two nitriles **14** and **15** will be expected to be the *anti* or *syn* isomer of 7-cyanonorbornene and 2-cyanotricyclo[4.1.0.0^{3,7}]heptane, respectively.

By a study of the n.m.r. spectra of 7-substituted norbornadienes and norbornenes, several criteria for configuration assignment of the 7-substituent with respect to the double bond were recently reported by Snyder and Franzus.[15] As shown in Figure 1, the vinyl proton resonance of **14** at τ 4.01 approximated a triplet, which suggested the 7-cyano group may be *anti*. In order to obtain a chemical proof as to the orientation of the 7-cyano group, **14** was reduced by lithium aluminum hydride to the unsaturated methylamine **22**. Deamination of **22** with nitrous acid in glacial acetic acid followed by hydrolysis with methylmagnesium iodide yielded the expected methanol derivative **23** accompanying some unidentified byproducts. For identification, authentic *anti* and *syn* isomers of 2-norbornene-7-methanol[16] were prepared by lithium aluminum hydride reductions of the corresponding isomers of 7-carbomethoxynorbornene which were available according to the method of Sauers.[16b,17] As reported recently,[18] since the infrared spectrum of the *syn*-7-methanol does not exhibit an interaction between the hydroxyl group and the π-electrons of the double bond, the use of infrared spectroscopy would not be convincing to distinguish these isomeric methanols. The most characteristic property to assign configurations to these methanols was the gas chromatographic behaviors. In a column of 15% diethylene glycol succinate polyester on Chromosorb W, we observed that retention time of *anti*-7-carbomethoxynorbornene was shorter than that of *syn*-7-carbomethoxynorbornene and that, in agreement with Sauers' observation,[16b] 2-norbornene-*syn*-7-methanol was more rapidly eluted than 2-norbornene-*anti*-7-methanol which had the freer hydroxyl group and thus was bound more strongly to the column. Accordingly, retention time analysis confirmed the above methanol derivative **23** as 2-norbornene-*anti*-7-methanol and no formation of the *syn*-7-methanol in the deamination products (see Experimental).

Only one question in the reactions employed for the above structure proof might be a possibility of rearrangement on the deamination. Recently, some workers[16b,19] reported that acetolysis of the *p*-bromobenzenesulfonates of 2-norbornene-*syn*-7-methanol and 2-norbornene-*anti*-7-methanol proceeded without rearrangement yielding the corresponding acetates in more than 90% yield. Therefore, even if there are some different characters between these carbonium ion type reactions, that is deamination and acetolysis, the abundant formation of the unrearranged alcohol **23** on the deamination of **22** would be a sufficient proof for the assignment of orientation of the 7-cyano group of **14**. Consequently, the nitrile **14** was established as *anti*-7-cyanonorbornene.

The existence of a cyclopropyl ring in the structure of **15** was evidenced as follows. The n.m.r. spectrum of **15** exhibited no vinyl hydrogen. Although the isolation of a pure sample of **15** was not successful, gas chromatography and elementary analysis of a crude sample showed no impurity other than a little amount of the structural isomer **14**. Unfortunately, the evidence of a cyclopropyl ring was not clean-cut on the n.m.r. spectrum of **15**.[20] It is known that the near-infrared spectrum of cyclopropylmethylene group shows a characteristic first overtone in the 1.64-μ region and a combination band in the 2.24-μ region.[22] Although the spectrum of **14** exhibits two weak bands

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[14] (a) K. Alder, K. Heimbach, and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958); (b) H. Krieger, *Suomen Kemistilehti*, **B35**, 4 (1962); (c) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959).

[15] E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

[16] (a) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963); (b) R. R. Sauers and R. M. Hawthorne, Jr., *ibid.*, **29**, 1685 (1964).

[17] R. R. Sauers, *Chem. Ind.* (London), 176 (1960).

[18] L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, Jr., and L. Eberson, *J. Am. Chem. Soc.*, **86**, 650 (1964); also, see ref. 16b.

[19] R. K. Bly, R. S. Bly, and J. E. Goldberg, Abstracts of Papers, the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 6C.

[20] A tertiary cyclopropyl proton does not appear at the unusually high-field characteristic of the cyclopropyl methylene protons[21]: refer to ref. 22b. We observed this fact in the cases of some tricyclene and quadricyclene derivatives.

[21] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y. 1959, p. 52.

[22] (a) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958); (b) J. Meinwald, A. Lewis, and P. G. Gassman, *ibid.*, **84**, 977 (1962).

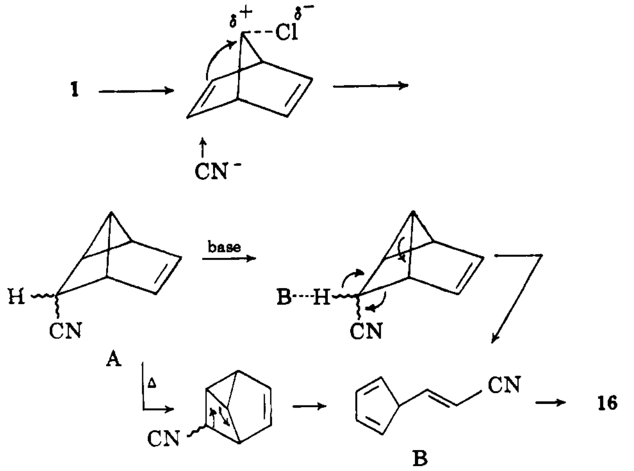
at 1.67 and 2.27 μ due to the double bond, much stronger bands observed at the same positions in the spectrum of **15** were assigned to a cyclopropane ring. Therefore, though it is somewhat nebulous, the structure of 2-cyanotricyclo[4.1.0.0^{3,7}]heptane was assigned for the nitrile **15**.[23] The orientation of the cyano group remained unknown.

To study the precise nature of this reaction, the rate was measured. The reaction of **2** with the equivalent quantity of sodium cyanide in 50% aqueous ethanol at 24.9° was followed to 70% completion by measuring the decreasing amount of the cyanide according to the method of Liebig and Dènigés (see Experimental). The reaction was determined to be first order, the rate constant being given by $k_1 = (1.54 \pm 0.12) \times 10^{-4}$ sec.$^{-1}$. The products and their ratio observed on this condition was the same to the above-mentioned results. A reference experiment, solvolysis of **2** in 50% aqueous ethanol at 26.5°, gave $k_1 = (3.02 \pm 0.06) \times 10^{-4}$ sec.$^{-1}$, that is a little higher than that obtained in the reaction with cyanide.

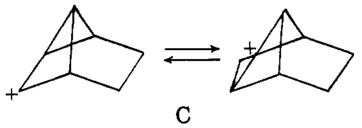
Discussion

The determination of the stereochemistry of the major product **14** formed in the reaction of **2** with sodium cyanide demonstrated convincingly retention of configuration in this reaction. No acceleration of the rate with the cyanide indicated that the reaction of **2** with sodium cyanide would be the S$_N$1 mechanism. It may be argued that the cyanide anions trapped carbonium ion intermediates formed in solvolysis. Therefore, the stereochemistry of this reaction and the high reactivities of **1** and **2** and the low reactivities of **3**, **4**, and **5** in this study are likely to be due to the presence or absence of participation in the transition state.[3,24]

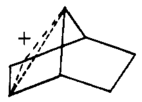
The formation of β-cyclopentadienylacrylonitrile (**6**) may be reasonably illustrated as follows. An intermediate A initially formed by the attack of a cyanide ion at the C-2 might be transformed into B by base-catalyzed rearrangement or by thermodynamic isomerization possibly due to the relief of the ring strain of A. The isomerization of B to a long conjugated form **16** in a protic solvent would be thermodynamically favored; however, we cannot decide whether this isomerization completely occurred in the solvent or in the transition state of the formation of maleic anhydride adduct **11**.[25-28]



Of considerable interest is that the ratios of the products formed by the attack of cyanide ions on C-2 and C-7 are significantly different between the reactions of **1** and **2**. Although we do not attempt to rationalize these observations at the present time, the repulsive forces between the negative charge on the attacking cyanide anion and the π-electrons of the anchimerically unassisted double bond of **1** might interfere with the front-side attack at C-7. Such an interference does not exist in the reaction of **2**, which results in the predominant attack of cyanide ions at C-7. Sauers[16b,17] demonstrated that almost equal amounts of *anti* and *syn* isomers of 7-carbomethoxynorbornene were found in a thermodynamically equilibrated mixture. The steric requirement of a cyano group is smaller than a carbomethoxyl group, so that the thermodynamic stabilities of *anti* and *syn* isomers of 7-cyanonorbornene would not be significantly different. Therefore, there is no reason to assume that the cyanide ions entering from the front side toward C-7 would be sterically more hindered by the $C_{5,6}$ ethylenic group of **1** than by the $C_{5,6}$ ethanic group of **2**. Consequently, steric effects do not appear to play an important role for the product distribution in this study.



C



D

An attempt to discuss the ideas of Brown's rapid equilibrium of the classical cation C[4a] and of Winstein's nonclassical cation D[4b] on the basis of our products formation was postponed until we have a more suitable evidence.

Experimental[29]

Materials—7-Chloronorbornadiene (**1**) and *syn*-7-chloronorbornene (**3**) were prepared by the methods of Winstein[30] and Roberts,[31] respectively. 7-Chloronorbornane (**4**)[31] was prepared by catalytic hydrogenation of **1** over platinum oxide.

***anti*-7-Chloronorbornene (2)**.—*anti*-7-Norbornenol[32] (5.8 g.) was treated with 6.28 g. of thionyl chloride in 25 ml. of anhydrous ether. After refluxing for 1 hr., the solution was washed with ice-water and distilled. There was obtained 2.5 g. (37%) of **2**, b.p.

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(23) As a referee pointed out, we do not estimate that this procedure is a complete structural elucidation of **15**. However, at the present time we have failed to find a more powerful technique to prove the cyclopropyl ring of the minor product **15**.

(24) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

(25) This is hydrogen shift like those of carboalkoxycyclopentadienes[26,27] and alkylcyclopentadienes.[28]

(26) (a) K. Alder, F. H. Flock, A. Hausweiler, and R. Reeber, *Chem. Ber.*, **87**, 1752 (1954); (b) D. Peters, *J. Chem. Soc*, 1761 (1959), and references therein cited.

(27) J. A. Berson and E. S. Hand, *J. Am. Chem. Soc.*, **86**, 1978 (1964).

(28) (a) R. Riemschneider, A. Reisch, and H. Horak, *Monatsh.*, **91**, 805 (1960); (b) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

(29) Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Unless stated otherwise, infrared spectra were determined with a Nippon Bunko IR-S spectrometer in carbon tetrachloride and carbon disulfide. N.m.r. spectra were determined at 60 Mc. with a Varian-60 spectrometer using tetramethylsilane as internal standard in deuteriochloroform.

(30) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(31) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

(32) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

70.5–71.5° at 60 mm., $n^{23}\mathrm{D}$ 1.4937, which was identified with an authentic sample prepared by the method of Roberts, *et al.*[31]

Similarly, 3-chloronortricyclene (**5**) was prepared from 3-nortricyclanol[33] by the reaction with thionyl chloride.

The Reaction of 7-Chloronorbornadiene (1) with Sodium Cyanide.—A solution of 2.2 g. (0.0175 mole) of **1** in 5 ml. of ethanol was slowly added to a stirred solution of 4 g. of sodium cyanide in 20 ml. of water and 50 ml. of ethanol under nitrogen atmosphere with ice cooling. After 0.5 hr. of stirring, the reaction mixture was poured into 300 ml. of water and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo* leaving *ca.* 2 g. of an oily residue, which was immediately transformed into β-cyclopentylpropionitrile (**7**) by catalytic hydrogenation over palladium on charcoal in ethanol or into 1-(β-cyanovinyl)-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**11**) by treatment with a benzene solution of maleic anhydride. The yield of **7** was 1.07 g. (50% from **1**), b.p. 96–96.5° at 19 mm., $n^{26}\mathrm{D}$ 1.4520 (lit.[9] b.p. 98–100° at 19 mm.).

Anal. Calcd. for $C_8H_{13}N$: C, 77.99; H, 10.64; N, 11.37. Found: C, 78.28; H, 10.52; N, 11.71.

The nitrile **7** was identified by comparison of infrared spectra and retention time analysis on gas chromatography with an authentic sample.

1-(β-Cyanovinyl)-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**11**) was recrystallized from methanol to give colorless crystals, m.p. 159°. The yield was 50% from **1**.

Anal. Calcd. for $C_{12}H_{19}NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.97; H, 4.47; N, 6.47.

β-Cyclopentylpropionic Acid (8) and Its Derivatives 9 and 10.—β-Cyclopentylpropionitrile (**7**) (2.2 g.) was heated under reflux with a solution of 1 g. of sodium hydroxide in 1 ml. of water and 5 ml. of ethanol. An acidic fraction was distilled to give 0.36 g. of **8** (60%), b.p. 100–101° at 4 mm., $n^{24}\mathrm{D}$ 1.4584 (lit. b.p. 134–136° at 14 mm.,[9] b.p. 131° at 6 mm.,[10] $n^{17.5}\mathrm{D}$ 1.4594[10]). Anilide **9** (prepared from β-cyclopentylpropionic chloride) had m.p. 107–109° (lit.[10] m.p. 110°); toluidide **10**, m.p. 97°.

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.75; H, 9.13; N, 6.01.

These three compounds were identified with authentic samples by mixture melting point, comparison of infrared spectra, and retention time analysis on gas chromatography.

1-(β-Cyanovinyl)-5-norbornene-*endo*-2,3-dicarboxylic Acid Monomethyl Ester (12).—A mixture of 0.41 g. of **11** in 1 ml. of methanol was heated under reflux for 4 hr. The reaction mixture was poured into water and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and evaporated leaving *ca.* 0.4 g. of crystals. Repeated recrystallization from a mixed solvent of cyclohexane and benzene gave 0.35 g. of colorless crystals of **12**, m.p. 127°.

Anal. Calcd. for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 62.96; H, 5.46; N, 5.34.

The Reaction of *anti*-7-Chloronorbornene (2) with Sodium Cyanide.—A solution of 10 g. (0.073 mole) of **2** in 10 ml. of ethanol was added to a stirred solution of 13.4 g. of sodium cyanide in 50 ml. of water and 120 ml. of ethanol under nitrogen atmosphere and refluxed for 3 hr. The reaction mixture was poured into *ca.* 1 l. of water and extracted with ether. The ether solution was washed with water, dried, and evaporated *in vacuo* leaving an oily residue. Elution chromatography of the residue on Merck neutral alumina isolated the minor product, *anti*-7-norbornenol, m.p. 117–118°, as the last isolable elute, whose identification was carried out with an authentic sample.[32] *anti*-7-Cyanonorbornene (**14**), b.p. 86° at 28 mm., $n^{25}\mathrm{D}$ 1.4815, was isolated as a main product by preparative gas chromatography from the residue.

The preparative gas chromatography was carried out at 150° with 14 mm. × 3 m. stainless steel U-type tube in a Yanagimoto gas chromatograph Model G.C.G. 3D and with a flow rate of 600 cc./min. of helium; the column was packed with 25% by weight of silicon 550 suspended on 30–60-mesh Shimalite. The retention time of **14** and **15** were 7 and 12 min.

The infrared spectrum of **14** showed bands at 3080 (m), 2960 (s), 2880 (m), 2260 (m), 1620 (s), 1575 (s), 1465 (m), 1455 (m), 1325 (s), 1130 (m), 980 (m), 910 (m), 875 (m), and 710 (s) cm.$^{-1}$.

Anal. Calcd. for C_8H_9N: C, 80.63; H, 7.61; N, 11.76. Found: C, 80.25; H, 7.61; N, 11.55.

In another run, the above oily residue was hydrogenated over palladium on charcoal in ethanol. After evaporation of the solvent, the saturated nitriles were distilled to give 7.3 g. of the fraction at b.p. 80–86° (24 mm.). It was the mixture of three compounds which were 7-norbornanol, 7-cyanonorbornane (**16**), and 2-cyanonorbornane (**17**) in the relative ratio of 33:49:18 on the basis of comparison of peak areas on gas chromatography.

7-Norbornanol, m.p. 150–151° (lit.[34] m.p. 150–151°), was removed by elution chromatography using Merck neutral alumina and petroleum ether. The mixture of **16** and **17** (1.05 g.) in a ratio of 79:21 was heated under reflux for 15 hr. with a mixture of 20 g. of 25% aqueous sodium hydroxide and 2 ml. of methanol. Precipitated norbornane-7-carboxamide (**18**) was obtained by filtration, and the aqueous layer was acidified and extracted with ether to obtain *exo*-2-norbornanecarboxylic acid (**19**). The amide **18** was purified by recrystallization from ethanol, 0.6 g. (60%) of colorless crystals, m.p. 199.5° (lit.[13] m.p. 198.5–199.5°).

Anal. Calcd. for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.36; H, 9.49; N, 10.00.

The yield of **19**, m.p. 48–49°, was 0.234 g. (94% from **17**) (lit.[14a] m.p. 56–57°). The acid **19** was converted into *exo*-2-norbornanecarboxanilide (**21**), m.p. 130° (lit.[14c] m.p. 130°), by treatment with thionyl chloride and aniline. Identifications of **18**, **19**, and **21** were carried out with authentic samples independently prepared.[13,14a,c]

7-Norbornylmethylamine (20).—In a Soxhlet extraction apparatus, 0.61 g. of **18** were extracted with 30 ml. of boiling ether charged with 0.515 g. of lithium aluminum hydride. After decomposition of excess lithium aluminum hydride with water, the ether layer was filtered to remove inorganic salts. Passing of dry hydrogen chloride gas into the ether solution precipitated 0.7 g. (99%) of the **20** HCl salt as colorless crystals, m.p. >240°.

The infrared spectrum (in Nujol) of **20** showed absorption bands at 3100 (s), 1600 (m), 1490 (m), 1310 (w), 1210 (w), 1130 (w), 1020 (w), 970 (w), 930 (w), 920 (w), 880 (w), 870 (w), and 800 (w) cm.$^{-1}$.

Anal. Calcd. for $C_8H_{15}N\cdot HCl$: C, 59.45; H, 9.98; N, 8.67. Found: C, 59.30; H, 9.82; N, 8.49.

***anti*-7-Norbornenylmethylamine (22).**—To a solution of 0.4 g. (3.4 mmoles) of **14**, 5 ml. of anhydrous ether, and 2 ml. of benzene was slowly added a solution of 114 mg. (3 mmoles) of lithium aluminum hydride in 3 ml. of anhydrous ether. The mixture was refluxed for 2 hr. with stirring, cooled, and treated with water and 2 *N* sodium hydroxide solution. The ether layer was separated and dried over anhydrous sodium sulfate. Passing of hydrogen chloride gas into the ether solution at Dry Ice–acetone temperature gave colorless crystals. Recrystallization from a solvent mixture consisting of ethanol and ether yielded 175 mg. (32%) of pure **22** HCl salt, m.p. >240°.

Anal. Calcd. for $C_8H_{14}ClN$: C, 60.18; H, 8.84; Cl, 22.21. Found: C, 60.20; H, 8.95; Cl, 22.00.

Deamination of 22.—To a solution of 55 mg. of **22** HCl salt, 2 ml. of glacial acetic acid, and 0.2 ml. of acetic anhydride was added 55 mg. of powdered sodium nitrite. After stirring for 5 hr. at room temperature, the reaction mixture was poured into water and extracted with petroleum ether. The petroleum ether solution was washed with aqueous sodium carbonate, dried over anhydrous sodium carbonate, and evaporated leaving an oil. The gas chromatography of this oil showed four peaks in the relative proportions 1:45:12:42 at the retention times of 8.2, 9.7, 11.3, and 13.5 min. in the acetate region after elution of about 10% of materials of short retention time (probably hydrocarbons). The largest peak was completely overlapped with that of the crude acetate obtained by treatment of the authentic 2-norbornene-*anti*-7-methanol[16b] with acetic anhydride. However, since the retention time of the crude samples of the *anti* and *syn* isomers of the acetate were almost same, the above oil was hydrolyzed without purification by treatment with excess methylmagnesium iodide in anhydrous ether followed by a usual work-up procedure.[35]

Gas chromatography of the hydrolyzed oily product exhibited five peaks in the relative proportions 8:11:45:30:6 at the retention times of 11.3, 13.4, 14.4, and 16.2 min. in the alcohol region. Retention time analyses with authentic samples of the *anti* and *syn* isomers of 2-norbornene-7-methanol prepared by the method of Sauers[16b,17] confirmed that the largest peak was that of 2-norbornene-*anti*-methanol (**23**) and that the *syn* isomer was not

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[33] L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

[34] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[35] As a standard procedure, for example, refer to H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 852 (1964).

present. A sample of **23** isolated by gas chromatography had the same retention time as that of the crude **23**, proving no change in the column, and had n^{25}_{D} 1.4974 (lit.[16b] b.p. 61° at 0.25 mm., n^{27}_{D} 1.4970) and infrared spectrum identical with that of the authentic *anti* sample.

The other peaks were not identified. Their appearance may be due to the rearranged products on the deamination, to the isomerization products of **22** HCl salt, or to the by-products on the hydrolysis step.[36]

The gas chromatographic analyses were carried out at 180° with 6 mm. × 3 m. stainless steel tube in a Shimadzu gas chromatograph Model GC-1B and with a flow rate of 100 ml./min. of helium. Retention times on a column of 15 wt.% of diethylene glycol succinate polyester on acid-washed, 30–60-mesh Chromosorb W were for 2-norbornene-*syn*-7-methanol, 11.9 min., and for the *anti*-7-methanol **23**, 14.4 min.

Kinetic Measurements of the Reaction of *anti*-7-chloronorbornene (2) with Sodium Cyanide.—As a solvent for kinetics, 50% aqueous ethanol was prepared by mixing equal parts by volume of absolute ethanol and water. Samples of approximately 0.04 mole each of **2** were weighed into eight 10-ml. volumetric flasks. Then each of the flasks was filled with a solution of 49.40 mmoles of sodium cyanide in 10 ml. of 50% aqueous ethanol, already equibrated thermally in a thermostat at 24.9°. The dissolution of **2** was facilitated by shaking. The flasks were kept in the thermostat, and at recorded times the contents of each flask were drained into a titration flask containing 20 ml. of cold acetone. The amount of remaining sodium cyanide, and thereby the amount of remaining **2**, was determined by titrating with 0.01 N silver nitrate solution according to the Liebig–Dènigés method.[38]

A plot of $\ln a/(a - x)$ *vs.* time was a straight line; a was the initial concentration of **2**, and x was the amount of **2** that had reacted. The rate constant, $(1.54 \pm 0.12) \times 10^{-4}$ sec.$^{-1}$ at 24.9°, was obtained from the slope of the linear plot. A plot of

$$\frac{1}{b - a} \ln \frac{a(b - x)}{b(a - x)} \textit{ vs. } t$$

resulted in upwards curvature; a and b were the initial concentrations of **2** and sodium cyanide, respectively, x was the amount of the substrates that had reacted, and t was time.

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[36] Since the submission of our first draft, Berson and Gajewski[37] noticed the formation of various kinds of the rearranged products on the deamination of **22**. Their observation does not contrast with our results.

[37] J. A. Berson and J. J. Gajewski, *J. Am. Chem. Soc.*, **86**, 5020 (1964).

[38] Refer to F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1935, p. 657.

Quinone Dehydrogenation. I. The Oxidation of Monohydric Phenols

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2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is found to be a powerful oxidizing agent for phenols. The high yield reaction proceeds smoothly at room temperature in methanol solution and, depending on the structure of the phenol, leads to oxidative dimerization by either C–C or C–O coupling, oxidative debromination, or oxidative cleavage of hydroquinone monoethers and *p*-hydroxybenzyl ethers, as well as to benzylic oxidation. 2,4,6-Tri-*t*-butylphenol reacts with DDQ to yield 4-(2,3-dichloro-5,6-dicyano-4-hydroxyphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one which easily dissociates into radicals as demonstrated by an interesting aryloxy exchange reaction. 2,6-Di-*t*-butyl-4-methylphenol upon treatment with DDQ yields a crystalline dimer of 2,6-di-*t*-butyl-4-methylphenoxy radical, which in solution dissociates into the blue-colored monomer. Its disproportionation into 2,6-di-*t*-butyl-4-methylphenol and 2,6-di-*t*-butyl-1,4-quinone methide has been studied by spectroscopic and chemical means. The mechanism for the oxidation of phenols by DDQ is discussed.

Numerous papers, including several recent review articles, published during the last 15 years on the oxidation of natural and synthetic antioxidants reflect the general interest in this field of organic chemistry.[1–3] A large number of oxidizing agents of both heterolytic and homolytic nature have been employed in the oxidation of phenols. Quinones, however, apparently have not been used previously for the oxidation of monohydric phenols since "the scope of quinone dehydrogenation has not been fully established."[4] In this study 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (abbreviated henceforth DDQ) is introduced as an oxidizing agent for phenols.

DDQ was first synthesized almost 60 years ago by Thiele and Günther,[5] but only during the last decade was its usefulness in the dehydrogenation of hydroaromatic systems recognized.[6] The oxidation potential of DDQ is *ca.* 1.0 compared with 0.71 v. for chloranil.[4] In the dehydrogenation of tetraline, for instance, DDQ reacts 5500 times faster than chloranil that is commonly used in dehydrogenation reactions.[4] DDQ was employed successfully in dehydrogenating steroids,[7,8] the selective oxidation of steroidal allylic[9] alcohols, and also recently in the cleavage of steroidal enol ethers.[10]

When DDQ was applied earlier in the selective oxidation of benzyl alcohols, it was found to convert secondary *p*-hydroxybenzyl alcohols smoothly into the corresponding *p*-hydroxyphenyl alkyl ketones, a reaction in which the phenolic group appeared unattacked.[11] It has now been found that phenols are easily oxidized by DDQ. The present paper deals with the oxidation of substituted monohydric phenols and some reactions observed on highly reactive quinol ethers prepared in the course of this study.

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[4] L. M. Jackman in "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 329.

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[8] See also H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

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