The Reaction of Norbornene with Polyhalomethanes and the Behavior of the Adducts towards Acid and Base

ERICH TOBLER AND DONALD J. FOSTER

Research and Development Department, Olefins Division, Union Carbide Corporation, South Charleston, West Virginia

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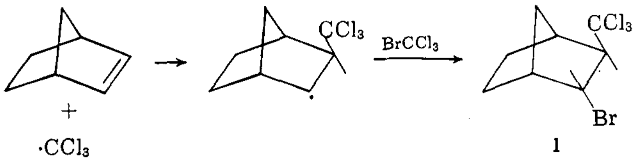
The radical-catalyzed addition of chloroform, carbon tetrachloride, and bromotrichloromethane to norbornene has been studied and evidence has been obtained indicating that the latter two add in a *trans* manner. Dehydrohalogenation of the adducts results in the formation of the corresponding dichloromethylene compounds. The *exo* and *endo* isomers of 2-dichloromethylene-3-halobicyclo[2.2.1]heptanes yield 2-dichloromethylene-3-*exo*-hydroxybicyclo[2.2.1]heptane upon hydrolysis. The corresponding *endo*-hydroxy isomer is obtained by oxidation of the *exo* isomer and subsequent reduction with sodium borohydride.

In studying the reactivity of olefinic double bonds in free-radical reactions, Kharasch and Friedlander[1] reported the results of their investigations of the ultraviolet light catalyzed radical addition of bromotrichloromethane to a series of olefins. All of the addition products, with the exception of those from bicyclic olefins, lost halogen easily when treated with base. Fawcett[2] suggested that the addition was a *trans* process with the trichloromethyl radical attacking from the less hindered *exo* side and the bromotrichloromethane molecule approaching the intermediate from the side opposite to the trichloromethyl group in the chain transfer step. The stability of the bicyclic adducts was explained in terms of the fact, that hydrogen halide cannot be eliminated, because the only hydrogen which could be lost without producing a bridgehead olefin (Bredt's rule) lies *cis* to the bromine. However, later data suggested[3] that such a generalization is doubtful in the case of bridged-ring compounds, thus rendering invalid a proof of the *trans* conformation of the adduct on these grounds. Since literature data on the reaction of norbornenes with free radicals seem to indicate a preference for *exo-cis* addition[4,5,6] and because of the claim that the dipole moment of the chloroform and bromotrichloromethane addition product also suggested *cis* addition,[7] we reinvestigated the addition of polyhalomethanes to norbornene.



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Treatment of norbornene with carbon tetrachloride in the presence of benzoyl peroxide gives a single addition product[8] (as shown by v.p.c. analysis of the original reaction product) in 91% yield. Whereas the adduct is very stable towards aqueous base, the trichloromethyl group is readily hydrolyzed to the carboxyl group by 96–97% sulfuric acid. Although some structural changes have to be expected under such harsh conditions, the formation of 3-*endo*-chlorobicyclo[2.2.1]-heptane-2-*exo*-carboxylic acid (**3**, identical with the chloro acid obtained by Alder, *et al.*[9]) in a 75% yield is in support of the *trans* configuration of the norbornene–carbon tetrachloride adduct (**2**). Additional evidence for the *endo* position of the chlorine atom in **2** is the formation of 2-dichloromethylene-3-endo-chlorobicyclo-[2.2.1]heptane (**7**) when **2** is treated with alcoholic base. The *endo*-chloro structure of **7** can be established by a comparison of its n.m.r. spectrum with that of its *exo*-chloro isomer **9** (see below.)

The structure proof of **2** by n.m.r. analysis is less straightforward. The n.m.r. spectrum of the adduct shows a poorly resolved triplet (relative area 1) at 4.22 p.p.m. which is assigned to the chloro proton H-3, a quartet at 2.58 p.p.m. which is assigned to the trichloromethyl proton H-2 and which is superimposed on the two bridgehead proton signals (combined relative area 3), and a complex band at high field (relative area 6) representing three methylene groups. The quartet has coupling constants of 1.7 and 6.1 c.p.s. The absence of a coupling constant approximating 4.0–4.5 c.p.s. is indicative of an *endo* configuration for the proton, thus establishing the trichloromethyl group as *exo*. The center peak of the triplet is broadened and exhibits fine splitting, signs that this signal may be in reality a quartet whose inner lines are coincident. Although coupling constants cannot be measured accurately, the splittings appear to be ~6 and ~4.5 c.p.s. with an additional fine splitting of ~1–2 c.p.s. The 6.1-c.p.s. coupling constant of the quartet seems too large to assign to a *trans* H-2–H-3 interaction; and, if the 1.7 c.p.s. coupling is assigned to this interaction, the 6.1-c.p.s. coupling is too large for a $J_{1,2}$ which should approach zero,[10] or a $J_{2,7\text{-}anti}$[11] which is expected to have a value of 3 c.p.s. or less. On the other hand, if the 6.1-c.p.s. coupling of the quartet is assigned to a *cis* H-2–H-3 interaction, the 1.7-c.p.s. coupling can be assigned to a $J_{2,7\text{-}anti}$. The ~6-c.p.s. splitting of the triplet is consistent with this, but its ~4.5-c.p.s. splitting is higher than normal for a $J_{3,7\text{-}anti}$. However, in view of the uncertainty in the measurement of the ~4.5-c.p.s. value, this assignment cannot be ruled out. Williamson[12] and Laszlo and Schleyer[13] have demonstrated that

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[1] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[2] E. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

[3] (a) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952); (b) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

[4] S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957).

[5] J. A. Berson and R. Swidler, *ibid.*, **75**, 4366 (1953); **76**, 4060 (1954); J. A. Berson, *ibid.*, **76**, 5748 (1954).

[6] J. Weinstock, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept., 1955, p. 19O.

[7] V. A. Rolleri, *Dissertation Abstr.*, **19**, 960 (1958).

[8] This addition product of "unspecified stereochemistry" has been described by F. D. Greene and W. W. Rees [*J. Am. Chem. Soc.*, **82**, 890 (1960)].

[9] K. Alder, R. Hartmann, and W. Roth, *Ann.*, **613**, 6 (1958).

[10] F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

[11] J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, 18th National Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June, 1963; *J. Am. Chem. Soc.*, **85**, 2514 (1963).

[12] K. L. Williamson, *ibid.*, **85**, 516 (1963).

[13] P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2709 (1963).

the magnitude of coupling constants between protons on vicinal saturated carbon atoms depends significantly on substituent electronegativities; and Flautt and Erman[14] have reported trans splittings of 6.0 c.p.s. in *o*-bornylphenol and *o*-bornylanisole. If a 6.1-c.p.s. coupling constant is reasonable for the *trans* proton in **2**, the ~4.5-c.p.s. splitting in the triplet is readily assigned to $J_{4,3\text{-}exo}$ and the ~1–2-c.p.s. splitting (if it is real) may be assigned to $J_{3\text{-}exo,5\text{-}exo}$.

A similar stereochemistry may be inferred for the addition of bromotrichloromethane to norbornene to give 2-*exo*-trichloromethyl-3-*endo*-bromobicyclo[2.2.1]-heptane[1] (**1**). Chloroform adds either in a *cis* or a *trans* manner to afford 2-*exo*-trichloromethylbicyclo-[2.2.1]heptane[7] (**4**).

All three adducts (**1**, **2**, and **4**) eliminate 1 mole of hydrogen halide when treated with potassium hydroxide in refluxing methanol or ethanol. In the case of **4**, the dehydrochlorination product must be the dichloromethylene compound[7] (**5**). A similar elimination takes place in **1** and **2** to give 2-dichloromethylene-3-*endo*-bromobicyclo[2.2.1]heptane (**6**) and 2-dichloromethylene-3-*endo*-chlorobicyclo[2.2.1]heptane (**7**), respectively. If elimination of hydrogen halide would occur in such a manner as to give a 2,3-double bond, the dehydrohalogenation products of **1** and **2** would be identical (**8**). The findings are supported by the infrared spectra (strong absorption band in the 6.05–6.10- and two strong bands in the 11.0–11.3-μ region) and by the n.m.r. spectrum of **7**. A peak at 4.63 p.p.m. is consistent with a proton (position 3) having a chlorine atom on the same carbon and a double bond at position 2. In the case of a vinyl proton as in **8**, the signal would fall at lower field. These results are in agreement with the findings of Davies,[15] who found that the addition products of carbon tetrachloride and bromotrichloromethane to aldrin upon treatment with base eliminate hydrogen chloride in the same manner.

On long-continued heating the *endo* compound **7** is isomerized to the thermodynamically more stable *exo* compound **9**. Woodward,[16,17] Craig,[18] Berson,[19] Alder,[20] Kwart,[21] and Rondestvedt[22] have reported examples of this phenomenon and a detailed description of the events that occur in the interconversion of *endo–exo* isomers has been reported by Craig,[18] Woodward,[16] Alder,[23] and Berson.[24]

The n.m.r. spectra of the isomers are very similar except for the chloro proton resonances H-3 occurring at 4.63 p.p.m. (*endo* isomer **7**) and 4.27 p.p.m. (*exo* isomer **9**). The paramagnetic shift of this resonance with respect to an unsubstituted methylene group arises from the deshielding effect of the chlorine atom attached to the same carbon. The observed chemical shifts are reasonable for an allylic proton having a chlorine atom on the same carbon.[25] The 4.63-p.p.m. signal has a coupling constant J = 4.4 c.p.s. and the 4.27-p.p.m. signal has a coupling constant J = 2.0 c.p.s. Anet[10] has shown (in the case of the camphane-2,3-diol isomers) that the coupling constant between the bridgehead proton H-4 and the adjacent proton H-3 is of the order of 4.0–4.4 c.p.s. if the adjacent proton is *exo* and zero if it is *endo*. The apparent discrepancy in the case of **9** (nonzero coupling constant of the *endo* proton H-3) could be explained by the fact, that the combined presence of an *exo*-chloro atom on the C-3 and an exocyclic dichloromethylene on the C-2 introduces sufficient strain in the ring to distort the protons in question from their normal dihedral angle. A similar distortion of the ring has been observed in the case of the oxymercuration product of norbornene, in which the *endo* proton H-3 was found to have a nonzero coupling constant (J = 2.1 c.p.s.).[26] However, in the light of more recent investigations it seems more likely, that the nonzero coupling constant arises by long-range spin–spin coupling between the *endo*-3- and *anti*-7-protons. It has been demonstrated in the case of 3-*exo*-halobicyclo-[2.2.1]heptan-2-ones (J = 3 c.p.s.) that when a methoxy group is introduced into the *anti*-7-position the J value becomes indeed zero.[11]

The allylic halogen atom in **6**, **7**, and **9** does not seem to be quite so labile as in other allylic systems.[27] Refluxing with aqueous acetone for 24 hr. results only in 10–20% of hydrolysis. However, with aqueous silver nitrate at room temperature, the three compounds are converted in high yields to a mixture of a hydroxy compound **10**, m.p. 72–72.5°, and the corresponding nitrate ester **11**. The hydroxy compound **10** is the only product formed (in yields exceeding 90%) when any of the three compounds is refluxed with aqueous lithium carbonate for 25 hr. Subsequent reactions of **10** confirmed its structure as 2-dichloromethylene-3-*exo*-hydroxybicyclo[2.2.1]heptane, the normal substitution product, formed by *exo* attack of the hydroxyl ion. (See Chart I.)

Heating **10** with nitric acid for a short period of time yields the nitrate ester **11** as the main product, indicating that the hydroxyl group is in the *exo* position. According to Toivonen,[28] the *endo* forms are oxidized to the ketones, whereas the *exo* forms are esterified to the nitrate esters in this reaction. Oxidation of **10** with nitric acid under more vigorous reaction conditions affords the ketone **12** as the main product. The ketone was isolated as the semicarbazone and subsequently regenerated by steam distillation in the presence of oxalic acid. The absence of a carbonyl band lower than 5.70 μ in the infrared excludes the presence of the carbonyl group in the 7-position.[29] The absence of a band at 7.11 μ excludes all ketones having a methylene group adjacent to the ketone carbonyl,[30] thus leaving as the only possible structure that of 2-dichloromethylene-bicyclo[2.2.1]heptan-3-one (**12**).

Reduction of **12** with sodium borohydride affords a new hydroxy compound **13**, m.p. 48–49°, in 76% yield. Ketones in the norbornene series are known to be reduced by *exo* attack of the reagent giving the more

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[14] T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963).

[15] D. I. Davies, *J. Chem. Soc.*, **1960**, 3669.

[16] R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1945).

[17] R. B. Woodward and H. Baer, *ibid.*, **70**, 1161 (1948).

[18] D. Craig, *ibid.*, **73**, 4889 (1951).

[19] J. A. Berson and R. Swidler, *ibid.*, **75**, 1721 (1953).

[20] K. Alder, *et. al.*, *Ann.*, **504**, 219 (1933).

[21] H. Kwart and I. Burchuk, *J. Am. Chem. Soc.*, **74**, 3094 (1952).

[22] C. S. Rondestvedt and C. D. Ver Nooy, *ibid.*, **77**, 4878 (1955).

[23] K. Alder and W. Trimborn, *Ann.*, **566**, 58 (1950).

[24] J. A. Berson, R. D. Reynolds, and W. M. Jones, *J. Am. Chem. Soc.*, **78**, 6049 (1956); J. A. Berson and A. Remanick, *ibid.*, **83**, 4947 (1961).

[25] Compare 4.15 p.p.m. for 2,3-dichloropropene.

[26] M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961).

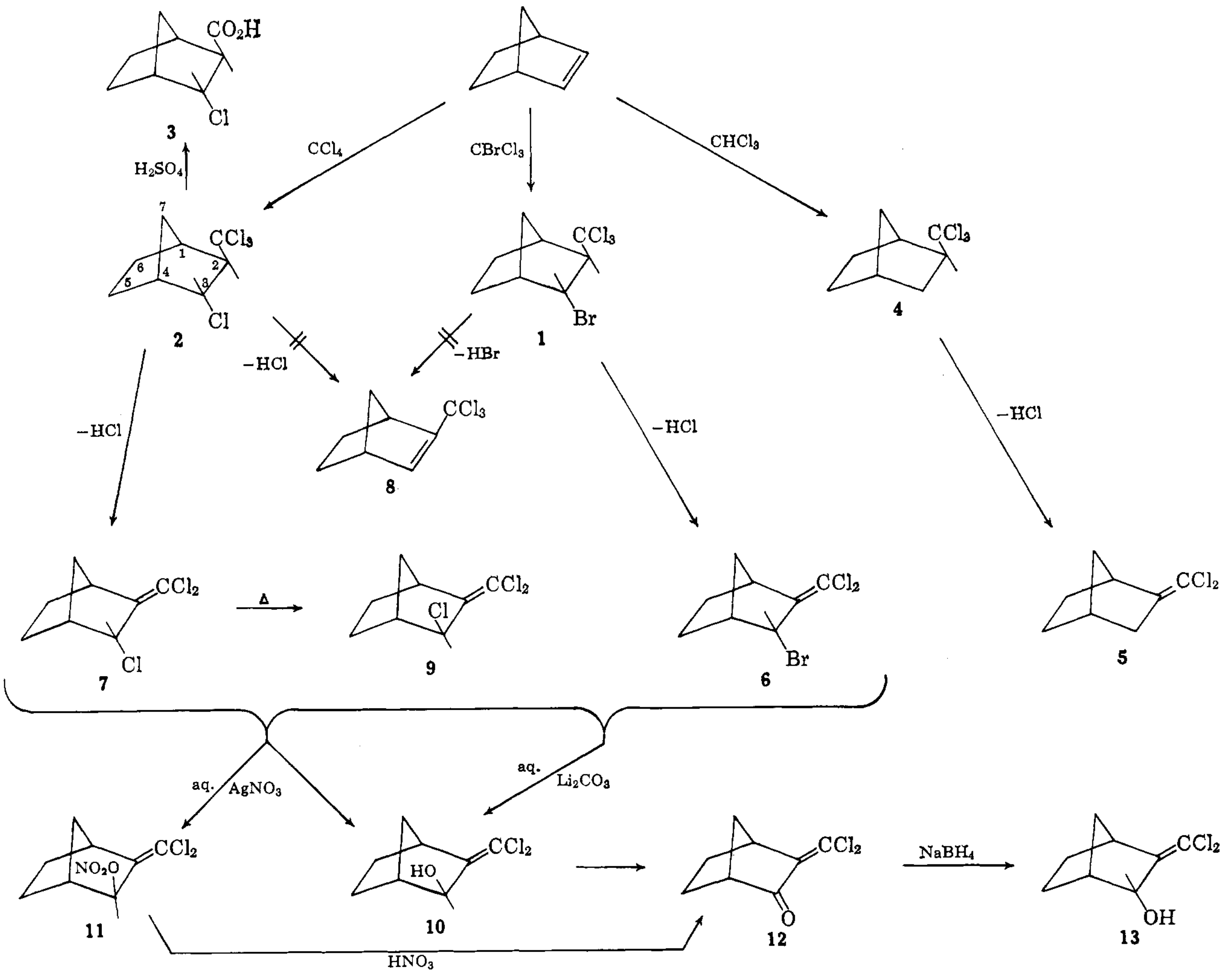
[27] See for instance 2,3-dibromocyclohexene, J. Sonnenberg and S. Winstein *J. Org. Chem.*, **27**, 748 (1962).

[28] H. Toivonen, *Suomen Kemistilethi*, **25B**, 69 (1952).

[29] C. H. Depuy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960), and references cited.

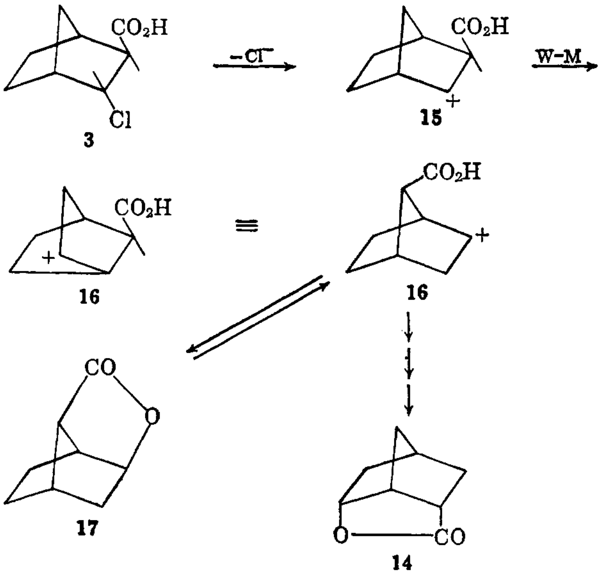
[30] S. A. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

Chart I



hindered alcohol in high proportions.[31] The n.m.r. spectra of the two isomeric hydroxy compounds **10** (*exo*) and **13** (*endo*) are consistent with the assigned structures. The spectrum of **13** in pyridine solution shows a doublet with a relative area of 1 at 4.66 p.p.m. for the proton H-3. The value of the coupling constant, $J = 4.5$ c.p.s., is characteristic of the interaction between an *exo* proton and its neighboring bridgehead proton in a norbornene system.[10] Furthermore, the paramagnetic shift of the H-3 resonance frequency in **13** with respect to **10** (4.35 p.p.m.) establishes H-3 as having an *exo* conformation in **13** and an *endo* conformation in **10**. In **10** the H-3 signal is a multiplet, probably a poorly resolved quartet with approximate coupling constants of 0.8 and 2.0 c.p.s. The large coupling probably involves the *anti*-7-proton,[11] the value being identical with that found for the corresponding *exo*-chloro compound **9**. The identity of the other proton involved in the small coupling is conjectural.

Upon hydrolysis of **2** with sulfuric acid, a small amount of a lactone is obtained, which was subsequently identified as **14**. Apparently **14** is formed from the chloro acid **3** since treatment of **3** with 50% sulfuric acid at room temperature results also in the formation of **14**. Evidently the formation of **14** proceeds *via* the carbonium ions **15** and **16** or by the way of the corresponding nonclassical carbonium ions. The anhydride **17**, which was actually the expected product or at least an intermediate in the formation of **14**, could not be detected. However, it is feasible that the carbonium ion **16** leads to the lactone **14** either by a combination of Wagner–Meerwein rearrangements and a series of hydride shifts or *via* the intermediate formation of the unsaturated acid **18**. It has been demonstrated,



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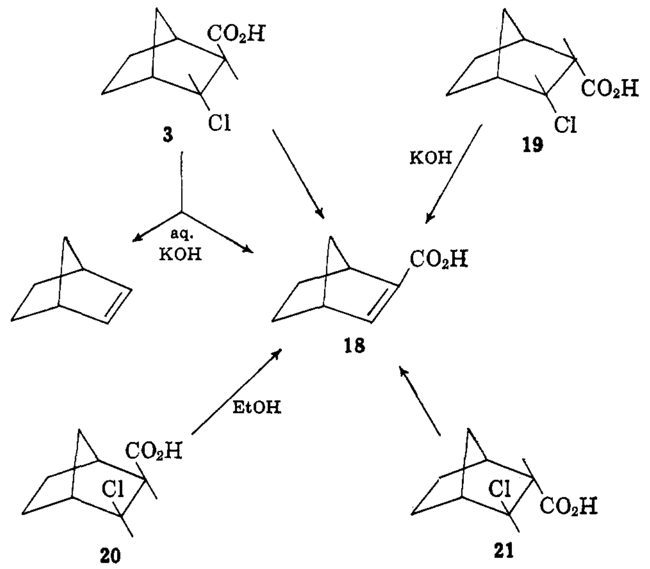
[31] J. Meinwald, J. K. Crandall, and P. G. Gassmann, *Tetrahedron*, **18**, 815 (1962), and references cited.

that **17** is readily converted to **14** and that the latter is the only stable end product.[32]

Similarly, hydrolysis of **7** with 96% sulfuric acid gives a mixture of compounds consisting mainly of **14**. The reaction probably proceeds through the intermediate formation of the chloro acid **3**, or the isomeric acid **19**, which is then transformed to the lactone **14**.

The chloro acid **3** appears to be more resistant towards hydrogen chloride elimination than the addition product **2**. After refluxing **3** in methanolic potassium hydroxide for 3 hr., 89.5% of the starting material is recovered unchanged. However, when the reaction is carried out in refluxing ethanol, a 72% yield of the unsaturated acid **18** is obtained. This acid is also obtained by similar treatment of the isomeric chloro acids **19**, **20**, and **21**.[9] The physical data of **18** are identical with those of the acid described by Finnegan and McNees[33] and by Witt and Schneider.[34] When **3** is refluxed in aqueous potassium hydroxide the formation of **18** is accompanied by an appreciable amount of norbornene. Refluxing the unsaturated acid **18** in aqueous potassium hydroxide for 5 hr. results in a mixture of starting material and a hydroxy acid (**22**), m.p. 134–135°,[35] whereas norbornene is not formed in this reaction. This indicates, that norbornene is formed directly from the chloro acid **3** by decarboxylative dechlorination[36] rather than by decarboxylation of the unsaturated acid **18**.



The present investigation shows clearly that the free-radical addition of polyhalomethanes to norbornenes is highly stereospecific favoring *trans* addition. Exclusive *trans* addition was also reported for the addition of polyhalomethanes to aldrin[15] and for the addition of *p*-toluenesulfonyl chloride to norbornene and aldrin.[37] On the other hand, exclusive *exo-cis* addition of *p*-thiocresol to 6-chloroaldrin has been observed,[4] and ethyl bromoacetate has been reported to give *exo-cis* addition with norbornene.[6]

In order to explain early stereospecific additions of hydrogen bromide, a bridged intermediate radical, similar in nature to the bromonium ion, was proposed [38] Berson and Swidler[5] have suggested a mesomeric radical, analogous to the nonclassical carbonium ion, to explain the formation of their *exo-cis* dibromide by the free-radical bromination of various substituted norbornenes (and 7-oxa analogs), a result opposite in nature to the exclusive *trans* addition observed in the free-radical addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene.[38] A possible explanation for the substantial number of nonspecific reactions is that an equilibrium exists between bridged and nonbridged intermediates such that one isomer would be formed from the bridged structure and the other isomer from the open intermediate radical. However, this explanation offers no particular advantage and stereochemical results of addition reactions can be accounted for satisfactorily in terms of an open (classical) radical[4] and the fact that the direction from which chain transfer occurs is controlled by steric factors. The exclusive *trans* addition observed in the present investigation can thus be explained by the large steric requirement for the trichloromethyl group. Models indicate that the approach of a molecule of carbon tetrachloride or bromotrichloromethane to the intermediate radical is inhibited in the *exo* direction by steric interference from the large trichloromethyl group. Thus the occurrence of chain transfer from the *endo* direction is favored. Similar conclusions have been advanced for the principal *trans* addition observed with *p*-toluenesulfonyl chloride.[37]

Experimental

All melting points are corrected. Infrared spectra (Beckman infrared 4) were determined in carbon tetrachloride and carbon disulfide solution or by the KBr disk technique. N.m.r. spectra were determined with a Varian A60 spectrometer with tetramethylsilane as an internal standard. Vapor phase chromatography (Beckman GC-2A gas chromatograph) was performed on a 4-m. column containing silicone DC550 on Chromosorb W (30–60) at 190° and a helium pressure of 55 p.s.i.

2-*exo*-Trichloromethyl-3-*endo*-chlorobicyclo[2.2.1]heptane (2).—A mixture of 94.0 g. of norbornene (1.0 mole), 1250 ml. of carbon tetrachloride, and 1.0 g. of benzoyl peroxide was refluxed for 24 hr. Vapor phase chromatography of the crude product (after removal of the carbon tetrachloride) showed a single peak with a retention time of 24 min. Distillation of the reaction product gave 225.2 g. (91%) of **2**, b.p. 75–76° at 0.4 mm., n^{24}_{D} 1.5325 (lit.[8] b.p. 132–135° at 9 mm., n^{30}_{D} 1.5298).

Anal. Calcd. for $C_8H_{10}Cl_4$: C, 38.74; H, 4.06; Cl, 57.20. Found: C, 39.26; H, 4.11; Cl, 56.84.

2-*exo*-Trichloromethylbicyclo[2.2.1]heptane (4).—A mixture of 94.0 g. of norbornene (1.0 mole), 1250 ml. of chloroform, and 1.0 g. of benzoyl peroxide was refluxed for 45 hr. Distillation of the reaction product afforded 180.8 g. (85%) of **4**, b.p. 46–48° at 0.3 mm., n^{25}_{D} 1.5140.

Anal. Calcd. for $C_8H_{11}Cl_3$: C, 45.01; H, 5.19; Cl, 49.81. Found: C, 45.41; H, 4.49; Cl, 49.53.

2-*exo*-Trichloromethyl-3-*endo*-bromobicyclo[2.2.1]heptane (1).—A mixture of 47.0 g. of norbornene (0.5 mole), 325 g. of bromotrichloromethane (1.64 mole), and 0.5 g. of benzoyl peroxide was refluxed for 7 hr. Distillation of the reaction mixture gave 112.7 g. (77%) of **1**, b.p. 88–89° at 0.3 mm., n^{25}_{D} 1.5517 (lit.[1] b.p. 70–75° at 0.1 mm., n^{20}_{D} 1.5538).

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(32) S. Beckmann and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).

(33) R. A. Finnegan and R. S. McNees, *Chem. Ind.* (London), 1450 (1961).

(34) J. W. Witt and C. A. Schneider, *ibid.*, 951 (1963).

(35) The hydroxybicyclo[2.2.1]heptanecarboxylic acid (**22**) of unknown spacial configuration is also obtained by refluxing the chloro acid **19** with aqueous lithium carbonate, whereas a similar treatment of **3** and its *exo*-chloro isomer **20** results in the formation of a hydroxy acid (**23**), m.p. 144–144.5°.

(36) For examples of the concurrent elimination of HX and CO_2, see, *e.g.*, W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd Ed., Longmans, Green and Co., London, 1948, p. 237.

(37) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).

(38) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

Anal. Calcd. for $C_8H_{10}BrCl_3$: C, 32.86; H, 3.45; Br, 27.33; Cl, 36.37. Found: C, 32.94; H, 2.77; Br, 27.01; Cl, 35.93.

2-Dichloromethylenebicyclo[2.2.1]heptane (5).—To 106.8 g. of **4** (0.5 mole) was added from a dropping funnel within 2 hr. a solution of 56 g. of potassium hydroxide (1.0 mole) in 300 ml. of methanol. At the end of the addition, the mixture was refluxed for 4 hr. After cooling to room temperature, 70 ml. of water was added. The organic layer was removed, the aqueous layer was extracted four times with ether, and the combined organic layers were washed four times with water. After drying over calcium chloride, the ether was distilled off at atmospheric pressure and the residue was fractionated at 0.2 mm. to give 40.7 g. (46%) of **5**, b.p. 33–34° at 0.2 mm., $n^{25}D$ 1.5200. Compound **5** was also obtained by thermal decomposition of **4** (refluxing at atmospheric pressure).

Anal. Calcd. for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69; Cl, 40.04. Found: C, 53.77; H, 5.19; Cl, 39.80.

The infrared spectrum of **5** shows an intense C═C stretching vibration at 6.05 and strong absorptions at 11.03 and 11.22 μ.

2-Dichloromethylene-3-*endo*-bromobicyclo[2.2.1]heptane (6).—The adduct **1** (87.8 g., 0.3 mole) was treated with a solution of 33.6 g. of potassium hydroxide (0.6 mole) in 150 ml. of methanol as described above for the conversion of **4** to **5**. Fractional distillation afforded 41.5 g. (54%) of **6**, b.p. 70–71° at 0.3 mm., $n^{25}D$ 1.5670.

Anal. Calcd. for $C_8H_9BrCl_2$: C, 37.53; H, 3.54; Br, 31.22; Cl, 27.70. Found: C, 37.66; H, 3.01; Br, 30.58; Cl, 28.02.

Strong infrared absorptions were at 6.10, 10.99, and 11.17 μ.

2-Dichloromethylene-3-*endo*-chlorobicyclo[2.2.1]heptane (7) and 2-Dichloromethylene-3-*exo*-chlorobicyclo[2.2.1]heptane (9). A.—The adduct **2** (102.5 g., 0.414 mole) was treated with a solution of 47.0 g. of potassium hydroxide (0.840 mole) in 250 ml. of methanol as described above for the conversion of **4** to **5**. Fractional distillation gave 80.1 g. (91%) of **7**, b.p. 64–65° at 0.3 mm., $n^{20}D$ 1.5445.

Anal. Calcd. for $C_8H_9Cl_3$: C, 45.43; H, 4.29; Cl, 50.28. Found: C, 45.29; H, 4.14; Cl, 49.74.

Characteristic infrared absorptions were at 6.04, 10.92, 11.12, 12.40, 12.73 and 13.30 μ.

According to the n.m.r. spectrum, this sample contained approximately 6% of the corresponding *exo*-chloro compound **9**.

B.—Compound **2** (24.9 g., 0.1 mole) was heated to reflux for 8 hr. During this time, the kettle temperature dropped from 272 to 255°. After work-up, distillation yielded 14.5 g. of distillate, containing 77% **7** plus **9** according to vapor phase chromatography. N.m.r. analysis indicated the mixture to consist of 56% **7** and 44% **9**.

C.—A 30-g. sample of **7** (containing 6% of **9**) was heated to 160° for 3 hr. in the presence of steel column packing. According to n.m.r., the sample analyzed for 16.5% **7** and 83.5% **9**. Compound **9** exhibits characteristic infrared absorptions at 6.05, 11.02, 11.19, 12.30, 12.55, 13.01, and 13.33 μ.

2-Dichloromethylene-3-*exo*-hydroxybicyclo[2.2.1]heptane (10). Hydrolysis of 2-Dichloromethylene-3-*endo*-bromobicyclo[2.2.1]heptane (6). A.—A mixture of 12.8 g. of **6** (0.05 mole), 200 ml. of acetone, and 100 ml. of water was refluxed for 24 hr. After cooling, water was added and the reaction mixture was neutralized with potassium carbonate. The amount of potassium carbonate required for neutralization (0.6 g., calcd. 2.65 g.) indicated that only 23% of **6** had hydrolyzed.

B.—The above mixture was treated with an aqueous silver nitrate solution. There was an immediate precipitate of yellowish silver bromide. After stirring at room temperature for 0.5 hr., the precipitate (7.2 g.) was filtered and the filtrate was extracted with ether. The combined ether extracts were washed with water and dried. Evaporation of the ether *in vacuo* left 8.5 g. of a white solid, m.p. 57–70°. Three recrystallizations from pentane afforded 7.5 g. (77.8%) of 2-dichloromethylene-3-*exo*-hydroxybicyclo[2.2.1]heptane (**10**), m.p. 72.0–72.5°.

Anal. Calcd. for $C_8H_{10}Cl_2O$: C, 49.76; H, 5.22; Cl, 36.72. Found: C, 50.12; H, 4.68; Cl, 36.62.

The infrared spectrum of the combined mother liquors (1.0 g.) showed strong absorptions at 6.08, 7.64, 7.82 and 11.7 μ, indicating the presence of a covalent nitrate (**11**).[27,39]

Hydrolysis of 2-Dichloromethylene-3-*endo*-chlorobicyclo[2.2.1]heptane (7). A.—Refluxing 10.6 g. of **7** (0.05 mole) with 200 ml. of acetone and 100 ml. of water for 24 hr. hydrolyzed **7** to the extent of 11.3%, as indicated by the amount of potassium carbonate utilized for neutralization.

B.—Treatment of the above reaction mixture with aqueous silver nitrate gave 9.1 g. of a viscous oil which solidified upon standing. The solid was filtered and twice recrystallized from pentane to give 7.9 g. (81.8%) of **10**, m.p. 72.0–72.5°, identical with **10** obtained from **6**. The mother liquor (1.2 g.) consisted mainly of the corresponding nitrate ester **11**.

C.—A mixture of 5.3 g. of **7** (0.025 mole), 10 g. of lithium carbonate, and 100 ml. of water was refluxed for 20 hr. After cooling, the mixture was extracted with ether; the ether extract was washed with water and dried over anhydrous sodium carbonate. Evaporation of the ether left 4.5 g. (94%) of a crystalline solid, which after two recrystallizations from pentane melted at 72–72.5°. The product was identical (mixture melting point and infrared spectrum) with the hydroxy compound **10**.

Hydrolysis of 2-Dichloromethylene-3-*exo*-chlorobicyclo[2.2.1]heptane (9). A.—To a solution of 10.8 g. of **9** (0.051 mole) in 150 ml. of acetone and 50 ml. of water was added a solution of 17 g. of silver nitrate (0.1 mole) in 20 ml. of water and the mixture was stirred at room temperature for 2 hr. After work-up, 10.3 g. of a yellowish oil was obtained, which partially crystallized. The slurry was cooled and then filtered, leaving 3.0 g. (31%) of a white solid, m.p. 59–69°. This compound, which after two recrystallizations from pentane melted at 72–72.5°, was identical with the hydroxy compound **10**. The filtrate (7.3 g., 61%) was again the corresponding nitrate ester **11**.

B.—A mixture of 10.6 g. of **9** (0.05 mole), 20 g. of lithium carbonate, and 200 ml. of water was refluxed for 20 hr. After work-up, 9.6 g. (99%) of a white solid, m.p. 57–72°, was obtained. After two recrystallizations from pentane, the solid had m.p. 72–72.5° and was found to be identical with **10**.

2-Dichloromethylenebicyclo[2.2.1]heptan-3-one (12). Treatment of 2-Dichloromethylene-3-*exo*-hydroxybicyclo[2.2.1]heptane with Nitric Acid. A.—A mixture of 7.6 g. of **10** (0.0393 mole), 17.5 ml. of water, and 32.5 ml. of concentrated nitric acid was heated on the steam bath for 15 min. After cooling, the reaction mixture was extracted three times with ether; the combined ether layers were washed with water, sodium carbonate solution, and again with water. After drying, evaporation of the ether left 7.4 g. of a viscous liquid. Bulb distillation at 0.2 mm. and an air bath temperature of 60–70° yielded 5.4 g. of a yellowish distillate, $n^{20}D$ 1.5375. The infrared spectrum indicated that this material consisted mainly of the nitrate ester **11**, with minor amounts of starting material (**10**) and ketone (**12**).

B.—The crude nitrate ester **11** (14.0 g., 0.059 mole), together with 35 ml. of water and 65 ml. of concentrated nitric acid, was heated on the steam bath for 3 hr. After work-up as above, 7.8 g. of a yellow oil was obtained, which according to its infrared spectrum consisted mainly of the expected ketone **12**.

Semicarbazone of 12.—The crude reaction product (5.5 g.) was treated with semicarbazide hydrochloride to give 5.5 g. (77%) of crude semicarbazone, melting at 215–217° with decomposition. After one recrystallization from aqueous ethanol, the melting point was 215–215.5° dec.

Anal. Calcd. for $C_9H_{11}Cl_2N_3O$: C, 43.57; H, 4.47; Cl, 28.58; N, 16.94. Found: C, 43.26; H, 4.42; Cl, 28.21; N, 16.53.

Regeneration of 12 from Its Semicarbazone.—The semicarbazone (2.5 g.) was steam distilled in the presence of an oxalic acid solution. The steam distillate was exhaustively extracted with ether and the combined ether extracts were dried over calcium sulfate. Evaporation of the ether afforded 1.57 g. (81.4%) of **12** as a pale yellow oil, $n^{20}D$ 1.5490, λ_{max} 252 and 345 mμ, 2,4-dinitrophenylhydrazone m.p. 235.5–236° dec., λ_{max}^{MeOH} 376 mμ (ϵ 1488).

Anal. Calcd. for $C_{14}H_{12}Cl_2N_4O_4$: C, 45.30; H, 3.26; Cl, 19.10; N, 15.09. Found: C, 45.56; H, 3.24; Cl, 19.03; N, 15.03.

The infrared spectrum of **12** is characterized by strong absorptions at 5.73, 6.18, 8.31, 9.22, 10.98, and 13.45 μ.

2-Dichloromethylene-3-*endo*-hydroxybicyclo[2.2.1]heptane (13).—To a stirred solution of 1.30 g. of **12** (6.8 mmoles) in 50 ml. of methanol was added a solution of 1.0 g. of sodium borohydride in 10 ml. of water. There was a slight exothermic reaction. The mixture was stirred at room temperature for 2 hr. and acidified with dilute sulfuric acid, water and ether were added, the ether layer was separated, the aqueous layer was extracted twice with ether, and the combined organic layers were washed three times with water and dried. Evaporation of the ether left 1.20 g. of a viscous residue which crystallized upon addition of cold pentane.

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(39) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen, London, 1958, p. 301.

Filtration afforded 1.00 g. (76%) of white crystals, m.p. 47–49°. After one recrystallization from pentane, **13** had m.p. 48–49°.

Anal. Calcd. for $C_8H_{10}Cl_2O$: C, 49.76; H, 5.22; Cl, 36.72. Found: C, 49.72; H, 4.75; Cl, 36.57.

3-*endo*-Chlorobicyclo[2.2.1]heptane-2-*exo*-carboxylic Acid (3). Acid Hydrolysis of 2-*exo*-Trichloromethyl-3-*endo*-chlorobicyclo-[2.2.1]heptane (2).—A mixture of 13.4 g. of **2** (0.54 mole), 75 ml. of concentrated sulfuric acid, and 0.75 ml. of water was stirred on a boiling water bath for 5.5 hr. During all this time, hydrogen chloride was evolved. The dark reaction mixture was cooled and poured onto 225 g. of cracked ice. After the ice had melted, the mixture was filtered through a course sintered-glass funnel, and the filtrate was extracted five times with ether. The combined ether extracts were extracted four times with a sodium carbonate solution and washed with water. After drying, the ether was evaporated leaving 0.43 g. of a solid residue, which after three recrystallizations from hexane melted at 149–152°. The infrared spectrum of this compound was identical with that obtained from a pure sample of the γ-lactone **14**. The sodium carbonate extract was acidified with sulfuric acid and extracted five times with ether. After drying, the ether was evaporated *in vacuo* to give 6.00 g. (75%) of **3**, m.p. 66–71°. After one recrystallization from pentane, the melting point was 70.5–71.5°.

An authentic sample of **3** was synthesized according to Alder, *et al.*,[9] and the two compounds were identical in all respects (melting point, mixture melting point, and infrared spectrum).

Reaction of 3 with Sulfuric Acid (γ-Lactone 14 Formation).—A 1.00-g. sample of **3** and 10 ml. of 50% sulfuric acid were shaken for 8 hr. at room temperature. The mixture was then extracted with ether and the ether extract was extracted with aqueous sodium carbonate and washed with water. After drying, the ether was evaporated to give 100 mg. (12.6%) of the γ-lactone **14**. After one recrystallization from hexane and subsequent sublimation at 100° (atmospheric pressure), **14** had m.p. 155–156°. The compound was identical in all respects (melting point, mixture melting point, and infrared spectrum) with **14** synthesized according to Alder, *et al.*[40]

Acid Hydrolysis of 7.—A stirred mixture of 16.5 g. of **7** (0.078 mole), 70 ml. of concentrated sulfuric acid, and 0.70 ml. of water was heated on a water bath to 40° for 5 hr. HCl was evolved during all this time. After addition of water, the reaction mixture was extracted five times with ether; the ether extract was extracted with aqueous sodium carbonate, washed with water, and dried. Evaporation of the ether gave 10.0 g. of a residue consisting of starting material, the γ-lactone **14**, and an unknown carbonyl compound ($\lambda_{C=O}$ 5.81 μ), as indicated by the infrared spectrum. No separation of the compounds occurred, when the sample was distilled. Acidification of the sodium carbonate extract and subsequent extraction with ether afforded 0.2 g. of a mixture, which according to the infrared spectrum consisted mainly of the γ-lactone **14** and the chloro acid **3**.

Reaction of 3 with Base. A.—A mixture of 17.0 g. of **3** (0.1 mole) and 16.2 g. of potassium hydroxide (0.3 mole) in 100 ml. of methanol was refluxed for 3 hr. After cooling, water was added and the mixture was washed with ether. The aqueous phase was acidified with sulfuric acid and extracted four times with ether; the combined ether layers were washed with water and dried. Evaporation of the ether gave 15.2 g. (89.5%) of solid starting material, m.p. 69–72°.

B.—A mixture of 15.2 g. of **3** (0.0872 mole) and 16.2 g. of potassium hydroxide (0.3 mole) in 100 ml. of ethanol was refluxed for 4 hr. After work-up as described above, 13.1 g. of an orange-colored liquid was obtained. Fractional distillation afforded 8.6 g. (71.6%) of bicyclo[2.2.1]hept-2-ene-2-carboxylic acid (**18**), b.p. 97–98° at 0.7 mm., n^{20}D 1.5112, λ_{max}^{MeOH} 229 mμ (log ε 3.86), infrared absorptions at 5.9 (C=O) and 6.27 μ (C=C), amide m.p. 143–5° (lit.[33] b.p. 96° at 0.6 mm.), λ_{max}^{EtOH} 229 mμ (log ε 3.85), ν_{max}^{film} 1678 cm.$^{-1}$, amide m.p. 142.7–144.6°.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.52; H, 7.29. Found: C, 69.79; H, 6.99.

C.—A mixture of 1.74 g. of **3** (0.01 mole) and 1.62 g. of potassium hydroxide (0.03 mole) in 5 ml. of water was refluxed for 3.5 hr. During this time 0.16 g. of a white waxy material had collected in the condenser neck. It melted at 45.5–46.5° and its infrared spectrum was identical with that obtained from norbornene. The brown reaction mixture was acidified with sulfuric acid and extracted with ether. After drying the extract, the ether was evaporated to give 0.80 g. of crude **18**.

D.—A mixture of 0.50 g. of **3** (0.0028 mole), 1.0 g. of lithium carbonate, and 25 ml. of water was refluxed for 24 hr., the reaction mixture was extracted with ether, and the aqueous phase was acidified with dilute sulfuric acid, extracted with ether, and dried over anhydrous sodium sulfate. Evaporation of the ether *in vacuo* left a viscous oil which crystallized after addition of a benzene–hexane mixture. The crude hydroxy acid **23** (0.26 g., 58%) melted at 135–137°. Repeated recrystallizations from benzene gave an analytical sample, m.p. 144–144.5°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.51; H, 7.74. Found: C, 61.63; H, 8.26.

Strong infrared absorptions (KBr disk) were at 2.97, 3.33, 5.88, 8.20, 9.18, 10.17, and 14.17 μ.

Reaction of 18 with Aqueous Potassium Hydroxide.—A mixture of 1.36 g. of **18** (0.01 mole) and 1.60 g. of potassium hydroxide (0.03 mole) in 10 ml. of water was refluxed for 5 hr. No sublimate was formed in the condenser and norbornene could not be detected in the ether extract. The acidic ether extract gave 1.12 g. of a viscous oil. Addition of hexane precipitated a white solid, which was filtered after standing overnight and twice recrystallized from CCl_4 to give a hydroxy acid (**22**), m.p. 134–135°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.51; H, 7.74. Found: C, 61.58; H, 7.66.

Strong infrared absorptions (KBr disk) were at 2.90, 3.33, 5.78, 6.95, 7.29, 7.65, 7.85, 8.20, 8.88, 9.30, 9.82, and 13.79 μ.

The filtrate consisted of unreacted starting material (**18**).

Reaction of 19 with Base. A.—A mixture of 4.4 g. of **19** (prepared according to Alder, *et al.*[9]) (0.025 mole), 10 g. of lithium carbonate, and 200 ml. of water was refluxed for 24 hr. Acidification of the reaction mixture and subsequent extraction with ether afforded a viscous oil. The oil was dissolved in a small amount of ether and hexane and was added to the ether solution until it was slightly turbid. After standing over night, the crystals (2.2 g., 56%) were collected and recrystallized from benzene, m.p. 132.5–134°. Renewed recrystallization gave an analytical sample, m.p. 134–135°, identical with the hydroxy acid obtained from the hydration of **18**.

B.—Treatment of **19** with ethanolic potassium hydroxide as described for the isomeric chloro acid **3** gave exclusively the unsaturated acid **18**.

Reaction of 20 with Aqueous Lithium Carbonate.—Refluxing **20** (prepared according to Alder, *et al.*[9]) with aqueous lithium carbonate as described for **3** (reaction D) afforded a hydroxy acid which was identical with the one (**23**) obtained from **3**.

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[40] K. Alder, G. Stein, M. Liebmann, and E. Rolland, *Ann.*, **514**, 197 (1934).