photoisomerizations of such ketones in solution. Norcamphor gives (2-cyclopentenyl)ethanal but not (3-cyclopentenyl)ethanal,[19,20] formally through a selective abstraction of the *syn*-7-H from diradical **4** in preference to the *endo*-6-H. Carvonecamphor is photoisomerized in methanol to an aldoketene intermediate which in turn is converted into the corresponding ester. Only the *α-exo*-H is abstracted intramolecularly as the ketene forms.[21] Photolysis of bicyclo[5.2.1]decan-10-one in pentane gives products derived from octamethyleneketene but no unsaturated aldehyde.[22] The reported facile and stereoselective conversions in solution of *l*-thujone and other ketones having special structural features[23] may be considered as exceptional cases.[24]

Experimental Section

Mass spectra were secured by Mr. J. A. Wrona with an Atlas CH-4 instrument. Preparative-scale chromatographic separations were carried out on Aerograph 90-P and 90-P3 instruments. Deuterium analyses were determined by Mr. J. Nemeth, Urbana, Ill. Analytical, mass spectral, and nmr data for the deuterium-labeled compounds are summarized in the tables.

3,3-Dideuterionorcamphor.—Deuterium oxide (34.6 g, 1.98 mol) was cautiously transferred to a 1.6-cm i.d. by 50-cm combustion tube containing 3.95 g (0.036 mol) of redistilled norcamphor and 41.6 g (0.198 mol) of trifluoroacetic anhydride. The tube was sealed, heated at 130° for 8.5 days, cooled, and opened; its contents were cautiously neutralized with anhydrous potassium carbonate and extracted with pentane. The combined extracts were dried over magnesium sulfate, filtered, and carefully concentrated by slow distillation. Sublimation of the residue at 90° gave 2.62 g (65%) of material. Analysis of the two major sublimation fractions by glpc showed them to be 98+% norcamphor.

exo-**3-Deuterionorcamphor.**—A solution containing 1.73 g of redistilled norcamphor, 2.83 ml of deuterium oxide, and 11.9 ml of deuteriotrifluoroacetic acid was sealed in a dry combustion tube, heated at 83 ± 1° for 22 hr, cooled, and transferred to a separatory funnel. The reaction mixture was saturated with potassium bicarbonate and extracted four times with pentane. The combined extracts were dried over sodium sulfate, filtered, and concentrated cautiously. The solid residue was sublimed to give 0.93 g (53%) of colorless product.

endo-**3-Deuterionorcamphor.**—A solution containing 1.16 g of 3,3-dideuterionorcamphor, 1.99 ml of water, and 8.97 ml of trifluoroacetic acid was subjected to the reaction conditions (83 ± 1° for 20 hr) and work-up as described directly above. The colorless sublimed product weighed 0.62 g (54%).

Gas Phase Photolysis of 3,3-Dideuterionorcamphor.—The mercury-sensitized gas phase photolysis of 1.34 g of 3,3-dideuterionorcamphor in a reaction vessel previously dried for 3 hr at 10^{-4} mm was carried out as described in detail for the unlabeled ketone.[6b] Flash distillation of the photolyzate gave 0.282 g of clear colorless liquid from which samples of deuterium-labeled 1,5-hexadiene, bicyclo[2.1.1]hexane, and allylcyclopropane were obtained through preparative glpc. Control experiments showed no deuterium exchange occurred during chromatography of the hydrocarbons. The recovered norcamphor was purified by sublimation.

Solutions of 0.045 ml of hydrocarbon in 0.20 ml of carbon tetrachloride were used in determining nmr and infrared spectra for these three products.[6b] The spectral solutions were rechromatographed to provide pure samples of the hydrocarbons for microanalytical deuterium determinations.

Gas Phase Photolysis of *exo*- and *endo*-3-Deuterionorcamphor.—*exo*- and *endo*-3-deuterionorcamphor (458 and 525 mg, respectively) were separately photolyzed and the three major hydrocarbons were isolated as previously described.[6b]

Registry No.—**1**, 18153-61-2; *exo*-3-deuterionorcamphor, 18139-04-3; *endo*-3-deuterionorcamphor, 18139-05-4.

(19) Reference 6b, note 10.

(20) But camphor does give the *endo*-6-H abstraction product, α-campholenic aldehyde; G. Ciamician and P. Silber, *Ber.*, **43**, 1340 (1910); R. Srinivasan, *J. Amer. Chem. Soc.*, **81**, 2604 (1959); see also W. C. Agosta and D. K. Herron, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P164.

(21) J. Meinwald, R. A. Schneider, and A. F. Thomas, *J. Amer. Chem. Soc.*, **89**, 70 (1967).

(22) C. D. Gutsche and J. W. Baum, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, P163; *J. Amer. Chem. Soc.*, **90**, 5862 (1968). We thank Professor Gutsche for making available to us a preprint of the full paper on this work.

(23) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966), and references therein.

(24) *Cf.* J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).

The *cis–exo* Addition of Isothiocyanic Acid to Norbornenes. Synthesis and Isomeric Configuration of the Herbicide Norea

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Isothiocyanic acid (HNCS) adds predominantly *cis* and *exo* to six norbornenes studied, producing norbornyl isothiocyanates in good to excellent yields. This *cis–exo* addition of HNCS to *endo*-dicyclopentadiene is utilized to prepare *exo*-5-isothiocyano-5,6-dihydro-*endo*-dicyclopentadiene, an intermediate used in the synthesis of the herbicide norea. Norea, which is predominantly *exo*-5-(3,3-dimethylureido)tetrahydro-*endo*-dicyclopentadiene, is prepared from the isothiocyanate in three steps: (1) the isothiocyanate is allowed to react with dimethylamine; (2) the resulting thiourea is converted into the corresponding urea by phosgenolysis and hydrolysis; and (3) the urea is catalytically hydrogenated to norea. Nonpolar media and moderate temperatures favor the *cis–exo* addition of isothiocyanic acid to *endo*-dicyclopentadiene.

The mode of addition of isothiocyanic acid (HNCS) to norbornenes was determined as part of our research on norea, a selective agricultural herbicide, and some of its analogs.[1] Under favorable reaction conditions, HNCS adds to six norbornenes *cis* and *exo* predominantly, producing norbornyl isothiocyanates in good to excellent yields without rearrangement of the norbornane ring structure.

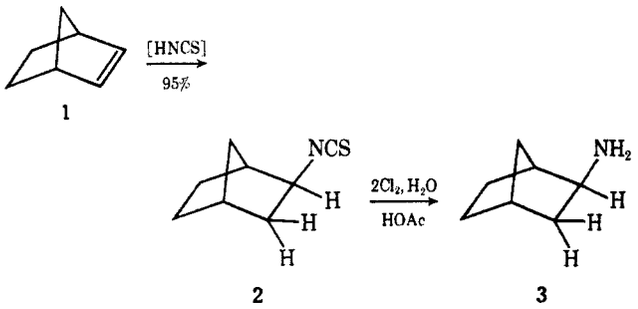
Although the additions of many acidic reagents to norbornenes have been investigated, the addition of isothiocyanic acid has received relatively little attention. Moreover, those results reported on the additions of HNCS to norbornenes are not in agreement. Bruson and Riener, first to report an addition of this

(1) (a) Norea is the common name and Herban is the registered trademark for 3-(hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea. (b) G. A. Buntin and W. R. Diveley (to Hercules, Inc.), U. S. Patent 3,304,167 (Feb 14, 1967).

type, concluded that HNCS reacts with *endo*-dicyclopentadiene to give an isothiocyanate with a rearranged ring system.[2a] It was established later that strong acids react with *endo*-dicyclopentadiene in a typical Wagner–Meerwein rearrangement.[2b] Based on the latter work, Riemschneider apparently assumed that isothiocyanic acid reacts with *endo*-dicyclopentadiene with rearrangement.[3] Luskin and coworkers disclosed that HNCS adds to camphene to give 2-isothiocyanoisocamphane.[4] Recently, and concurrently with our work, Ramey and Silvermann reported that HNCS adds to norbornadiene to give 5,6-dehydronorbornyl isothiocyanate, but the geometric configuration of the isothiocyanate group was not determined.[5]

Our interest in the mode of addition of HNCS to norbornenes arose from the observation that norea isomers, prepared from *endo*- and *exo*-dicyclopentadiene *via* their isothiocyanic acid adducts, were different compounds with different herbicidal activities. Previously reported work[2,6] indicated that both dicyclopentadiene isomers should give the same norea isomer. When this was found not to be the case, an investigation of the mode of addition of isothiocyanic acid to norbornenes was initiated.

Isothiocyanic acid, generated *in situ*, reacts with norbornene to give *exo*-2-norbornyl isothiocyanate (**2**) in excellent yield. That the isothiocyanate group is *exo* was shown by the conversion of **2** into the known *exo*-2-norbornylamine (**3**), identified as its acetamide, *via* reactions which should not affect the isomeric configuration. The chlorinolysis of **2** in the presence

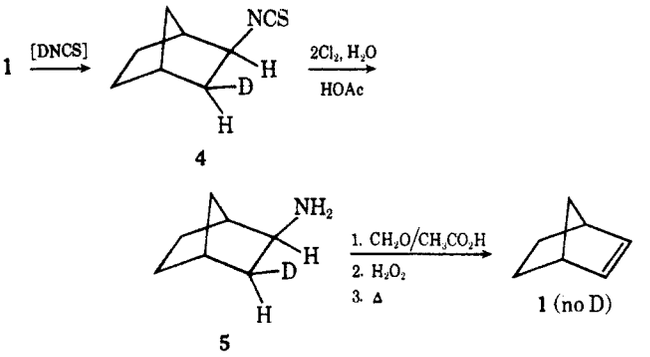


of water is a new and convenient method for conversion of an isothiocyanate into an amine and provides a simple synthesis of **3**.[7] Chlorinolysis of **2** under anhydrous conditions gives norbornyl iminodichloride (R—N=C=Cl_2), which is readily hydrolyzed to **3**.

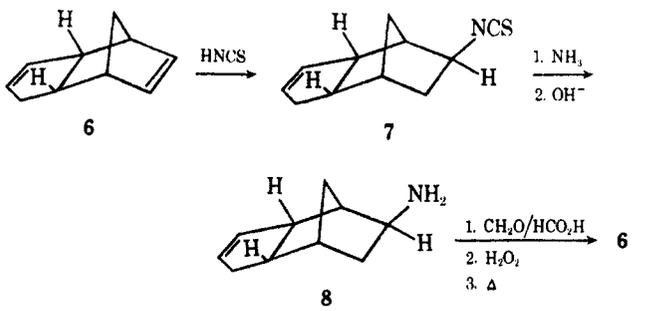
To obtain further information on the nature of the HNCS addition, deuterated isothiocyanic acid (DNCS) was added to norbornene. The nmr spectrum of the resulting deuterated isothiocyanate (**4**), which has a doublet equivalent to one proton at τ 6.5 and a coupling constant of 8.3 cps, indicated that the C-2 and C-3 hydrogens are *cis*.[8] The absence of further splitting indicated that these hydrogens are also *endo*.[8] We established chemically that the deuterium is on C-3.

(2) (a) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **67**, 1178 (1945); (b) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).
(3) R. Riemschneider, *Z. Naturforsch.*, **14b**, 814 (1959).
(4) L. S. Luskin, *et al.*, *J. Org. Chem.*, **21**, 1430 (1956).
(5) D. E. Ramey and M. Silvermann (to Shell Oil Co.), U. S. Patent 3,006,954 (Oct 31, 1961); *Chem. Abstr.*, **56**, 5854 (1962).
(6) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **67**, 726 (1945).
(7) G. A. Buntin (to Hercules, Inc.), U. S. Patent 3,150,183 (Sept 22, 1964).
(8) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

It was known that the isothiocyanate group is *exo* in the 2 position. Therefore, the results indicated that the hydrogens on C-2 and C-3 are *cis* and *endo* and the the isothiocyanate group and deuterium are *cis* and *exo*. This was confirmed chemically by converting **4** into **5** using the chlorinolysis procedure described above, then pyrolyzing the dimethylamine oxide of **5**.[9] The resulting product was norbornene containing no deuterium, thus indicating that deuterium had been on C-3. Because the amine oxide pyrolysis is a *cis* elimination, these results also indicated that the isothiocyanate group and deuterium are *cis* and *exo* on C-2 and C-3 respectively.



Similar results were obtained with *endo*-dicyclopentadiene (**6**), the starting material for norea. The isothiocyanate (**7**) from this norbornene (**6**) was allowed to react with ammonia, and the resulting thiourea was hydrolyzed to the corresponding amine (**8**). The dimethylamine oxide of the resulting amine was then pyrolyzed, and *endo*-dicyclopentadiene (**6**) was obtained as the predominant product. These results indicated



that no rearrangement of the ring system had occurred, in disagreement with the conclusions reported in earlier work.[2a]

exo-Dicyclopentadiene, when subjected to the same series of reactions, except that the isothiocyanate rather than the thiourea was hydrolyzed to the amine, gave predominantly *exo*-dicyclopentadiene as the product, indicating also that no change in the ring structure had occurred in the addition of isothiocyanic acid. Gas–liquid partition chromatographic (glpc) analyses of the isothiocyanates from the two dicyclopentadiene isomers gave essentially homogeneous and different isothiocyanates.

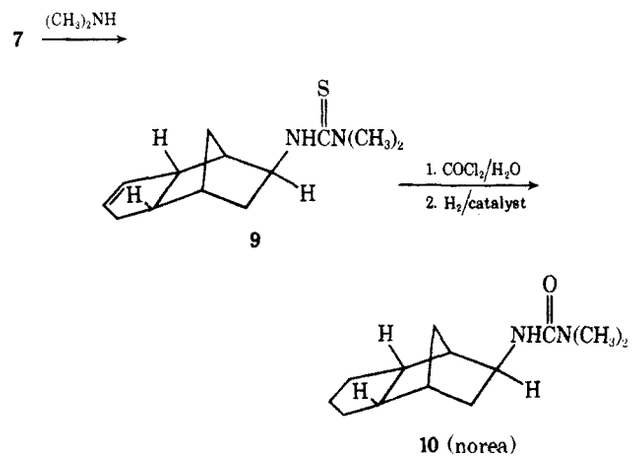
It was established that *endo*- and *exo*-5-chloronorbornene also react with HNCS similarly, the chlorines remaining predominantly in their original *endo* and *exo* configurations in the isothiocyanate products.

(9) C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 410 (1963).

The addition of HNCS to norbornadiene was observed to proceed also without rearrangement of the bicyclic ring system, producing 5,6-dehydro-*exo*-2-norbornyl isothiocyanate in 80% yield. This was shown by reaction of the product with nitrosyl chloride to form a dimeric adduct; also, hydrolysis of the thiourea, prepared from the norbornadiene–HNCS adduct and ammonia, yielded the corresponding unsaturated amine. This amine on hydrogenation gave *exo*-2-norbornylamine, thereby establishing the *exo* configuration of the original isothiocyanate group.

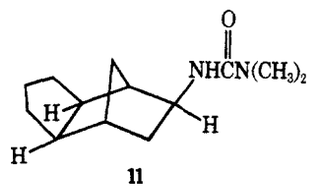
Thus, the accumulated evidence indicates that HNCS adds predominantly *cis* and *exo* to norbornenes, presumably *via* a concerted process, to produce norbornyl isothiocyanates without rearrangement of the bicyclic ring structure. We conclude that HNCS reacts with norbornenes differently from other strong acids.[2]

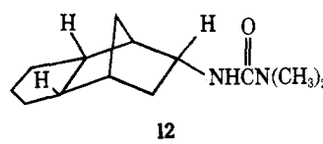
Norea (**10**) is prepared from **6** *via* **7** by reactions which do not affect the ring or isothiocyanate configuration and therefore has the *endo*-ring, *exo*-urea configuration.

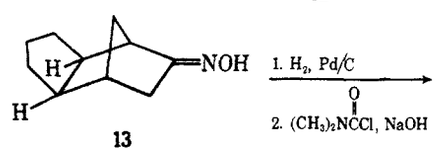


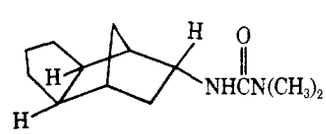
Norea may be synthesized also by the catalytic hydrogenation of **8**, conversion of the resulting saturated amine into the corresponding isocyanate, and reaction of the isocyanate with dimethylamine. Other norea isomers were prepared as follows. The *exo*-ring, *exo*-urea isomer (**11**) was prepared from *exo*-dicyclopentadiene *via* the isothiocyanate by the same reactions used to prepare norea. The *endo*-ring, *endo*-urea isomer (**12**) was prepared by reaction of the known corresponding amine[10] with phosgene in the presence of HCl to obtain the isocyanate and reaction of the isocyanate with dimethylamine. The fourth isomer was prepared from *endo*-dicyclopentadiene (**6**) *via* the known oxime of 5-ketotetrahydro-*exo*-dicyclopentadiene (**13**).[6] Catalytic hydrogenation of this oxime gave predominantly the *exo*-ring, *endo*-amine, which was converted into the corresponding urea isomer (**14**). Thus, the four possible isomeric 3-(hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylureas have been synthesized and identified. It is significant that the *endo*-ring, *exo*-urea isomer has the best combination of high herbicidal activity and crop tolerance.

To obtain *endo*-5-chloronorbornene containing a









minimum of the corresponding *exo* isomer for reaction with isothiocyanic acid, a 53:6:41 *endo*-5-chloronorbornene–*exo*-5-chloronorbornene–nortricyclyl chloride mixture was prepared by reaction of vinyl chloride with cyclopentadiene in a steel autoclave. Nortricyclyl chloride does not interfere because it does not react with HNCS under the conditions used. When the Diels–Alder reaction between vinyl chloride and cyclopentadiene was carried out in glass equipment, a 64:36 *endo*-5-chloronorbornene–*exo*-5-chloronorbornene mixture resulted. The conversions of 1:1 cyclopentadiene–vinyl chloride products obtained in iron and in glass equipment were essentially the same, *i.e.*, ~65% based on cyclopentadiene. We suspected that the different products resulted from the conversion of the *exo*-5-chloronorbornene isomer produced into nortricyclyl chloride by iron in the autoclave. This was confirmed by heating the 64:36 *endo*–5-chloronorbornene–*exo*-5-chloronorbornene mixture with iron powder under the same conditions used in the Diels–Alder reaction. Almost all of the *exo* isomer disappeared, whereas nortricyclyl chloride appeared about proportionately, and the *endo* isomer content remained essentially unchanged. To obtain *exo*-chloronorbornene free of the *endo* isomer for reaction with HNCS, anhydrous HCl was added to norbornadiene in methylene chloride at low temperature; this reaction gave a 77:23 *exo*-5-chloronorbornene–nortricyclyl chloride mixture.[11]

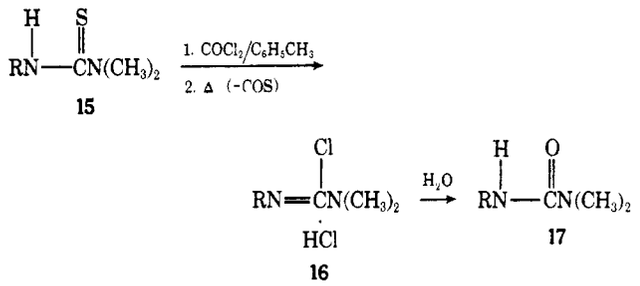
An observation of interest was that *endo*-5-chloronorbornene appeared to react with HNCS faster than did the corresponding *exo* isomer, but more slowly than norbornene. This observation was based on per cent yields of products obtained and the amounts of polymeric HNCS formed. The polymerization of HNCS is competitive with the addition reaction. That HNCS reacts more rapidly with *endo*-5-chloronorbornene than with the corresponding *exo* isomer was indicated also in a competitive experiment in which a known mixture of

(10) P. Wilder, Jr., C. F. Culberson, and G. T. Youngblood, *J. Amer. Chem. Soc.*, **81**, 655 (1959).

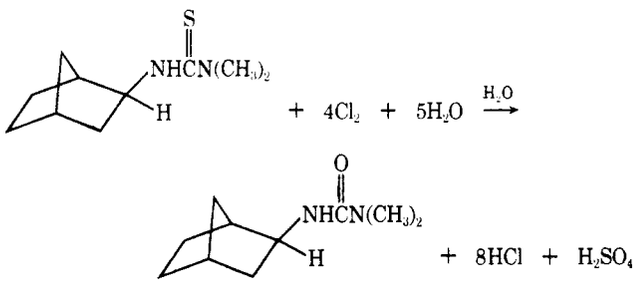
(11) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).

64:36 *endo*- and *exo*-5-chloronorbornene isomers was allowed to react with HNCS; the unreacted chloronorbornenes, analyzed by glpc, contained more of the *exo* (55%) than of the *endo* (45%) isomer. It was also of interest that HNCS did not add to 5,6-dichloronorbornene at all; only polymeric HNCS was formed. The 5,6-dichloro-2-norbornyl isothiocyanate may be prepared by another method, however. Transannular chlorines in norbornenes have a profound effect on the addition of HNCS. Other electron-withdrawing substituents, such as –CN, $-CO_2R$, $-NO_2$, etc., located in the 5 and/or 6 position in norbornenes, also retard the HNCS addition so much that HNCS polymerization becomes the predominant reaction. In contrast, alkyl substituents in the same positions have little if any effect, compared with the addition of HNCS to norbornene; very little HNCS polymerization occurs in these reactions; and the yields of isothiocyanate products are generally high.

The conversion of thioureas into ureas was also studied and two general methods appear to work well. A phosgenolysis–hydrolysis procedure has the widest applicability.[12] Phosgene passed into a solution of the thiourea (**15**) in a hydrocarbon solvent at 0–30° forms a thiouronium salt, which, on warming, loses COS. The resulting chloroformamidine salt (**16**) is readily hydrolyzed to the urea (**17**). A chlorinolysis–



hydrolysis procedure is also effective in converting thioureas into the corresponding ureas, as illustrated by the following example.[13] The ureas, soluble in the



concentrated acid solution formed, are isolated easily by dilution or preferably neutralization.

Both of the above procedures were limited only by the presence of other functional groups or moieties which react with phosgene or chlorine.

The ureas can be prepared also from the corresponding amines *via* isocyanate intermediates, followed by reaction of the isocyanates with dimethylamine.

The products obtained in reaction of HNCS with *endo*-dicyclopentadiene may be controlled in a limited way by varying the conditions under which the reaction is carried out. For example, the reaction of HNCS with *endo*-dicyclopentadiene in benzene at 25–30° produces a product which consists of 94.3% unrearranged *endo*-ring, *exo*-isothiocyanate, 1.3% rearranged *exo*-ring, *exo*-isothiocyanate, 0.7% thiocyanate of undetermined ring configuration, and 3.7% other components, as determined by glpc. The same reaction carried out in a more polar aqueous system at 90° results in a product which analyzes as 68.7% *endo*-ring, *exo*-isothiocyanate, 5.2% *exo*-ring, *exo*-isothiocyanate, 9.6% thiocyanate, and 16.5% other components. These results are similar, though the extreme limits are closer together, to the control of products possible in the addition of HCl to norbornadiene by varying reaction conditions; *e.g.*, anhydrous HCl reacts with norbornadiene at 0° to form a mixture of 77:23 *exo*-5-chloronorbornene–nortricyclyl chloride,[11] but concentrated hydrochloric acid at 25° produces almost a reverse ratio of products, *i.e.*, 87:13 nortricyclyl chloride–*exo*-5-chloronorbornene. Inasmuch as we learned how to produce almost exclusively the *endo*-ring, *exo*-isothiocyanate intermediate needed for the preparation of norea in high yield, the effect of solvent polarity and other reaction variables on the course of HNCS addition to norbornenes was not pursued further.

Experimental Section[14]

Norbornenes.—Commercial 95+% dicyclopentadiene (Enjay Chemical Co.) was used except where noted; glpc analysis indicated a 99:1 ratio of *endo* to *exo* isomers in this commercial product.[15] Norbornene was prepared as described in *Organic Syntheses*[17] or was purchased from Aldrich Chemical Co. Norbornadiene was obtained from Shell Chemical Co. *exo*-Dicyclopentadiene was prepared as described by Bartlett, *et al.*,[16] or was obtained from Carbide Olefins Corp.

5-Chloronorbornene. Preparation in Glass Equipment.—A Carius tube was charged with 77 g (1.23 mol) of vinyl chloride and 41.0 g (0.31 mol) of dicyclopentadiene, and heated at 250° for 5 hr. After removal of the excess vinyl chloride by evaporation, the residue was distilled through a short Vigreux column, and 53.5 g (67%) of product was collected, bp 46–48° (15–16 mm). Glpc analysis indicated that the product was a 64:36 mixture of *endo*- and *exo*-5-chloronorbornenes.[18]

5-Chloronorbornene. Preparation in Steel Equipment.—A mixture of 2500 g (19.0 mol) of dicyclopentadiene and 3500 g (56.0 mol) of vinyl chloride was heated in a 5-gal rocking steel autoclave at 200° for 15 hr. Fractionation of the reaction mixture through a glass-packed column of 20 theoretical plates resulted in 3144 g (65% based on dicyclopentadiene) of water-white liquid product, bp 91.6–94.0° (100 mm). Glpc analysis

(12) G. A. Buntin (to Hercules, Inc.), U. S. Patent 3,163,674 (Dec 29, 1964).

(13) W. R. Diveley and M. M. Pombo (to Hercules, Inc.), U. S. Patent 3,150,179 (Sept 24, 1964).

(14) Melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord Model 137B. Nmr spectra were recorded on a Varian A-60 instrument using carbon tetrachloride solvent and tetramethylsilane as internal standard.

(15) The gas chromatographic column used for this determination was a 4.0 m × 4 mm (i.d.) 15% β,β-oxydipropionitrile on Chromosorb W stainless steel column operated at 85° and 60 ml of He/min. Peak assignments were based on the major peaks in commercial *endo*-dicyclopentadiene (V_R = 3.01) and in *exo*-dicyclopentadiene (V_R = 2.56) prepared according to ref 16; V_R values are relative to benzene (V_R = 1.00).

(16) P. D. Bartlett and I. S. Goldstein, *J. Amer. Chem. Soc.*, **69**, 2553 (1947).

(17) J. Meinwald and N. J. Hudak, *Org. Syn.*, **37**, 65 (1957).

(18) The gas chromatographic column used for this determination was a 4.0 m × 4 mm (i.d.) dicarbitol phthalate on Chromosorb W stainless steel column operated at 148° and 60 ml of He/min. Peak assignments for *exo*-5-chloronorbornene (V_R = 1.5) and nortricyclyl chloride (V_R = 2.1) are based on the major and minor peaks in the products prepared according to ref 11. The peak for *endo*-5-chloronorbornene (V_R = 1.9) is based on the major peak of the Diels–Alder 1:1 cyclopentadiene–vinyl chloride product. V_R values are relative to *p*-xylene (V_R = 1.0).

indicated that the product was 53% *endo*-5-chloronorbornene, 6% the corresponding *exo* isomer, and 41% nortricyclyl chloride.[18]

Conversion of *exo*-5-Chloronorbornene into Nortricyclyl Chloride Using Iron.—A mixture of 20 g of a 64:36 *endo*–*exo*-5-chloronorbornene product (see preparation above) and 1 g of iron powder was sealed in a Carius tube and heated at 200° for 15 hr. The iron was filtered off and the filtrate was distilled to give 10.9 g of product, bp 51–56° (18 mm). Glpc analysis indicated that the product was 52% *endo*-5-chloronorbornene, 4% the corresponding *exo* isomer, and 44% nortricyclyl chloride.[18]

77:23 *exo*-5-Chloronorbornene–Nortricyclyl Chloride Product.—This mixture was prepared in 88% yield by the addition of anhydrous HCl to norbornadiene in methylene chloride as described by Winstein and Shatavsky:[11] bp 43–44° (17 mm). Glpc analysis indicated that the product was a 77:23 mixture of the two isomers.[18]

87:13 Nortricyclyl Chloride–*exo*-5-Chloronorbornene Product.—To 3 l. of concentrated HCl stirred and maintained at 25–28° was added dropwise 500 g of norbornadiene over a 3-hr period. After 2 hr more, water and benzene were added; the benzene layer was separated, water washed, dried, and distilled to give 391 g of water-white liquid product, bp 60–68° (20 mm). Glpc analysis indicated that the product was 87% nortricyclyl chloride and 13% *exo*-5-chloronorbornene.[18] A residue of 195 g of higher boiling liquid remained.

Nortricyclyl Chloride.—Nitrosyl chloride (11 g) was passed slowly into a stirred solution of 20 g of the above-described 87:13 nortricyclyl chloride–*exo*-5-chloronorbornene mixture in 40 ml of hexane at 20°. The precipitated product was filtered, and the filtrate was distilled to give 10 g of product, bp 59–61° (20 mm). Glpc analysis indicated that this product was 100% nortricyclyl chloride.[18] Nortricyclyl chloride does not react with isothiocyanic acid using the general procedure described below.

Isothiocyanates.—The following procedure, except where noted, is typical for preparation of the isothiocyanates which follow.

***exo*-2-Norbornyl Isothiocyanate (2).**—A solution of 384 g of concentrated sulfuric acid and 120 ml of water was added dropwise over 2 hr to a well-stirred mixture of 525 g (5.6 mol) of norbornene, 1500 ml of benzene, and 575 g (5.9 mol) of potassium thiocyanate maintained at 35–40°. The reaction mixture was kept at 35–40° for 3 hr longer and cooled, water was added, and the mixture was filtered to remove insolubles. The organic layer was separated with the aid of ether, washed with water, and dried; removal of the solvent left a tan liquid, 829 g (96.5%). Almost all of this product distilled at 76–78° (0.5 mm), $n^{20}D$ 1.5494. Its infrared (ir) spectrum had a strong, wide band centered at 4.8 μ (–N=C=S).

Anal. Calcd for $C_8H_{11}NS$: S, 20.9. Found: S, 21.0.

Anhydrous dimethylamine, passed into a 20% solution of the above isothiocyanate in hexane until heat no longer evolved, yielded a pale yellow crystalline thiourea derivative, 1,1-dimethyl-3-(*exo*-2-norbornyl)-2-thiourea, mp 100–101° (ethanol–water).

Anal. Calcd for $C_{10}H_{18}N_2S$: C, 60.61; H, 9.09; N, 14.1; S, 16.2. Found: C, 60.90; H, 9.15; 14.1; S, 16.1.

***exo*-5-Isothiocyano-5,6-dihydro-*endo*-dicyclopentadiene (7).**—This preparation was carried out using four different conditions, and the products obtained were analyzed by glpc.[19]

Method A.—The isothiocyanate was prepared from commercial dicyclopentadiene by the general procedure described above. The distilled product, a light yellow liquid, was obtained in 90% yield, bp 97–98° (0.2 mm). Its ir spectrum had the expected strong, wide band centered at 4.8 μ (–N=C=S). Glpc analysis indicated that this product was 91.3% *endo*-ring, *exo*-isothiocyanate, 2.5% *exo*-ring, *exo*-isothiocyanate, 2.2% thiocyanate, and 4.0% other components.[19] The isothiocyanate assignments are based on structure studies given later. The thiocyanate assignment was based on ir spectral data also given later. Retention times relative to the *endo*-ring, *exo*-isothiocyanate (1.00) were 0.83 for the *exo*-ring, *exo*-isothiocyanate and 0.75 for the thiocyanate.

Anal. Calcd for $C_{11}H_{13}NS$: N, 7.3; S, 16.8. Found: N, 7.2; S, 16.5.

Method B.—The product, prepared by the method of Bruson and Riener,[2a] analyzed as 87.3% *endo*-ring, *exo*-isothiocyanate, 6.1% *exo*-ring, *exo*-isothiocyanate, 4.3% thiocyanate, and 2.3% other components.[19]

Method C.—To a mixture of 250 ml of benzene and 100 g (1.0 mol) of KSCN, stirred and cooled at 25–30°, was added dropwise a solution of 51.0 g (0.5 mol) of concentrated sulfuric acid and 15 ml of water. After another 5 min, the benzene layer was separated, and 66.0 g (0.5 mol) of dicyclopentadiene was added dropwise over 30 min with stirring and cooling to maintain a temperature of 25–30°. When the reaction subsided, it was permitted to proceed overnight at ambient temperature, and the product was isolated as described above. On distillation, 82.4 g (86%) of light yellow product was collected at 102–104° (0.2 mm). Glpc analyses indicated that the product was 94.3% *endo*-ring, *exo*-isothiocyanate, 1.3% *exo*-ring, *exo*-isothiocyanate, 0.7% thiocyanate, and 3.7% other components.[19]

Method D.—A solution of 51.0 g (0.5 mol) of concentrated sulfuric acid and 15 ml of water was added dropwise to a stirred mixture of 100 g (1.0 mol) of KSCN and 500 ml of water with cooling to maintain the temperature at 25–30°. The resulting solution was stirred and heated at 90°, 132 g (1.0 mol) of dicyclopentadiene was added dropwise over 30 min, and the mixture was heated at 90° for 3 hr. After cooling, the product was extracted into benzene and isolated as described above. Distillation at 0.25 mm yielded 63.5 g of lower boiling components at 30–105° and 48.3 g of tan liquid product at 106–112°. Glpc analysis indicated that this product was 68.7% *endo*-ring, *exo*-isothiocyanate, 5.2% *exo*-ring, *exo*-isothiocyanate, 9.6% thiocyanate, and 16.5% other components.[19]

***exo*-5-Thioureido-5,6-dihydro-*endo*-dicyclopentadiene.**—This thiourea, mp 203° (lit.[2a] mp 202–204°), was prepared in 69% yield by saturating a 20% ethanol solution of the corresponding isothiocyanate, made by method A above, with anhydrous ammonia. The isothiocyanates prepared by methods B and C above gave the same derivative, as determined by melting point and mixture melting point.

Identification of 5-Thiocyano-5,6-dihydrodicyclopentadiene Peak in Glpc Assignments.—A dicyclopentadiene–HNCS product (90.0 g), prepared according to Bruson and Riener (see method B above),[2a] was dissolved in 510 g of hexane, and the solution was treated with anhydrous dimethylamine until no more solid thiourea derivative separated. After cooling, the solid product was removed by filtration. The solvent was removed from the filtrate by aspiration, and the residue was distilled; 4.1 g of light tan liquid was collected at 110–119° (0.55 mm). Glpc analysis indicated that this product was 6.2% *endo*-ring, *exo*-isothiocyanate (V_R = 1.00), 41.3% *exo*-ring, *exo*-isothiocyanate (V_R = 0.83), 38.3% thiocyanate (V_R = 0.75), and 14.2% other components.[19] The thiocyanate assignment is based on the ir spectrum of the distillate which had a sharp, narrow band at 4.62 μ (–SCN). This band was partially obscured by a weaker, broad –NCS band in the same region.

***exo*-5-(3,3-Dimethylthioureido)-5,6-dihydro-*endo*-dicyclopentadiene (9).**—This thiourea derivative was prepared by reaction of the corresponding isothiocyanate (prepared by method A above) with anhydrous dimethylamine in hexane as described above. The yield of crude product was 95%; white crystals, mp 100–101°, were obtained after recrystallization from benzene.

Anal. Calcd for $C_{13}H_{20}N_2S$: S, 13.5. Found: S, 13.8.

***exo*-5-Isothiocyano-5,6-dihydro-*exo*-dicyclopentadiene.**—This isothiocyanate was prepared from *exo*-dicyclopentadiene by the general procedure described above. The light tan liquid, bp 107–108° (0.3 mm), was obtained in 65% yield. Its ir spectrum had a wide, strong band at 4.5–5.0 μ (–N=C=S). Glpc indicated that this product contained no *endo*-ring, *exo*-isothiocyanate, and that it was essentially homogeneous.[19]

Anal. Calcd for $C_{11}H_{13}NS$: N, 7.3; S, 16.8. Found: N, 7.2; S, 16.8.

A thiourea derivative of this isothiocyanate was prepared by passing an excess of anhydrous ammonia into an ethanol solution of the isothiocyanate with cooling, then precipitating the product with water. The white crystalline derivative melted at 150–151° after two recrystallizations from benzene.

***exo*-5-(3,3-Dimethylthioureido)-5,6-dihydro-*exo*-dicyclopentadiene.**—This thiourea was prepared from the corresponding isothiocyanate and anhydrous dimethylamine in hexane. The crude product, mp 127–131°, was obtained in 88% yield. Recrystallization from benzene gave white crystals, mp 131–133°.

(19) The gas chromatographic column used for this determination was a 2.5 m × 4 mm (i.d.) borosilicate column packed with silicone rubber (SE-30) on Gas Chrom Z operated at 158° and 80 ml of He/min.

Anal. Calcd for $C_{13}H_{20}N_2S$: N, 11.9; S, 13.5. Found: N, 11.7; S, 13.2.

5,6-Dehydro-*exo*-2-norbornyl Isothiocyanate.—This isothiocyanate was pepared from norbornadiene using the general procedure described above in 80% yield. It was a pale yellow liquid, bp 78–80° (1.5 mm), $n^{20}D$ 1.5738.[5]

Anal. Calcd for C_8H_9NS: N, 9.3. Found: N, 9.2.

Reaction of this isothiocyanate with dimethylamine in hexane gave the expected thiourea, mp 105–106° (ethanol).

Anal. Calcd for $C_{10}H_{16}N_2S$: S, 16.3. Found: S, 16.5.

A nitrosyl chloride dimer adduct was prepared by slowly passing nitrosyl chloride (22 g) into a stirred mixture of 50 g (0.33 mol) of the isothiocyanate in 350 ml of hexane maintained at 20°. The white solid product was filtered, washed with hexane, and dried to give 51.5 g of dimer (72%), mp 145.5–146.5°. Its ir spectrum (Fractol mull) had a strong wide band centered at 4.7 μ (–N=C=S).

Anal. Calcd for $C_{16}H_{18}Cl_2N_4O_2S_2$: S, 14.8; Cl, 16.5. Found: S, 14.5; Cl, 16.4.

***endo*-5- (or 6-) Chloro-*exo*-2-norbornyl Isothiocyanate.**—This isothiocyanate was prepared from a 53:6:41 *endo*-5-chloronorbornene–*exo*-5-chloronorbornene–nortricyclyl chloride mixture (see preparation above) using the general procedure described above. The product was a pale yellow liquid obtained in 67% conversion: bp 101–102° (0.5 mm), $n^{20}D$ 1.5732, ir 4.7 μ (–N=C=S).

Anal. Calcd for $C_8H_{10}ClNS$: S, 17.1. Found: S, 17.2.

Reaction of this isothiocyanate with anhydrous dimethylamine in hexane gave the expected thiourea, mp 109–112° (ethanol–water).

Anal. Calcd for $C_{10}H_{17}ClN_2S$: Cl, 15.3; S, 13.7. Found: Cl, 15.0; S, 13.7.

***exo*-5- (or 6-) Chloro-*exo*-2-norbornyl Isothiocyanate.**—This isothiocyanate was prepared from a 77:23 *exo*-5-chloronorbornene–nortricyclyl chloride mixture (see preparation above) using the general procedure described above. It was a pale yellow liquid obtained in 53% conversion: bp 82–86° (0.15 mm), $n^{20}D$ 1.5718, ir 4.7 μ (–N=C=S).

Anal. Calcd for $C_8H_{10}ClNS$: Cl, 18.9; S, 17.1. Found: Cl, 18.8; S, 17.1.

Reaction of this isothiocyanate with anhydrous dimethylamine in hexane gave the expected thiourea derivative, mp 141–143° (ethanol).

Anal. Calcd for $C_{10}H_{17}ClN_2S$: Cl, 15.3; S, 13.7. Found: Cl, 15.1; S, 14.0.

Competitive Addition of Isothiocyanic Acid to *endo*- and *exo*-5-Chloronorbornenes.—The general procedure described above was followed using 610 g (4.75 mol) of a 64:36 *endo*–*exo*-5-chloronorbornene mixture, 500 ml of benzene, 525 g (5.25 mol) of potassium thiocyanate, and a solution of 390 g of concentrated sulfuric acid in 110 ml of water. The isothiocyanate obtained weighed 568 g (64% conversion). Distillation yielded 132 g (1.03 mol) of 5-chloronorbornenes (45:55 *endo*–*exo* as determined by glpc).[18]

HNCS Additions to 5-Cyanonorbornene, 5-Carbethoxynorbornene, and 5-Nitronorbornene.—Addition of HNCS to these substituted norbornenes, using the general procedure described above, gave low conversions (<20%) of isothiocyanate products, identified by the broad, stong isothiocyanate band (~4.7 μ) in their ir spectra. Large amounts of polymeric HNCS formed in each case.

Amines. ***exo*-2-Norbornylamine (3).**—Chlorine (371 g, 5.24 mol) was passed into a stirred mixture of 400 g (2.62 mol) of *exo*-2-norbornyl isothiocyanate, 2 l. of glacial acetic acid, and 47 ml of water with cooling to maintain the temperature at 25 ± 5°. The solvent was removed under reduced pressure, and the resulting white salt was dissolved in water. A small amount of insoluble material was removed by filtration, and the filtrate was made strongly basic with aqueous sodium hydroxide. The liberated amine was extracted into benzene (twice), dried, and distilled as a water-white liquid, 171 g (67%), bp 55–56° (25 mm), $n^{20}D$ 1.4849.

Anal. Calcd for $C_7H_{13}N$: N, 12.6; neut equiv, 111. Found: N, 12.6; neut equiv, 112.

The acetamide, prepared by reaction of **3** with acetic anhydride, melted at 143–144° (ethanol–water) (lit.[20] mp 143–144°). The acetamide of the corresponding *endo*-amine melts at 132°.[20]

(20) J. A. Berson and D. A. Ben-Efraim, *J. Amer. Chem. Soc.*, **81**, 4098 (1961).

***exo*-2-Norbornyl Iminodichloride.**—Chlorine (100 g, 1.41 mol) was introduced over 1 hr into a stirred mixture of 100 g (0.66 mol) of *exo*-2-norbornyl isothiocyanate and 500 ml of carbon tetrachloride maintained at 25°. Distillation of the reaction mixture gave 80 g (64%) of clear liquid, bp 100–102° (15 mm), $n^{20}D$ 1.5135.

Anal. Calcd for $C_8H_{11}Cl_2N$: N, 7.3. Found: N, 7.3.

Hydrolysis of *exo*-2-Norbornyl Iminodichloride.—To a stirred mixture of 40 ml of glacial acetic acid and 2 ml of water was added dropwise 10 g (0.052 mol) of the above iminodichloride. The addition was exothermic. After 3 hr, 4.0 g (69%) of *exo*-2-norbornylamine, bp 65° (28 mm), was isolated as described above. An acetamide of this amine was prepared: mp 143–144° (lit.[20] mp 143–144°).

***endo*-5- (or 6-) Chloro-*exo*-2-norbornylamine.**—This amine, prepared by chlorinolysis of the corresponding isothiocyanate in a solution of acetic acid and water as described above, was a water-white liquid, bp 70–73° (1.3 mm) (62% yield).

Anal. Calcd for $C_7H_{12}ClN$: neut equiv, 145.5. Found: neut equiv, 148.

Reaction of this amine with phenyl isothiocyanate gave the phenylthiourea, mp 138–139° (ethanol), *p*-toluenesulfonamide derivative mp 136.5–137.5° (aqueous ethanol).

***exo*-5- (or 6-) Chloro-*exo*-norbornylamine.**—This amine, prepared from the corresponding isothiocyanate by chlorinolysis in a solution of acetic acid and water, was a water-white liquid, bp 50–54° (0.3 mm) (46% yield).

Anal. Calcd for $C_7H_{12}ClN$: neut equiv, 145.5. Found: neut equiv, 150.

Its phenylthiourea derivative melted at 164.5–165.5° (ethanol), and its *p*-toluenesulfonamide derivative melted at 143.5–144.5° (aqueous ethanol).

***exo*-5-Amino-5,6-dihydro-*endo*-dicyclopentadiene (8).**—A mixture of 958 g (4.60 mol) of *exo*-5-thioureido-5,6-dihydro-*endo*-dicyclopentadiene, 750 g (13.4 mol) of potassium hydroxide, and 2.4 l. of ethylene glycol was stirred and heated at reflux for 10 hr. After cooling, water and benzene were added. The benzene layer was separated and extracted with 10% HCl, the acidic extract was made basic, and the liberated amine was extracted into benzene. After drying, the benzene was removed by aspiration, and the amine distilled to give 473 g (69%) water-white liquid, bp 72–76° (1.25 mm), $n^{20}D$ 1.5281 (lit.[3] $n^{21}D$ 1.5285).

Anal. Calcd for $C_{10}H_{15}N$: N, 9.4. Found: N, 9.2.

The acetamide of this amine, prepared by reaction with acetic anhydride, melted at 133–134° (petroleum ether) (lit.[2a] mp 129–130°). Its phenylthiourea derivative, prepared by reaction with phenyl isothiocyanate, melted at 160–162° (lit.[3] mp 160–161°), after two recrystallizations from ethanol.

***exo*-5-Amino-5,6-dihydro-*exo*-dicyclopentadiene.**—This amine was prepared in 41% yield by basic hydrolysis of the corresponding isothiocyanate with sodium hydroxide in ethylene glycol using conditions described in the preceding experiment: bp 67–70° (1 mm), $n^{20}D$ 1.5209.

Anal. Calcd for $C_{10}H_{15}N$: neut equiv, 149. Found: neut equiv, 150.

A phenylthiourea derivative, prepared by reaction of this amine with phenyl isothiocyanate, melted at 134–136° (ethanol).

5,6-Dehydro-*exo*-2-norbornylamine.—This amine was prepared in 28% yield by basic hydrolysis of the corresponding thiourea using potassium hydroxide in ethylene glycol as described above: bp 53–54° (18 mm).

Anal. Calcd for $C_7H_{11}N$: neut equiv, 109. Found: neut equiv, 116.

This unsaturated amine was hydrogenated in ethanol using Raney nickel catalyst at 124° and 3000-psi hydrogen pressure. The product, *exo*-2-norbornylamine, distilled at 59° (22 mm) (56% yield). An acetamide of this norbornylamine was prepared using acetic anhydride: mp 144° (lit.[20] mp 143–144°).

***exo*-5-Aminotetrahydro-*endo*-dicyclopentadiene.**—The unsaturated amine, *exo*-5-amino-5,6-dihydro-*endo*-dicyclopentadiene (400 g), was catalytically hydrogenated using 5% palladium on carbon and 3000-psi hydrogen pressure at 100° to give 401 g of dark liquid product, $n^{20}D$ 1.5180, neut equiv 152.5. A portion of this product (147 g) was distilled to give 142 g of water-white liquid, bp 72–74° (0.5 mm), $n^{20}D$ 1.5181. An ir spectrum of the product had no C=C absorption.

Anal. Calcd for $C_{10}H_{17}N$: neut equiv, 151. Found: neut equiv, 152.

***exo*-5-Aminotetrahydro-*exo*-dicyclopentadiene.**—This amine

was prepared by catalytically hydrogenating *exo*-5-amino-5,6-dihydro-*exo*-dicyclopentadiene (39 g) in isopropyl alcohol using 5% palladium on carbon and 3000-psi hydrogen pressure at 100°. Distillation gave 26.5 g (67%) of water white product, bp 57–58° (0.3 mm), $n^{20}D$ 1.5085. Elemental analysis of its urea derivative is given later.

Isocyanates. ***exo*-2-Norbornyl Isocyanate.**—The following procedure is typical for preparation of the isocyanates from amines. Anhydrous HCl (16.0 g, 0.45 mol) was passed into a stirred mixture of 49.0 g (0.44 mol) of *exo*-2-norbornylamine and 400 ml of xylene. The resulting white paste was heated at 120° and 65.0 g(0.66 mol) of phosgene was introduced slowly. The mixture became clear as the reaction progressed. The mixture was distilled under reduced pressure and 40.6 g (67%) of water-white liquid product was collected: bp 80–83° (28 mm). The urea derivative was prepared by passing anhydrous ammonia into a hexane solution of the isocyanate: mp 188–190°. The corresponding urea derivative of *endo*-2-norbornyl isocyanate was reported to melt at 196–197°.[20]

The following isocyanates were prepared from the corresponding amines by the general procedure described above (elemental analyses were obtained on urea derivatives of these isocyanates): ***exo*-5-isocyanato-5,6-dihydro-*endo*-dicyclopentadiene**, 82% yield, bp 90–93° (1 mm), $n^{20}D$ 1.5178; *exo*-5-isocyanato-5,6-dihydro-*exo*-dicyclopentadiene, 55% yield, bp 79–81° (0.5 mm), $n^{20}D$ 1.5173; ***exo*-5-iocyanatotetrahydro-*endo*-dicyclopentadiene**, 82% yield, bp 86–88° (1.5 mm), $n^{20}D$ 1.5100; ***exo*-5-isocyanatotetrahydro-*exo*-dicyclopentadiene**, 71% yield, bp 85–87° (0.8 mm), $n^{20}D$ 1.5022; **5,6-dehydro-*exo*-norbornyl isocyanate**, 62% yield, bp 70–74° (24 mm).

Ureas. 1,1-Dimethyl-3-(*exo*-2-norbornyl)urea.—Three procedures were used to prepare this urea: (A) reaction of the corresponding isocyanate with anhydrous dimethylamine in hexane; (B) chlorinolysis of the corresponding thiourea in the presence of water; and (C) phosgenolysis of the corresponding thiourea followed by hydrolysis of the resulting intermediate. These procedures were used also for the preparation of other ureas which follow.

Method A.—Anhydrous dimethylamine was passed into a 25% solution of the corresponding isocyanate in hexane until heat no longer evolved. The mixture was maintained at 5–10° during the addition. The resulting white solid product which separated from the reaction mixture was obtained in 70% yield: mp 183.0–183.5° (ethyl acetate).

Anal. Calcd for $C_{10}H_{16}N_2O$: C, 65.93; H, 9.89; N, 15.4. Found: C, 65.88; H, 9.91; N, 15.2.

Method B.—Chlorine (40.0 g, 0.563 mol) was passed into a stirred suspension of 25.0 g (0.126 mol) of the corresponding thiourea in 150 ml of water with cooling to maintain <30°. The mixture eventually became clear. After being kept overnight, the mixture was neutralized with 20% sodium hydroxide with cooling to maintain <40°. The white solid which separated was filtered, washed with water, and dried in air: mp 168–173°. Recrystallization from ethyl acetate gave 21.8 g (95%), mp 183°.

Method C.—To a stirred mixture of 142.5 g (0.72 mol) of the corresponding thiourea and 100 ml of toluene maintained at 20–25° was added slowly under the surface of the mixture 93.0 g (0.94 mol) of phosgene; the heterogeneous mixture became homogeneous, then again heterogeneous. The mixture was warmed for 30 min at 50° and cooled, and water was added dropwise. After 1 hr, the mixture was neutralized with aqueous sodium hydroxide, and the solid product was filtered, washed with water, and dried to give 110.2 g of white solid, mp 183–184°. Another 12.2 g of product, mp 175–180°, was obtained by evaporation of the toluene (93.5% yield).

***exo*-5-(3,3-Dimethylureido)-5,6-dihydro-*endo*-dicyclopentadiene** was prepared from the corresponding thiourea by phosgenolysis and hydrolysis. The product, a white solid, was obtained in 89% yield: mp 153–154°. This urea was also prepared by reaction of the corresponding isocyanate with dimethylamine in hexane.

Anal. Calcd for $C_{13}H_{20}N_2O$: C, 70.90; H, 9.09; N, 12.7. Found: C, 70.79; H, 8.99; N, 12.6.

***exo*-5-(3,3-Dimethylureido)-5,6-dihydro-*exo*-dicyclopentadiene** was prepared by reaction of the corresponding isocyanate with anhydrous dimethylamine in hexane; it was a white powder, mp 172–173° (ethyl acetate) (94% yield).

Anal. Calcd for $C_{13}H_{20}N_2O$: N, 12.7. Found: N, 12.5.

This same urea was prepared also by phosgenolysis and hydrolysis of the corresponding thiourea in 80% yield: mp 172–173° (ethyl acetate).

***exo*-5-(3,3-Dimethylureido)tetrahydro-*endo*-dicyclopentadiene (norea)** (**10**) was prepared by reaction of the corresponding isocyanate and anhydrous dimethylamine in hexane (96% yield): mp 168–169°; after recrystallization once from toluene and once from ethyl acetate, mp 171–172°; mmp 145–147° with the preceding compound.

Anal. Calcd for $C_{13}H_{22}N_2O$: C, 70.21; H, 9.98; N, 12.6. Found: C, 70.31; H, 10.01; N, 12.7.

This urea also was prepared in 96% yield by the catalytic hydrogenation of *exo*-5-(3,3-dimethylureido)-5,6-dihydro-*endo*-dicyclopentadiene. A 10% solution of the unsaturated urea in toluene and 5% by weight of G-69 catalyst (Ni and Zr on Kieselguhr) were hydrogenated at 120° and 400-psi hydrogen pressure to constant pressure. The product, isolated by removal of the catalyst by filtration and the solvent by aspiration, and recrystallization of the product from toluene and then from ethyl acetate, had mp 171°. A quantitative method for analysis of norea has been reported.[21]

***exo*-5-(3,3-Dimethylureido)tetrahydro-*exo*-dicyclopentadiene** (**11**) was prepared from the corresponding isocyanate in hexane and anhydrous dimethylamine in 94% yield: white crystals, after recrystallization from ethyl acetate; mp 204.5–205.5°.

Anal. Calcd for $C_{13}H_{22}N_2O$: N, 12.6. Found: N, 12.4.

3-(5,6-Dehydro-2-*exo*-norbornyl)-1,1-dimethylurea was prepared in 74% yield from the corresponding isocyanate and anhydrous dimethylamine in hexane: mp 182–183°.

Anal. Calcd for $C_{10}H_{16}N_2O$: N, 15.6. Found: N, 15.4.

This urea was prepared also in 91% yield by phosgenolysis of the corresponding thiourea followed by hydrolysis of the resulting chloroformamidine (method C): mp 182–184°.

***endo*-5-(3,3-Dimethylureido)tetrahydro-*exo*-dicyclopentadiene** (**14**).—The *endo*-5-aminotetrahydro-*exo*-dicyclopentadiene required for the synthesis of this urea was made by the catalytic hydrogenation of the known oxime of 5-ketotetrahydro-*exo*-dicyclopentadiene (**13**).[6] This oxime (125 g) in 200 ml of absolute ethanol was hydrogenated using 10 g of 5% palladium on carbon at 70° and 2000-psi hydrogen pressure. The catalyst was filtered off and the filtrate was distilled. A fraction, 16.5 g, was collected at 71–100° (0.3 mm). An ir spectrum indicated that this product contained an amine and also some carbonyl impurities. To prepare the urea, a solution of 16.0 g of this crude amine and 13.5 g (0.125 mol) of dimethylcarbamoyl chloride in 250 ml of chloroform was cooled at 0° and treated dropwise with a solution of 5.0 g (0.125 mol) of sodium hydroxide in 20 ml of water. The temperature was permitted to rise to 25°; after 2 hr the organic layer was separated, washed with water, and dried; and the solvent was evaporated. The resulting white solid product weighed 10.2 g, mp 130–150°. After two recrystallizations from ethyl acetate and one from toluene, 5.4 g of white crystals, mp 135–140°, resulted. This melting point is different from those of the other three isomers. Glpc analysis indicated that the product was ~80% *exo*-ring, *endo*-urea and ~20% *exo*-ring, *exo*-urea.[22]

Anal. Calcd for $C_{13}H_{22}N_2O$: N, 12.6. Found: N, 12.4.

***endo*-5-(3,3-Dimethylureido)tetrahydro-*endo*-dicyclopentadiene** (**12**) was prepared in 67% yield from the known *endo*-5-aminotetrahydro-*endo*-dicyclopentadiene[10] *via* the isocyanate using the procedure described above; it was a white powder, mp 95–97°.

Anal. Calcd for $C_{13}H_{22}N_2O$: N, 12.6. Found: N, 12.6.

Deuterium-Labeled Experiments. ***exo*-2-Norbornyl-*exo*-3-d_1 Isothiocyanate** (**4**).—To a stirred slurry of 76 g (0.81 mol) of norbornene, 85 g (0.88 mol) of potassium thiocyanate, and 100 ml of benzene under a nitrogen atmosphere was added dropwise over 1 hr a solution of 40.0 g (0.4 mol) of D_2SO_4 (99%, Merck and Co.) in 12.0 g of D_2O (99.7%, Nichem, Inc.). The temperature was maintained at ~40° during the addition and for 4 hr more. After cooling, the mixture was filtered and the cake was washed with benzene. The filtrate and washings were combined, washed with water, and dried. After removal of the solvent by aspiration, the residue was distilled *in vacuo* and 95 g (76%) of pale yellow liquid product was collected: bp 67–69° (0.6 mm). The nmr spectrum of this isothiocyanate has a doublet resonance at τ

(21) J. J. Ford, J. F. Gates Clarke, Jr., and R. T. Hall, *J. Agr. Food Chem.*, **14**, 307 (1966).

(22) J. G. Gates Clarke, Jr., glpc method to be published.

6.5, corresponding to one proton. It is assumed that this proton is on C-2 along with the isothiocyanate group because of its position downfield in the spectrum. The spin–spin splitting is 8.3 cps, indicating that the adjacent proton is *cis* to the proton on C-2. The absence of any further splitting indicates that the proton on C-2 is *endo*, so that coupling to the bridgehead hydrogen does not occur, and that there is an *exo*-deuterium on C-3, so that *trans* coupling does not occur.[8]

Anal. Calcd for $C_8H_{10}DNS$: N, 9.1. Found: N, 8.9.

***exo*-2-Norbornylamine-*exo*-3-d_1 (5).**—Chlorine (42.4 g, 0.5 mol) was passed into a stirred mixture of 46.0 g (0.3 mol) of deuterated isothiocyanate, 260 ml of acetic acid, and 5.4 ml of water maintained at 25–30°, and the product was isolated as described above for *exo*-2-norbornylamine: 16.44 g (49%), bp 51–53° (17 mm).

N,N-Dimethyl-*exo*-2-norbornylamine-*exo*-3-d_1.—To 37.4 g (0.715 mol) of 88% formic acid was added slowly with cooling 16.0 g (0.143 mol) of *exo*-2-norbornylamine-*exo*-3-d_1. Then 34.6 g (0.427 mol) of 37% formaldehyde was added with cooling, and the resulting mixture was heated to reflux. At about 65–70°, a vigorous evolution of gas occurred, lasting for ~15 min. Heating was continued for 8 hr at 90–95° After cooling, 100 ml of 4 *N* HCl was added and the volatiles were removed by aspiration until a solid began to separate. Water (75 ml) was added and the solid was dissolved. This solution was made strongly basic with 20% sodium hydroxide and extracted twice with ether. The ether was removed from the extract by aspiration and the residue was distilled under reduced pressure. At 69–72° (21–23 mm), 11.78 g (59%) of product was collected. The mass spectrum of this product had a base peak at *m/e* 58, a large parent peak at 140 (20.4% of base peak), and an isotope peak at 141 (3.0%). Undeuterated N,N-dimethyl-*exo*-2-norbornylamine had a base peak at *m/e* 58, parent peak at 139 (36.6% of base peak), and an isotope peak at 140 (3.7%).

Preparation and Pyrolysis of N,N-Dimethyl-*exo*-2-norbornylamine-*exo*-3-d_1 Oxide.—To a stirred mixture of 11.0 g (0.0785 mol) of the deuterated amine and 25 ml of methanol cooled at 15–20° was added dropwise 25 ml of 30% H_2O_2. The mixture was maintained at this temperature for 1 hr, another 4 ml of 30% H_2O_2 was added dropwise, and the resulting mixture was permitted to react overnight at ambient temperature. Excess H_2O_2 was decomposed with Pt gauze. The residue was then subjected to aspiration; when the temperature reached 25°, the pressure was adjusted to 170–175 mm, and heating was resumed. The residue solidified to a waxy solid, then melted, and pyrolyzed at 100–130°, mostly at 110–120°. The product, collected in a receiver cooled with Dry Ice, was extracted with ether and dried, and the ether was evaporated, finally at 80°. The product (3.22 g, 44%) had an nmr spectrum essentially identical with that of norbornene. Its mass spectrum had a *m/e* 95 to *m/e* 94 ratio of 0.10 compared with 0.073 for an authentic sample of norbornene.

Structure Studies. N,N-Dimethyl-*endo*-5- (or 6-) chloro-*exo*-2-norbornylamine.—The procedure described above to obtain dimethylated **5** was essentially followed using 51.4 g (0.35 mol) of *endo*-5- (or 6-) chloro-*exo*-2-norbornylamine, 106 g (2.03 mol) of 88% formic acid, and 64 g (0.79 mol) of formalin. The mixture was refluxed for 23 hr; then the product was isolated to give 46.4 g (76%) of water-white product, bp 49–50° (0.2 mm), $n^{20}D$ 1.4953.

Anal. Calcd for $C_9H_{16}ClN$: Cl, 20.4; neut equiv, 174. Found: Cl, 20.1; neut equiv, 182.

Preparation and Pyrolysis of N,N-Dimethyl-*endo*-5- (or 6-) chloro-*exo*-2-norbornylamine Oxide.—To a stirred mixture of 12.0 g (0.069 mol) of the corresponding dimethylamine in 20 ml of anhydrous methanol was added dropwise 24 ml of 30% H_2O_2 with cooling to keep the temperature at 15–20°. The mixture was stirred for 2 hr and then was permitted to react 24 hr without stirring. Excess H_2O_2 was decomposed with Pt gauze and the methanol was evaporated in a current of air. The residue was pyrolyzed as described above by heating slowly at 50–60 mm in the beginning and at 15–20 mm finally. Vapors from the pyrolysis were collected in a Dry Ice trap. The condensate was extracted with ether and the ether extract was washed with water, dried, and distilled to give 4.5 g (51%) water-white liquid, bp 49–50° (16 mm). Glpc analysis indicated that this product was 96% *endo*-5-chloronorbornene and 4% the corresponding *exo* isomer.[18]

N,N-Dimethyl-*exo*-5- (or 6-) chloro-*exo*-2-norbornylamine.—This amine was prepared in 65% yield as described above for the *endo-exo* isomer, except that the reaction time was 16 hr. It was a water-white liquid, bp 54–55° (0.3 mm), $n^{20}D$ 1.4935.

Anal. Calcd for $C_9H_{16}ClN$: neut equiv, 174. Found: neut equiv, 177.

Preparation and Pyrolysis of N,N-Dimethyl-*exo*-5- (or 6-) chloro-*exo*-2-norobornylamine Oxide.—These reactions were carried out as described above for the corresponding *endo-exo* isomer. From 12.0 g (0.069 mol) of the dimethylamine, 5.0 g (56%) of chloronorbornenes was collected at 61–63° (30 mm). Glpc analysis indicated that the product was 75% *exo*-5-chloronorbornene and 25% the corresponding *endo* isomer.[18]

***exo*-5-Dimethylamino-5,6-dihydro-*endo*-dicyclopentadiene** was prepared in 70% yield from the corresponding amine by the alkylation procedure described above: bp 72–78° (1.0 mm).

Anal. Calcd for $C_{12}H_{19}N$: neut equiv, 177. Found: neut equiv, 179.

Preparation and Pyrolysis of the Amine Oxide of *exo*-5-Dimethylamino-5,6-dihydro-*endo*-dicyclopentadiene.—The amine oxide was prepared from the corresponding dimethylamine (15.0 g) and pyrolyzed as described above to give 7.0 g (63%) of product, bp 75° (33 mm). Glpc analysis indicated that the product was 96% *endo*-dicyclopentadiene and 4% the corresponding *exo* isomer.[15] The product absorbed 2.92% hydrogen (calcd 3.02%).

***exo*-5-Dimethylamino-5,6-dihydro-*exo*-dicyclopentadiene** was prepared from the corresponding amine in 64% yield by the alkylation procedure described above: bp 69° (0.6 mm), $n^{20}D$ 1.5089.

Preparation and Pyrolysis of the Amine Oxide of *exo*-5-Dimethylamino-5,6-dihydro-*exo*-dicyclopentadiene.—The amine oxide was prepared from the corresponding dimethylamine (10.0 g) and pyrolyzed as described above to give 3.0 g (40%) of product, bp 74° (33 mm). Glpc analysis indicated that this product was >95% *exo*-dicyclopentadiene.[15] An ir spectrum was essentially identical with that of *exo*-dicyclopentadiene. The product absorbed 2.93% hydrogen (calcd 3.02%).

Registry No.—Isothiocyanic acid, 3129-90-6; **2,** 18530-33-1; 1,1-dimethyl-3-(*exo*-2-norbornyl)-2-thiourea, 18530-43-3; *exo*-5-isothiocyano-5,6-dihydro-*exo*-dicyclopentadiene, 18530-34-2; *exo*-5-(3,3-dimethylthioureido)-5,6-dihydro-*exo*-dicyclopentadiene, 18530-35-3; **3,** 7242-92-4; *exo*-2-norbornyl iminodichloride, 18598-39-5; 5,6-dehydro-*exo*-2-norbornyl isothiocyanate, 18598-40-8; thiourea derivative of 5,6-dihydro-*exo*-2-norbornyl isothiocyanate, 18530-36-4; **4,** 18530-38-6; thiourea derivative of **4,** 18530-49-9; **5,** 18530-39-7; **7,** 18530-40-0; *exo*-5-amino-5,6-dihydro-*exo*-dicyclopentadiene, 18530-41-1; **8,** 18530-42-2; **9,** 18530-44-4; 5,6-dehydro-*exo*-2-norbornylamine, 18530-45-5; *exo*-5-aminotetrahydro-*endo*-dicyclopentadiene, 18530-46-6; *exo*-5-aminotetrahydro-*exo*-dicyclopentadiene, 18530-47-7; *exo*-5-isocyanato-5,6-dihydro-*endo*-dicyclopentadiene, 18530-48-8; *exo*-5-isocyanato-5,6-dihydro-*exo*-dicyclopentadiene, 18530-50-2; *exo*-5-isocyanatotetrahydro-*endo*-dicyclopentadiene, 18530-51-3; *exo*-5-isocyanato-5,6-dihydro-*exo*-dicyclopentadiene, 18530-52-4; 5,6-dihydro-*exo*-norbornyl isocyanate, 18530-53-5; 1,1-dimethyl-3-(*exo*-2-norbornyl)urea, 18530-54-6; *exo*-5-(3,3-dimethylureido)-5,6-dihydro-*endo*-dicyclopentadiene, 18598-46-4; *exo*-5-(3,3-dimethylureido)-5,6-dihydro-*exo*-dicyclopentadiene, 18530-55-7; **10,** 18530-56-8; **11,** 18530-57-9; 3-(5,6-dihydro-2-*exo*-norbornyl)-1,1-dimethylurea, 18530-58-0; **12,** 18530-59-1; **14,** 18530-60-4; N,N-dimethyl-*exo*-2-norbornylamine-*exo*-3-d_1, 18530-61-5; *exo*-5-dimethylamino-5,6-dihydro-*endo*-dicyclopentadiene, 18530-62-6; N,N-dimethyl-*exo*-2-norbornylamine-*exo*-3-d_1 oxide, 18598-47-5; amine oxide of *exo*-5-dimethylamino-5,6-dihydro-*endo*-dicyclopentadiene, 18530-63-7;

exo-5-dimethylamino-5,6-dihydro-*exo*-dicyclopentadiene, 18530-64-8; amine oxide of *exo*-5-dimethylamino-5,6-dihydro-*exo*-dicyclopentadiene, 18530-65-9.

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Absolute Configurations and Rotations of 1-Methyl-2-methylenenorbornane and 1,2-Dimethyl-2-norbornyl Derivatives

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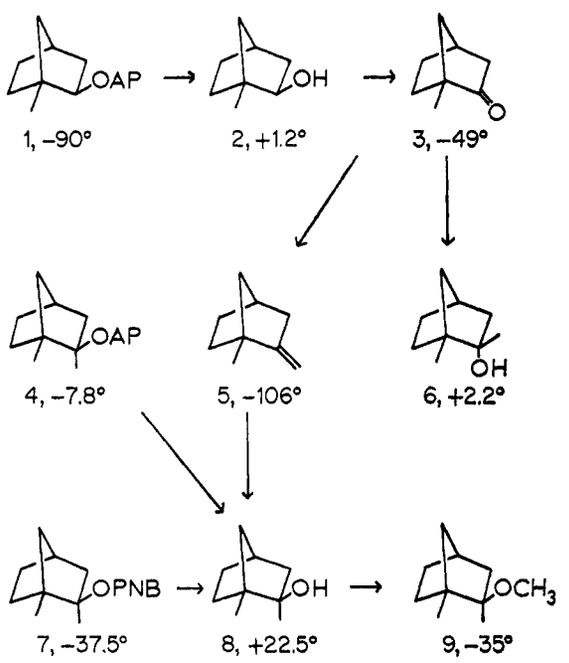
Absolute configurations of 1-methyl-2-methylenenorbornane (**5**) and *exo*- (**8**) and *endo*-1,2-dimethyl-2-norbornanol (**6**) have been established by correlation with 1-methyl-2-norboranone (**3**). The correlations also provide absolute rotations for these compounds. Optical resolutions of the 1-methyl-*exo*-2-norbornyl and 1,2-dimethyl-*exo*-2-norbornyl systems are described.

In connection with an investigation of the solvolysis of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (**7**)[1] we have had occasion to relate configurations and rotations of optically active 1,2-dimethyl-*exo*-2-norbornyl derivatives (**4** and **7**–**9**) and 1-methyl-2-methylenenorbornane (**5**). Configurations and rotations were correlated as outlined in Chart I. The absolute configuration of (−)-1-methyl-2-norbornanone (**3**) had been established earlier[2] by correlation with (−)-fenchone. The present correlations establish absolute configurations for the compounds included in Chart I.

CHART I



1-Methyl-*exo*-2-norbornanol (**2**) was prepared from norcamphor as described earlier[2] and the acid phthalate derivative, **1**, was resolved by recrystallization of the cinchonine salt. The most active sample of **1** was found to be about 40% optically pure by the correlation outlined below.

Saponification of (−)-1-methyl-*exo*-2-norbornyl acid phthalate (**1**), followed by oxidation (CrO_3) of the resulting (+) **2** by a method that has been shown[3] to convert *exo*-2-norbornanol into norcamphor with complete preservation of optical configuration, gave (−)-1-methyl-2-norbornanone (**3**). To avoid optical fractionation the intermediate solid (+) **2** was not isolated. An independent saponification was used to relate the rotations of **1** and **2**.

The ketone, (−) **3**, was converted into (+)-1,2-dimethyl-*endo*-2-norbornanol (**6**) by reaction with methylmagnesium bromide and into (−)-1-methyl-2-methylenenorbornane (**5**) by the Wittig reaction. Oxymercuration–demercuration of (−) **5** according to the method outlined by Brown and coworkers[4] gave (+)-1,2-dimethyl-*exo*-2-norbornanol (**8**). It has been shown[4] that oxymercuration–demercuration of 1-methyl-d_3-2-methylenenorbornane gives 1-methyl-d_3-2-methyl-*exo*-norbornanol without detectable scrambling of the methyl groups and from this, and the reproducible change in rotation for the conversion of active **5** to **8**, it seems that this step proceeds without loss of optical activity.

The rotations included in the chart[5] result from correlation with the highest observed rotations for the 1,2-dimethyl-*exo*-2-norbornyl derivatives. This correlation gives a rotation for 1-methyl-2-norbornanone (**3**) that is about 15% higher than that obtained[2] by correlation with *d*-fenchone. This discrepency could result from partial loss of activity for the two-step conversion of **3** into **8**. However, for reasons given above this seems unlikely. The changes in rotation for each step of the conversion of active **1** into active **8** were found to be reproducible by different investiga-

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(2) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961).
(3) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635 (1965).
(4) (a) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967); H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); (b) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).
(5) Optical rotations are $[\alpha]^{30}D$ for chloroform solutions.