268 (14,300), and 343 (8250). The nmr showed a phenyl multiplet at 6.85 ppm and the tertiary hydrogen as a singlet at 4.8 ppm.

Methyltetraphenylcyclopentadienyl Cation (IId). A solution of 0.5 g of 1-methyltetraphenylcyclopentadienol (Id) in methylene chloride was converted to the deep blue cation solution with BF_3 at −70°. After 5 min of standing at this temperature a purplish hue had developed. Then 0.23 g of cycloheptatriene was added, and after the usual work-up and chromatography 0.11 g (22%) of methyltetraphenylcyclopentadiene (IVd) was isolated, mp 177–179° (lit. mp 178.5–179.5°). In the ultraviolet the compound had $\lambda\lambda_{max}$ 243.5 (ϵ 18,000) and 336.5 mμ (ϵ 14,500). The nmr spectrum showed a broad phenyl multiplet at 7.22 ppm, the tertiary hydrogen at 5.04 ppm as a broad peak, and the methyl at 1.96 ppm as a doublet, $J = 2$ cps.

β-Naphthyltetraphenylcyclopentadienol (Ie). This compound was prepared in 75% yield by reaction of β-naphthylmagnesium bromide with tetracyclone. It was crystallized from benzene, mp 214–215°.

Anal. Calcd for $C_{39}H_{28}O$: C, 91.4; H, 5.5. Found: C, 91.1; H, 5.7.

Pentachlorocyclopentadienyl Cation (V). Hexachlorocyclopentadiene (1.0 g) was added to 8.0 g of SbF_5, and the mixture was shaken at room temperature for 2 min. This solution, containing pentachlorocyclopentadienyl cation (as revealed by the esr spectrum, see Discussion), could be stored at Dry Ice temperature.

Ten such mixtures were poured into well-stirred methanol at room temperature, and an excess of sodium bicarbonate was added. The methanol was then removed *in vacuo*, and the residue was taken up in methylene chloride, dried, and distilled. The major products were dimers of hexachlorocyclopentadiene, but 5% of the material was volatile *in vacuo*. The principal component of this volatile material was hexachlorocyclopentadiene, but about 20% was identified as 1,1-dimethoxytetrachlorocyclopentadiene (VI) by comparison of its vpc retention time, nmr, and mass spectrum with those of an authentic sample. A control experiment showed that the authentic ketal (VI) could be recovered in 70% yield if it was dissolved in the methanol and SbF_5 was then added as in the quenching experiment. When SbF_5 was quenched into methanol containing hexachlorocyclopentadiene, the volatile product was recovered hexachloro compound with no detectable trace of the ketal (VI).

Electron Spin Resonance Studies. Solutions of the carbonium ions were frozen at 77°K and then examined in a Varian esr spectrometer. The results are presented in the Discussion section.

Magnetic Susceptibility Measurements. The nmr method described by Evans[13] was used. Solutions of the cyclopentadienols and of the corresponding cations were prepared in CH_2Cl_2, and each solution was placed in an nmr tube along with a capillary containing pure CH_2Cl_2. The separation in the nmr between the CH_2Cl_2 line of pure solvent and that of solution as measured at room temperature and at −54.6° for the alcohols, and at −54.6° for the cations (temperature measured with a copper–constantan thermocouple inside the nmr tube). The results are presented in Table I. This method was also applied to diphenylpicrylhydrazyl and gave results in good agreement with the known magnetic susceptibility of this radical.

Acknowledgment. We want to thank Mr. W. H. Yoger for his aid in determining some of the esr spectra.

Rates of Reaction of *exo*- and *endo*-5-Norbornene-2-boronic Acid with Mercuric Chloride

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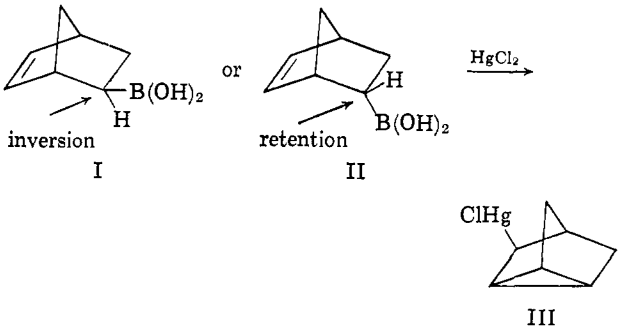
Abstract: The rates of reaction of mercuric chloride with *exo*- and *endo*-5-norbornene-2-boronic acid, both of which yield nortricyclylmercuric chloride, have been measured in the presence of excess chloride ion in aqueous acetone buffered with potassium acid phthalate and phthalic acid. Aliquots were analyzed for unreacted boronic acid by removal of the mercury(II) with stannous chloride oxidation of the boronic acid with hydrogen peroxide and gas chromatography of the resulting dehydronorborneol. The *exo*/*endo* rate ratio is 400 (±40) at 25°, 270 at 45°. The rate law is $-d[RB(OH)_2]/dt = k[RB(OH)_2][HgCl_3^-][RCO_2^-][RCO_2^-]/[Cl^-]$. The mechanism and its relation to other electrophilic displacements at saturated carbon are discussed.

Cyclopropane rings may be opened or closed by processes involving electrophilic displacement at one carbon atom, usually accompanied by nucleophilic displacement at the other. Electrophilic displacement with inversion occurs in the reaction of *exo*-5-norbornene-2-boronic acid (I) with mercuric chloride to yield nortricyclylmercuric chloride (III), and has been shown qualitatively to be much faster than the corresponding retention process with the *endo* isomer II.[2]



I II III

Although concerted electrophilic displacements ordinarily occur with retention, inversion has been observed recently in alkaline ring openings of cyclopropanols.[3,4] However, the transition states appear to have a high degree of carbanion or SE1 character. Ring opening by acid is clearly SE2 but occurs with retention. An SE2 reaction with preferred inversion evidently occurs in the bromination of quadricycloheptanedicarboxylic acid.[5]

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(1) (a) We thank the National Science Foundation for financial support, Grant GP-2953. (b) Alfred P. Sloan Foundation Fellow.

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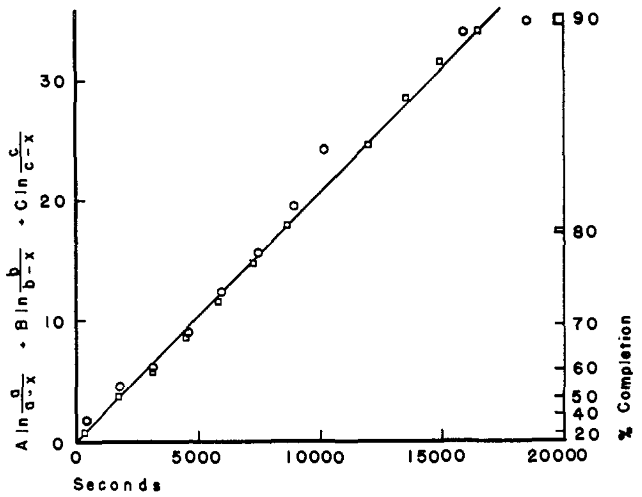

Figure 1. Plot of the reaction of *exo*-5-norbornene-2-boronic acid with mercuric chloride, runs 1 and 2 of Table I, according to eq 3 and 4. Values of a were 0.0726 and 0.0720 M; lines marking "% completion" are broadened when affected by the difference.

The objectives of the present study were to determine the relative rates of inversion and retention in the reactions of the norborneneboronic acids with mercuric chloride under conditions chosen for experimental convenience, and to obtain information about the rate law to put the mechanistic interpretation[2] on a sounder basis.

Results

The reactions were run in aqueous 75% acetone (by volume) under nitrogen. The initial concentration of *exo*- or *endo*-5-norbornene-2-boronic acid,[2,6] introduced as the more easily purified butyl ester, was about 0.07 M, and the other reactants were generally in the 0.1–0.2 M range. Mercuric chloride was used together with an excess of sodium chloride over that required for complete conversion of the mercury(II) to $HgCl_3^-$. Otherwise, the rate law was exceedingly complex, as observed previously in a direct displacement of boron by mercury(II).[7] The departure of boron is normally facilitated by bases.[7] We used potassium acid phthalate together with phthalic acid for buffering.

Aliquots were analyzed by stopping the reaction with stannous chloride, oxidizing the unreacted boronic acid with hydrogen peroxide in the presence of sodium carbonate, and gas chromatographing the resulting dehydronorborneol. A reference compound, cyclohexanol, added to the original reaction mixture permitted quantitative comparison. This analytical method was not suitable for boronic acid solutions much more dilute than those used, and the other reactants were about as concentrated as their solubilities would permit. Accordingly, the usual pseudo-first-order kinetic treatment could not be used. A further limitation of the analytical method was the instability of both dehydronorborneols to the hydrogen peroxide solution. It was necessary to inject the sample into the gas chromatograph within 5–10 min after adding the hydrogen peroxide to avoid erratic results. This limited the frequency of points to one in 25 min, the time required for chromatography, and precluded following rapid reactions or initial rates.

In order to obtain plots that could be interpreted, it was necessary to assume a rate law. It seemed likely that the rate would depend on the boronic acid, mercuric chloride, and the buffer anion.[7]

$$-d[RB(OH)_2]/dt = k[RB(OH)_2][HgCl_2][RCO_2^-] \quad (1)$$

Since our conditions included excess chloride ion, a fairly large stability constant for $HgCl_3^-$ would require replacement of $[HgCl_2]$ by $[HgCl_3^-]/[Cl^-]$ to obtain the observable rate law

$$-d[RB(OH)_2]/dt = k[RB(OH)_2][HgCl_3^-][RCO_2^-]/[Cl^-] \quad (2)$$

Although the stability constant for $HgCl_3^-$ is only 7 (±2) in water, it increases to 10^6 in acetonitrile[8] and could easily be large enough in 75% acetone to require eq 2, as was found to be the case.

Integration of eq 2 by partial fractions yields an equation of the form

$$kt = A \ln [a/(a-x)] + B \ln [b/(b-x)] + C \ln [c/(c-x)] \quad (3)$$

where x is the molarity of boronic acid consumed, a, b, and c are the initial concentrations of boronic acid mercuric chloride, and potassium acid phthalate, and A, B, and C are constants having the values

$$A = (a+d)/[(a-b)(a-c)];\ B = (b+d)/[(b-a)(b-c)];\ C = (c+d)/[(c-a)(c-b)] \quad (4)$$

where d is the sodium chloride in excess of that required for the formation of $HgCl_3^-$.

The reaction of *exo*-5-norbornene-2-boronic acid yielded a linear plot with eq 3 and 4 to 90% completion, as shown for the conditions with the most extensive data in Figure 1.

Although the plots based on the rate law of eq 2 are linear, simple third-order plots based on eq 1 fall off only slightly. (Integration of eq 1 also yields eq 3, but with $A = 1/[(a-b)(a-c)]$, $B = 1/[(b-a)\cdot(b-c)]$, and $C = 1/[(c-a)(c-b)]$.) A clear choice was indicated by varying the reagent concentrations. Values of k obtained graphically from eq 2 remained reasonably constant, but those from eq 1 did not, as shown in Table I.

The *endo*-boronic acid (II) also yielded linear plots with the rate law of eq 2, in one case to 64% completion (19 days at 25°). However, there was a somewhat erratic tendency for the plots to curve upward after long reaction times (see Discussion). The k's determined from the initial slopes of three runs ranged from 4.6 to 5.1×10^{-6}, average 4.9×10^{-6}, at 25.0°. The scatter of points was in about the same range as that of the *exo* isomer up to 70% completion (see Figure 1), a proportionately greater spread than found in the 70–85% completion range where most of the points for the *exo* isomer were taken.

At 45.2°, k for the *exo*-boronic acid was 8.1×10^{-3} (based on two three-point runs) and for the *endo* isomer was 3.0×10^{-5} (based on one eight-point run, with the

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(6) D. S. Matteson and J. O. Waldbillig, *J. Org. Chem.*, **28**, 366 (1963).

(7) H. G. Kuivila and T. C. Muller, *J. Am. Chem. Soc.*, **84**, 377 (1962).

(8) L. G. Sillén and A. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 293.

Table I. Rate Constants for the Reaction of *exo*-5-Norbornene-2-boronic Acid with Mercury(II) Chloride and Biphthalate Ion in 75% Acetone at 25°

Run	Reagent increased[a]	Concn, *M*	$10^3 k$, eq 2, l. mole^{-1} sec^{-1}	$10^3 k$, eq 1, l.^{2} mole^{-1} sec^{-1}
1	None	Stock[a]	2.12	30
2	None		2.05	29
3	NaCl	0.358	2.36	9.6
4	$HgCl_2$	0.164	1.8[b]	35[c]
5	Biphthalate	0.199	1.71	
6	Phthalic acid	0.186	2.95	
7	$NaNO_3$	0.426	3.10	

[a] Stock solution: $HgCl_2$, 0.137; total NaCl, 0.168; potassium acid phthalate, 0.110; phthalic acid, 0.031 *M*. [b] Curves upward from about 1.6 to 2.15. [c] After about 50% reaction. The slope to the first point (36%) is 120, to the second (69% reaction) is 43 over-all.

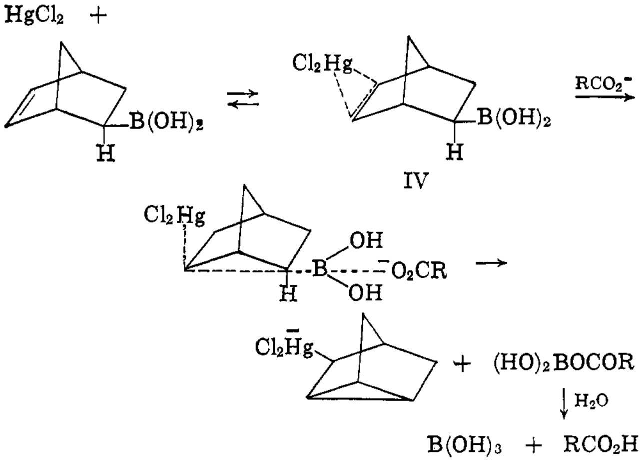
analysis at time zero as a check on initial boronic ester concentration), precision 3–5% in both cases. The calculated ΔE^* values are 12.7 kcal/mole for the *exo* and 16.9 for the *endo* isomer.

The k_{exo}/k_{endo} values. are 420 at 25°, 270 at 45.2°. Allowance for the slight curvature of the *exo* runs would lower the ratio at 25° to 400–410. The uncertainty in these ratios is estimated to be about 10%.

Discussion

The observed rate law supports a modification of the mechanism postulated previously,[2] illustrated with the *exo* isomer I.

$$HgCl_3^- \rightleftarrows HgCl_2 + Cl^-$$



The intermediate (IV) and transition state (V) are drawn as π complexes of mercuric chloride with the double bond. The possibility that a *cis–exo* adduct of mercuric chloride with the norbornene is an intermediate has been pointed out previously.[2] The kinetic results do not provide any evidence on this question. In either case, nucleophilic displacement occurs on that carbon from which mercury or chloride (assisted by mercury) departs, and the role of chloride would be rate inhibiting. Though our data unequivocally rule out $HgCl^+$ as the attacking electrophile (plots involving $[HgCl_2]^2$ curve sharply), data from conditions of low chloride concentration suggest that a much faster reaction involving such a species can occur.

We have made some simplifying assumptions in order to interpret the kinetics in terms of a small number of mercury(II) species. One is that formation of $HgCl_4^{2-}$ is negligible. This would require that its stability constant in 75% acetone be somewhat less than 10, the value in water.[8] This assumption seems reasonable and is in accord with the kinetic results. A second assumption is that the reaction product, nortricyclylmercuric chloride (III), complexes fairly strongly with one chloride ion. Otherwise, the reaction would release two chloride ions for every molecule of boronic acid consumed, and our plots assuming release of one chloride ion should show considerable curvature. Nortricyclylmercuric chloride crystallized at about 90% reaction of the *exo* boronic acid (runs 1 and 2), and it appeared that the reaction did slow down due to the chloride ion released at that time, but the points begin to scatter in this region.

The reciprocal dependence of the rates on chloride ion requires that the stability constant of $HgCl_3^-$ be about 10^3 or greater, while the curvature of run 4, Table I, indicates that it is below 10^4. A similar range, 2×10^3 to 10^4, was suggested by a reaction of the *endo*-boronic acid (II) with a 0.054 *M* excess of mercuric chloride over sodium chloride. After a very rapid initial reaction of the first 25% of the boronic ester, the rate fell off to yield a third-order *k* (eq 1) around 20 times that found when chloride was in slight excess, from which the stability constant for $HgCl_3^-$ could be calculated using arbitrary assumptions about the complexing ability of nortricyclylmercuric chloride. The figures given are the extremes, but rate errors or other mercury(II)–chloride equilibria add further uncertainty. In any event, this seems a reasonable range, greater than in water and less than in acetonitrile,[8] and the much higher rate of this run adds further support to the rate law of eq 2.

The apparent order in the initial concentration of potassium acid phthalate is somewhat less than one. In addition, *k* was increased 50% by a sixfold increase in phthalic acid concentration. The effects are too small to curve the plots according to the rate law of eq 2 appreciably. These results rule out hydroxide ion catalysis. The slight acceleration by acid may involve a secondary effect on the complexing of mercury(II).

Sodium nitrate probably accelerates the reaction by increasing the dissociation of $HgCl_3^-$. The effect on *k* correlates with that of increasing the sodium chloride concentration, run 3, Table I.

The tendency of the *endo k*'s to curve upward around 70% reaction, sometimes earlier, could result from several factors. Nortricyclylmercuric chloride from a long *endo* run was obtained in only moderate yield and appeared to contain some very high-melting contaminant, in contrast to the high yield and purity from an *exo* run. Decomposition of the product might have released mercuric chloride into the reaction mixture, which would account for the 50% rate increase. Escape of solvent through the silicone greased joints or rubber septum is another possibility. The final 25° *endo* run was terminated after 35% completion by failure of the thermal regulator to turn the heat off; no previous irregularity was observed.

The magnitudes of the k_{exo}/k_{endo} ratios, 400 at 25° and 270 at 45.2°, are consistent with previous qualitative observations[2] made with different reaction conditions. The difference between the heats of activation, 4.2 (±1) kcal/mole, is within experimental error of the difference in free energy of activation, 3.55 at both temperatures.

Part of the higher reactivity of the *exo*-boronic acid (I) is due to its greater Lewis acidity, but this steric effect is probably small. A previous measurement[2] showed that the *exo* glyceryl ester was stronger than the *endo* by a factor of three toward hydroxide ion in aqueous glycerol. The correlation between this somewhat questionable figure and the relative strengths of the free boronic acids toward biphthalate ion is unknown. Partial closure of the cyclopropane ring in the transition state would decrease the steric difference,[4] provided that the original attack of mercury(II) was *exo*.

Oxymercuration of norbornylene occurs readily and yields *exo* products.[9] On this basis, we have postulated initial *exo* complexing of mercury(II) with the double bond in norborneneboronic acids, which would be too weak to complex appreciably with biphthalate ion as the initial step. We have shown that bonding to boron is altered in the rate-determining step since there is a B^{10}/B^{11} isotope effect.[10] New evidence that the tricyclic mercury compound is the initial product, not an artifact resulting from rearrangement, has been obtained in a study of the bicycloocteneboronic acids.[11]

Interpretations involving carbanion intermediates (SE1 mechanisms) have been suggested for the "100%" inversion in the alkaline ring opening of cyclopropanols[3] and the *exo*/*endo* rate ratios of 17–50 for ring opening of 1-acetoxynortricyclene in various deuterated alkaline media.[4] However, we do not believe that the transition state can have much carbanion character in our transannular mercuri-deboronations. Salts of aliphatic boronic acids do not solvolyze readily to carbanions; for example, a synthetically useful purification of methaneboronic acid utilizes an aqueous solution of its sodium salt.[12] The unit negative charge on the transition state for the mercuri-deboronation must be highly delocalized, chiefly to electronegative atoms such as oxygen and chlorine, and the qualitative stereochemical result is not changed by conditions of more acid and less chloride ion.[2,11]

Our interpretation of the retention found in proton attack on cyclopropanes would emphasize the special stability of the C–H–C bridged system, isoelectronic with B–H–B bridged bonds, resulting from proton attack on the "banana bonds" of the ring.[3] The stability of such bridged systems falls off rapidly with increasing size or weaker bonding of the electrophile, allowing inversion in alkaline cyclopropanol cleavages,[3,4] quadricycloheptane bromination,[5] and transannular mercurideboronation. Electrophile attack or departure concerted with ring opening or closing is probably common to all these reactions, but carbanion character is not.

Still unexplained is the discrepancy between the usual preference for retention in electrophilic displacements and the inversions found in these reactions involving cyclopropane rings. To our previous literature review and speculations,[2,13] we would like to add the suggestion that norbornenyl cations, anions, and radicals or related transition states probably all favor *exo* attack or departure of any group at either end of the homoconjugated system. Electrophilic and nucleophilic displacement differ in the degree of filling of available molecular orbitals in the transition state,[13] but in the norbornenyl system this effect operates mainly at the terminal attacking and leaving atoms and is thus of only peripheral importance.

Experimental Section

Dibutyl *exo*- and *endo*-5-norbornene-2-boronate[2,6] were redistilled and stored under nitrogen. The *exo* sample was free from any detectable *endo* isomer. The first *endo* sample used was 88 ± 2% pure based on gas chromatography of the derived dehydronorborneols. The *exo* contaminant was removed completely from 10 g of this material by treatment with 1.8 g of mercuric chloride and 1.1 g of sodium acetate in 50 ml of aqueous 60% acetone. However, this left nortricyclylmercuric chloride as a contaminant. Part was removed by crystallization, perhaps more by extraction of a butyl alcohol–ether solution with aqueous sodium iodide, but even after distillation through a spinning-band column the dibutyl *endo*-norborneneboronate deposited a small amount of mercuric iodide. This material yielded the same rate constant as the other within experimental error.

Kinetics. A stock solution was prepared containing all the reactants except the boronic ester in 1:3 water–acetone (by volume). Also included was 0.4% cyclohexanol as the reference compound for gas chromatographic analysis. This solution showed no signs of deterioration in several months. Kinetics were run in a side-arm flask equipped with a magnetic stirrer, a nitrogen inlet which could be closed after flushing out the air, and a rubber septum for injection and removal of material with a hypodermic syringe. A 10-ml portion (measured by pipet) of stock solution was stirred vigorously and 0.2 ml of the boronic ester, weighed accurately in the syringe, was injected. Molarities (see Table I) were calculated assuming volumes additive. Temperature measurement and control were ±0.05°. In most runs, 6–9 points were taken.

Analyses were carried out by withdrawing a 0.55-ml sample and adding it quickly to a freshly prepared solution of 0.10 g of stannous chloride in 0.10 ml of water. Mercurous chloride and mercury precipitated immediately. After 30–60 sec, 1.0 ml of 1.6 *M* sodium carbonate was added. The suspension was centrifuged and the liquid decanted, then treated with 0.30 ml of 30% hydrogen peroxide. Some additional precipitate formed and was settled with the centrifuge. Within 5–8 min after the hydrogen peroxide addition, about 8 μl of the solution was injected into the gas chromatograph. An Aerograph Model 600-D with a Ucon polar column, a flame ionization detector, and a disk integrator were used. The column was kept between 125 and 130°. Integrals were carefully corrected for baseline drift. The dehydronorborneol/cyclohexanol peak area ratio was found. The fraction of boronic acid remaining was calculated by comparison with the peak area ratio at the start of the reaction. This initial measurement could be made only with the *endo* isomer, since the *exo* reacted significantly in less time than it took to withdraw the first sample. It was, therefore, assumed that a given concentration of *exo* isomer would yield the same initial integral as the same amount of *endo*. The constancy of the relation of initial concentration of *endo* boronic ester to the analytical result at "zero" time was better than ±2% in five determinations.

An *exo* run at 25° yielded an infinity point of zero remaining boronic acid after 26 hr and a yield of nortricyclylmercuric chloride above 90%, mp 150–151°. To obtain an *endo* infinity point, sodium carbonate was added to an aliquot in sufficient amount to greatly accelerate the reaction, which had reached 85% completion prior to this. The residual boronic acid was estimated to be 1.5 ± 1%. Nortricyclylmercuric chloride obtained from an *endo* run melted lower, 148–149°, and contained a small amount of very high melting impurity. The yield was only 50%, though separation problems caused some loss.

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