ing. The product was allowed to dry after being washed with water several times. Recrystallization from ethanol-water gave 0.75 g. (70%), m.p. 70–71°.

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Benkeser Reduction of Norbornadiene and Norbornene[1]

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The question of occurrence and extent of conjugation effects in norbornadiene has been of interest in recent years. Although conjugation effects are not manifested in heat of hydrogenation experiments[2] and in free radical addition reactions,[3] the products obtained in ionic addition reactions are well accounted for in terms of a bridged-ion intermediate with homoconjugative character.[4] The exclusive formation in aqueous solution of a 1:1 norbornadiene-silver ion complex suggested conjugation effects (orbital overlap)[5] and the abnormal ultraviolet spectrum[6] of the diene is strong evidence for such conjugation effects in the excited state.

Recently Benkeser has shown that lithium in ethylamine is a powerful and selective reducing reagent toward aromatic rings.[7] The aromatic systems are rapidly reduced to monoolefins which are themselves far more slowly reduced.[7,8] Implicit in the tentative mechanism proposed[7] is the facile reduction of nonaromatic conjugated systems, specifically 1,3-dienes. It seemed of interest then to use the Benkeser reagent with norbornadiene to provide a different system for evaluating conjugation effects in that compound. Since isolated double bonds are reduced with difficulty,[7,8] it was expected that if the compound were reduced readily, nortricyclene would be formed by homoconjugative 1,5-addition.

When reduction of norbornadiene with lithium in ethylamine was tried, rapid color changes, similar to those described for the reduction of aromatic systems,[7] took place and nortricyclene was indeed present in the product mixture. It constituted a surprisingly small portion (13%) of that mixture however. The principal reduction product (64%) was that formed by simple 1,2- addition, norbornene. An appreciable amount of norbornane was also formed; with a 50% excess of lithium it became the major product (55%).

Since the equilibrium mixture of norbornene and nortricyclene contains 77% nortricyclene,[9] it seems very unlikely that the small amount of nortricyclene comes from a rearrangement of initially-formed norbornene precursor. Instead it is most probably a primary product itself, formed by some 1,5- addition to the homoconjugative system. Were isomerization a probable path, one might well expect that far more of the thermodynamically-favored isomer would be formed.[10,11] Homoconjugative addition of lithium to norbornadiene then seems possible but is a minor path in the over-all reaction.

The appearance of norbornane in the product mixture suggested that norbornene should be reduced by the Benkeser reagent also. When the experiment was tried, the color changes were again rapid, reduction proceeded, and norbornane was the only product isolated. In view of the slow reductions of other monoolefins,[7,8] the rapid reaction of norbornene is unexpected and is another example of unusual properties of these strained bridgehead compounds.

Although homoconjugative reduction of norbornadiene occurs only to a minor extent, two observations indicate that reduction (principally 1,2- addition) of the diene is nonetheless a faster process than reduction of norbornene (also 1,2- addition). Both norbornadiene and norbornene were reduced rapidly, but the color changes accompanying the reductions seemed to take place more rapidly with the diene. Secondly, with a small

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[1] This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

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[10] This assumes of course that the rate of isomerization is sufficiently rapid to allow equilibrium to be approached during the time of experiment. Some support for this assumption comes from the reaction between chilled norbornadiene and *p*-thiocresol;[3] within thirty minutes, a product mixture is formed which consists of 60% substituted nortricyclene and 40% substituted norbornene. The nortricyclene derivative was shown to be formed by rearrangement of the substituted norbornene precursor.

[11] One can envision a process whereby norbornene might be formed other than by simple 1,2- addition. Half-protonation of the nortricyclene 2,6-dianion would give an anion that could be pictured as a hybrid of nortricyclenyl-2 anion and norbornenyl-5 anion; final protonation to product could conceivably be rate-controlled so that norbornene was formed predominantly rather than nortricyclene, even through the initial reduction was actually a 1,5- addition. It is difficult to see, however, why the kinetic factor should so strongly favor formation of the thermodynamically-unfavored isomer from a hybrid anion whose canonical structures are essentially equivalent in geometry and steric requirements.

excess of lithium, norbornene was the principal product and was itself reduced to norbornane only to a small extent. Thus norbornadiene apparently reacts more rapidly than does norbornene which apparently reacts more rapidly than other olefins such as cyclohexene.[7] A similar order of reactivity for these olefins toward *p*-thiocresoxy radical[3] and toward aqueous silver ion[5] has been reported. The relative degrees of strain in the olefinic compounds probably account in large measure for this order.[3,5] However, the fact that isolable quantities of norborane were formed even though unchanged norbornadiene was recovered in the product mixture indicates that the differences in reactivities of norbornadiene and norbornene toward lithium in ethylamine are not great.

If the reduction involves the addition of lithium atoms (or of solvated electrons), then perhaps it should not be surprising that the course of the reaction with the diene should be more similar to free radical additions[3] than to cationic ones[4] insofar as the manifestation of conjugative properties are concerned.

EXPERIMENTAL

Norbornadiene and *norbornene* were supplied without charge by Shell Chemical Corp. and by Du Pont Polychemicals Dept., respectively; they were freshly distilled from sodium before use. *Norbornane* was prepared by the low pressure hydrogenation of norbornene with Raney nickel catalyst. Gas chromatography[12] and infrared spectroscopy[13] revealed no contaminants in the norbornene and norbornane samples and only traces of contaminants in the norbornadiene sample. A sample containing 81% *nortricyclene* and 19% norbornene graciously was supplied by Dr. Paul R. Schleyer, Princeton University, and was used without further purification as the source of authentic nortricyclene for spectral comparisons.

Reduction of norbornadiene. Lithium shot (8 mesh, 6.25 g., 0.90 g.-atom) was added to 250 ml. of anhydrous ethylamine in a flask equipped with stirrer, dropping funnel, Dry Ice condenser, and nitrogen atmosphere. The characteristic deep blue color developed quickly and after 30 min. stirring, norbornadiene (36.8 g., 0.40 mole) was added rapidly dropwise. After about half of the diene had been added, the blue color suddenly disappeared. The mixture appeared white with a lump of lithium floating in it. After 15 min., a muddy tan color developed and after 30 min. the lithium was no longer visible. The mixture was stirred for a total of 7 hr. Solid ammonium chloride (49 g., 0.90 mole) was added (attended by considerable heat evolution and probably some loss of volatile product material by entrainment) and the thick mixture was left standing overnight. Water was added and the mixture was extracted twice with ether. The ether solution was washed twice with water, twice with dilute hydrochloric acid, and again with water. After being dried with magnesium sulfate, it was distilled to give 22.2 g. of material, b.p. 95–103°, nearly all of which solidified in the receiver. Gas chromotography[12] resolved the distillate into three fractions (besides carbon tetrachloride solvent) which were shown by comparison of retention times and infrared spectra[13] with those of authentic samples to be norbornadiene (25%), norbornene (48%), and a mixture of norbornane and nortricyclene (27%). Although the last peak was symmetrical, the infrared spectrum of this fraction showed absorption for both norbornane and nortricyclene. Comparison with spectra of standard mixtures (absorbancies at 12.27 μ and 12.51 μ for norbornane and nortricyclene, respectively) indicated that this fraction of the product mixture consisted of 63% norbornane and 37% nortricyclene.

The products from the Benkeser reduction of norbornadiene then were 64% norbornene, 23% norbornane, and 13% nortricyclene.

In another experiment, with a 50% excess of lithium, no diene was recovered. The product, obtained in 74% yield, was found to be 24% norbornene, 55% norbornane, and 21% nortricyclene. Because of inadvertent loss of material by evaporation prior to analysis, these figures are less reliable than those above.

In both experiments small amounts of high boiling residue remained in the pot undistilled.

Reduction of norbornene. The same procedure was used twice with lithium, ethylamine, and norbornene. The deep blue color faded during addition of olefin and was essentially gone when addition was complete. The blue color continually redeveloped around the floating lump of lithium and the stirred mixture was aqua to lavender in color during the entire reaction period (7 hr.). Except for a very small amount of recovered norbornene in one experiment, norbornane was obtained in about 33% yield as the only product (gas chromatographic and infrared spectral analyses). A little high boiling residue remained in the pot undistilled.

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[12] Beckman GC-2 instrument; 6-ft. silicone column, 70–100°, 40–60 ml./min. flow rate of He, CCl_4 solutions.

[13] Beckman IR-5 instrument; CS_2 solutions.

Preparation of 3-Fluorophthalic Anhydride

Adam Heller

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For the synthesis of some polycyclic fluorine compounds, substantial quantities of 3-fluorophthalic anhydride were required. The ease with which the readily accessible 3-nitrophthalic anhydride can be converted by gaseous chlorine into the 3-chloro-compound,[1–3] led us to suspect that the chlorine atom in the latter might be reactive enough for a nucleophilic substitution reaction with potassium fluoride. Indeed, at 280–290° this reaction gave a 50% yield of the hitherto unknown 3-fluorophthalic anhydride.[4]

Similar exchange reactions with potassium fluoride have been observed for chlorine activated by nitro groups[5–7] or by a combination of a nitro-

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