Factors Controlling the Reactions of Nortricyclyl and Dehydronorbornyl Chloride with Sodium and with Magnesium

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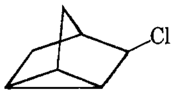
Three factors have been found which affect product composition in the reactions of nortricyclyl and dehydronorbornyl chloride with sodium and with magnesium: temperature, ionic character of the carbon–metal bond, and the presence of either a ring double bond or potential double bond. Evidence concerning these three factors is presented and a mechanism is suggested for the formation of 3- and 4-vinylcyclopentene in the reactions of nortricyclyl and dehydronorbornyl chloride with sodium.

Recently we have reported that treatment of either nortricyclyl chloride (I) or dehydronorbornyl chloride (II) with sodium in *n*-decane at 85–90° generates very nearly identical C_7 hydrocarbon fractions consisting of nortricyclene (III), norbornene (IV), 3-vinylcyclopentene (V), and 4-vinylcyclopentene (VI).[2] Further study of these and similar reactions has revealed three factors which control product composition: temperature, ionic character of the carbon–metal bond, and the presence of either a ring double bond (dehydronorbornyl chloride) or potential double bond (nortricyclyl chloride).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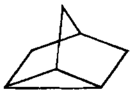
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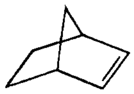
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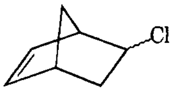
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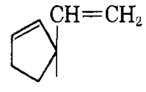
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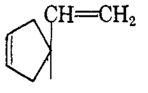
VI

Investigation of the effect of temperature demonstrated that, as the maximum reaction temperature is reduced, the percentage of the C_7 hydrocarbon fraction representing the ring cleavage products V and VI decreases from a total of 55.8% at 154 to 1.0% at 0° (Table I).

Roberts and co-workers[3] have reported that hydrolysis of the Grignard reagent prepared from either dehydronorbornyl or nortricyclyl bromide produces nortricyclene. Grignard reagents in these two systems were reinvestigated at temperatures equivalent to those used in the sodium reaction by preparing the Grignard reagents from the alkyl chlorides in di-*n*-butyl ether, and then subjecting them to heating at 130°. After hydrolysis the Grignard reagent prepared from dehydronorbornyl chloride (54% *endo*, 46% *exo*) produced a 48.1% yield of C_7 hydrocarbons: 92.3% nortricyclene, 7.2% norbornene, and a trace (0.5%) of 3- and 4-vinylcyclopentene. Nortricyclyl chloride resulted in a 15.2% yield of nortricyclene and norbornene in a similar ratio of 87.4:12.6 with no detectable 3- and 4-vinylcyclopentene present.

To rule out the possible influence of the different solvents used in the Grignard and sodium reactions, reactions of the alkyl chlorides with sodium in di-*n*-butyl ether at 85–90° were carried out. Vinylcyclopentenes were formed, and the product ratios were similar to those obtained in the *n*-decane solvent. The reaction of dehydronorbornyl chloride (II, 54% *endo*, 46% *exo*) leads to a C_7 hydrocarbon composition of 65.6% III, 14.2% IV, and 20.2% V and VI, while I produces a corresponding composition of 57.7% III, 9.5% IV, and 32.8% V and VI. The more highly ionic bond of the alkyl sodium compound,[4] then, is apparently necessary in order for the ring cleavage reaction to make any significant contribution to product composition. The greater density of negative charge available for rearrangement at the carbon atom of the more highly ionic bond would seem to point to a carbanionic rearrangement. This dependence upon the ionic character of the carbon–metal bond is consistent with the carbanionic rearrangements in the 2,2-diphenylpropyl system studied by Zimmerman and Zweig.[5,6] A final argument in favor of a carbanionic cleavage mechanism is that several studies of dehydronorbornyl and nortricyclyl free radicals have not revealed similar ring cleavages to that reported here.[7]

The question of whether or not the ring double bond or potential double bond is necessary in the starting chloride for ring cleavage was answered by investigating the reaction of norbornyl chloride (VII) with sodium. Norbornyl chloride (50% *exo*, 50% *endo*) when treated with sodium produces a 27% yield of C_7 hydrocarbons composed of 32.2% nortricyclene (III), 30.0% norbornene (IV), and 37.8% norbornane. No ring cleavage products were found. The nortricyclene seems best explained by an intramolecular insertion reaction of carbene intermediate VIII, generated as the

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[1] National Defense Act Fellow, 1959–1962.

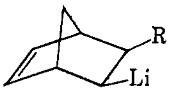
[2] P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, **28**, 3234 (1963).

[3] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

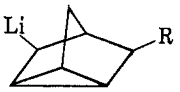
[4] The sodium–carbon bond has an estimated 47% ionic character while the magnesium–carbon bond has only 27% and the lithium–carbon bond is intermediate with 43% (E. G. Rochow, D. R. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 65, 77).

[5] H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

[6] The absence of ring cleavage following generation of intermediate i and ii by addition of alkyl and aryl lithium to norbornadiene, investigated by G. Wittig and E. Hahn [*Angew. Chem.*, **72**, 781 (1960)] and G. Wittig and J. Otten, [*Tetrahedron Letters*, **10**, 601 (1963)], may be explained on the basis of the first two factors. The reactions were, in general, carried out at lower temperatures and the carbon–lithium bond would be expected to be less susceptible to carbanionic rearrangement.


i

R = n-C_4H_9, C_6H_5


ii

R = n-C_4H_9, C_6H_5, i-C_3H_7, t-C_4H_9

[7] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); P. J. Graham, E. L. Buhle, and N. Pappas, *J. Org. Chem.*, **26**, 4658 (1961); E. S. Huyser and G. Echegaray, *ibid.*, **27**, 429 (1962); J. W. Wilt and A. A. Levin, *ibid.*, **27**, 2319 (1962).

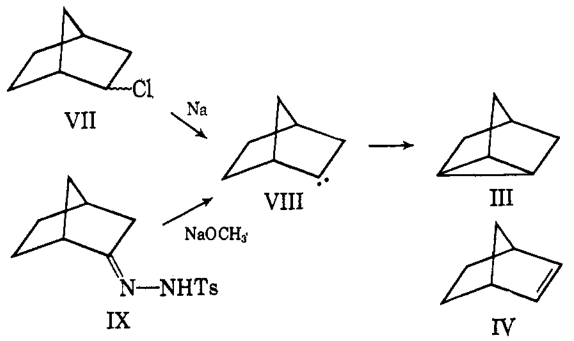
TABLE I

THE REACTIONS OF NORTRICYCLYL AND DEHYDRONORBORNYL CHLORIDE WITH SODIUM

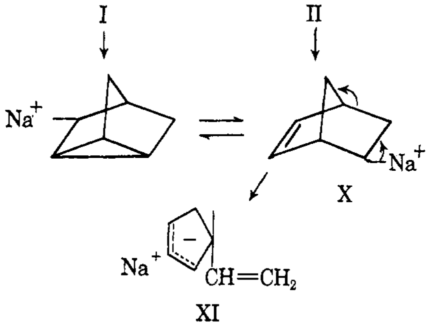
RCl	Oil-bath temp., °C.	Max. temp.,[a] °C.	Yield, %	III, %	IV, %	V, %	VI, %	Norbornadiene, %
I[b]	85–90	154	20.5	34.3	9.9	18.7	37.1	
I[c]	85–90	133	19.2	71.0	10.0	5.9	13.1	
II[c]	85–90	133	27.1	64.0	13.0	7.5	13.5	2.0
I[c]	25	108	21.8	85.6	8.5	1.7	4.2	
II[c]	25	108	29.5	80.2	11.7	2.3 (combined)		5.8
I[c]	0	0	8.3	93.0	6.0	1.3 (combined)		
II[c]	0	0	10.4	79.6	7.4	1.0 (combined)		12.0

[a] Maximum temperature reached inside the reaction flask. [b] No solvent used. [c] Alkyl chloride, 5.00 g.; *n*-decane, 12.5 ml.; 0.90 g. of sodium.

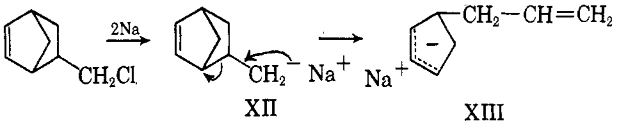
result of α-elimination induced by norbornylsodium, since carbenoid decomposition of the *p*-toluenesulfonylhydrazone of norcamphor results nearly exclusively in nortricyclene.[8] In spite of the fact that only trace amounts of norbornene are formed in basic decomposition of IX, α-elimination as well as β-elimination must be listed as a possible reaction pathway for the production of norbornene from VII. The different norbornene–nortricyclene ratios may be the result of different modes of formation of bivalent carbon intermediate VIII.[9]



The dependence of the ring cleavage on the presence of a double bond or potential double bond may be rationalized on the basis of two factors: stabilization of the carbanion by allylic resonance[10] and greater relief of strain in the more highly strained system.[11] Thus, the cleavage reaction may be viewed as the result of the electronic shifts pictured in X which produce mesomeric carbanion XI.[12]



Similar cleavage of a norbornyl carbanion would have produced a nonresonance-stabilized vinylcyclopentyl carbanion. Two additional examples of this type of ring cleavage are found in the generation of 3- and 4-allylcyclopentene upon treatment of dehydronorbornylmethyl chloride with sodium (XII → XIII),[13] and in the generation of Δ^3-cyclopentenylacetamide by cleavage of dehydronorcamphor with sodium amide.[14]



The ring cleavage reaction of norbornadiene recently reported by Finnegan and McNees[15] may also be classified with the above reactions. Treatment of norbornadiene with amylsodium results in the generation of cyclopentadiene and acetylene. The authors favor a cleavage mechanism involving proton abstraction at C-2 rather than C-7.[16] The cleavage of the C-3–C-4 bond, resulting from the shift of the pair of electrons at C-2 to form a C-2–C-3 triple bond (XIV) is analogous to those listed above. This bond cleavage is clearly dependent on the second double bond since 2-nor-

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[8] L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961); this decomposition was repeated in our laboratories with nearly identical results [a trace (0.5%) of norbornene was detected in the C_7 hydrocarbon fraction].

[9] While in some cases there is good agreement of product composition for reactions proceeding *via* a bivalent carbon intermediate formed by different routes [for example, see G. L. Closs, *ibid.*, **84**, 809 (1962)] in other instances significant differences in product composition are apparent [G. L. Closs and J. J. Cyle, *ibid.*, **84**, 4350 (1962); G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4984 (1962); G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962)].

[10] The usual order of stability of carbanions (allyl > vinyl > alkyl), as measured by preferential proton abstraction by alkyl sodium, is upset in the case of cyclopentene. A. A. Morton and R. A. Finnegan [*J. Polymer Sci.*, **38**, 19 (1959)] have found that cyclopentene undergoes vinyl rather than allylic proton abstraction. Nevertheless it seems reasonable to assume that an allylic cyclopentenyl carbanion will be more stable than a cyclopentyl carbanion either through resonance or inductive stabilization.

[11] R. B. Turner, W. R. Meador, and R. E. Winkler [*J. Am. Chem. Soc.*, **79**, 4116 (1957)] have found that, in spite of the nonbonded repulsions introduced as a result of the reduction of the norbornene double bond, the heat of hydrogenation of norbornene is 6 kcal. greater than that for cyclohexene, and 7.4 kcal. greater than that for cyclopentene.

[12] G. Wittig and G. Klumpp [*Tetrahedron Letters*, **10**, 607 (1963)] have recently reported a reaction which may be quite similar in mechanism to the dehydronorbornyl chloride–sodium reaction. Treatment of norbornadiene with lithium produced norbornene, nortricyclene, and 3-vinylcyclopentene.

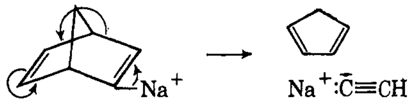
[13] P. K. Freeman, D. E. George, and V. N. M. Rao, preliminary experimental results concerning this reaction were presented at the Northwest Regional Meeting of the American Chemical Society, Bellingham, Wash., June, 1963, Abstracts, p. 25; complete details will be reported at a later date.

[14] S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).

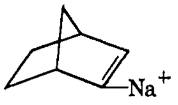
[15] R. A. Finnegan and R. S. McNees, *Tetrahedron Letters*, **17**, 755 (1962).

[16] This appears even more certain now, since A. Streitweiser, Jr., and R. A. Caldwell [*J. Org. Chem.*, **27**, 3360 (1962)] have found only C-2 proton abstraction when norbornadiene is treated with butyllithium with no evidence for C-7 proton abstraction.

bornenylsodium (XV), produced by treatment of norbornene with butylsodium in pentane[17] or as repeated in this laboratory in *n*-decane at 125–130°,[18] does not undergo ring cleavage.



XIV



XV

Finally, it is interesting to note that the lack of a second carbon–carbon bond cleavage following the transformation of X to XI may be due to the fact that a vinyl carbanion would not be expected to be so good a leaving group as an ethynyl carbanion.[19]

Experimental[20]

Reactions of Nortricyclyl Chloride and Dehydronorbornyl Chloride with Sodium.—These reactions were carried out in *n*-decane as solvent as previously described, isolating the C_7 hydrocarbon fraction directly by vacuum distillation.[2] The results are summarized in Table I.

In order to test the effect of changing solvent upon the ring cleavage reaction, nortricyclyl chloride and dehydronorbornyl chloride (54% *endo*, 46% *exo*) were treated with sodium in di-*n*-butyl ether. The procedure was essentially the same as that used above with *n*-decane as solvent. Alkyl chloride (5.0 g.), 0.9 g. of sodium, 12.5 ml. of di-*n*-butyl ether, and an oil-bath temperature of 85–90° were employed. After the 1-hr. stirring period was complete, the reaction mixture was neutralized with methanol, washed with water, and dried. Vapor phase chromatographic analysis of the resulting di-*n*-butyl ether solution on a 3-m. Dow Corning QF-1 silicone oil column showed that the C_7 hydrocarbon fractions had the following compositions: 65.6% nortricyclene, 14.2% norbornene, and 20.2% 3- and 4-vinylcyclopentene from dehydronorbornyl chloride; 57.7% nortricyclene, 9.5% norbornene, and 32.8% 3- and 4-vinylcyclopentene from nortricyclyl chloride.

Nortricyclyl and Dehydronorbornyl Grignard Reagents.—To 2.0 g. (0.083 g.-atom) of magnesium and a crystal of iodine in a dry 100-ml. flask fitted with a mechanical stirrer, a pressure-equalized dropping funnel, and a condenser attached to a calcium chloride drying tube, was added 1 g. of nortricyclyl or dehydronorbornyl chloride in 1 ml. of absolute di-*n*-butyl ether. The mixture was stirred mechanically at 50–55°, oil-bath temperature, and the reaction began immediately. After an additional 10 ml. of di-*n*-butyl ether was added, 9.0 g. of the alkyl chloride in 9 ml. of di-*n*-butyl ether was added dropwise at 50–60°. The mixture was heated with stirring at 85–90° for 2 hr. in the first pair of experiments and at 125–130° for 75 min. in the second pair of experiments.

The mixture then was cooled to room temperature and poured into an ice–water mixture saturated with ammonium chloride. After shaking in a separatory funnel, the organic layer was washed with water and dried. Vapor phase chromatographic analysis of the di-*n*-butyl ether solution was accomplished on a 3-m. Dow Corning QF-1 column.

Nortricyclyl Grignard reagent heated at 85–90° gave a 68.3% yield of C_7 hydrocarbons composed of 96.8% nortricyclene, 3.2% norbornene, and a trace (0.1%) of 3- and 4-vinylcyclopentene. Dehydronorbornyl Grignard reagent (from dehydronorbornyl chloride, 44% *exo*, 56% *endo*) heated at 85–90° gave a 70.4% yield of C_7 hydrocarbons: 91.4% nortricyclene, 8.6% norbornene, and no detectable 3- and 4-vinylcyclopentene. Heated at 125–130°, nortricyclyl Grignard reagent produced a 15.2% yield of C_7 hydrocarbons: 87.4% nortricyclene, 12.6% norbornene, and no detectable 3- and 4-vinylcyclopentene. At this same temperature the dehydronorbornyl Grignard reagent (from dehydronorbornyl chloride, 46% *exo*, 54% *endo*) gave a 48.1% yield of C_7 hydrocarbons: 92.3% nortricyclene, 7.2% norbornene, and 0.5% 3- and 4-vinylcyclopentane.

Reaction of Norbornyl Chloride with Sodium.—Using the same procedure and apparatus described previously for nortricyclyl chloride,[2] 5.0 g. (0.037 mole) of norbornyl chloride (50% *endo*, 50% *exo*) was allowed to react with 0.85 g. (0.037 g.-atom) of sodium in *n*-decane at 85–90°. The C_7 hydrocarbon fraction (1.0 g.), isolated directly from the reaction mixture by vacuum distillation, had the following composition: 37.8% norbornane, 30.0% norbornene, and 32.2% nortricyclene.

The percentage composition was obtained by vapor phase chromatographic analysis of the product mixture on two different columns. A 2-m. Dow Corning 200 silicone oil column gave two peaks in the ratio of 70:30. The infrared spectrum of the isolated 30% peak, showed it to be norbornene, while infrared analysis of the 70% component proved that it was a mixture of norbornane and nortricyclene. A Carbowax 1500 column also gave two peaks in a 67.8:32.2 ratio. The 32.2% component corresponded to nortricyclene; the 67.8% component was a mixture of norbornene and norbornane.

Norcamphor *p*-Toluenesulfonylhydrazone.—Norcamphor *p*-toluenesulfonylhydrazone was prepared by a procedure modeled after that used by Cristol for nortricyclenone.[21] An analytical sample prepared by recrystallization from ethanol melted at 201.5–202.5° dec.

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.47. Found: C, 60.55; H, 6.53.

Carbenoid Decomposition of Norcamphor *p*-Toluenesulfonylhydrazone.—This decomposition was carried out according to the procedure outlined for the sodium methoxide induced decomposition of nortricyclenone *p*-toluenesulfonylhydrazone.[21] The 28.7% yield of C_7 hydrocarbons obtained was principally nortricyclene (99.5%) with a trace of norbornene (0.5%).

Reaction of Norbornene with *n*-Butylsodium.—A solution of *n*-butylsodium in 70 ml. of *n*-decane was prepared from 7.3 g. of sodium (0.32 g.-atom) and 10.6 g. (0.115 mole) of *n*-butyl chloride using the procedure of Morton and co-workers.[22] A solution of 5.0 g. (0.053 mole) of norbornene in 10 ml. of *n*-decane was added dropwise to the *n*-butylsodium solution at 80–85°. After the addition was complete, the reaction flask was heated at an oil-bath temperature of 85–90° for 30 min. and then at 125–130° for 30 min. After washing the decane solution with water and drying, infrared analysis and vapor phase chromatographic analysis (on a 3-m. Dow Corning QF-1 silicone oil column and a 2-m. Dow Corning 200 silicone oil column) demonstrated that 3.74 g. of norbornene was present (a 75% recovery). There were no traces of any other C_7 hydrocarbons.

Acknowledgment.—The authors gratefully acknowledge the support of this research by the National Science Foundation (NSF-G13511).

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

[18] The result in *n*-decane rules out the possibility, perhaps somewhat unlikely, that XV is a precursor of the 3- and 4-vinylcyclopentenes in the dehydronorbornyl chloride–sodium or nortricyclyl chloride–sodium reaction.

[19] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt Rinehart and Winston, New York, N. Y., 1959, p. 258.

[20] Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[21] S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

[22] A. A. Morton, G. M. Richardson, and A. T. Hallowell, *J. Am. Chem. Soc.*, **63**, 327 (1941).