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## The Relative Stability of Bridged Hydrocarbons. Norbornene and Nortricyclene<sup>1</sup>

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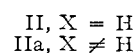
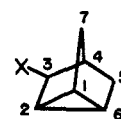
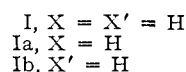
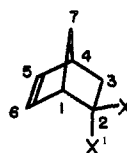
Nortricyclene (II), a compound containing a three-membered ring, was found to be more stable than the olefinic isomer norbornene (I). Equilibration of both pure materials at the temperature of reflux by means of a silica-alumina catalyst gave mixtures with identical composition, 23% I and 77% II. There was no evidence for the formation of isomers other than I and II in the reaction. The earlier methods of preparation of norbornene, involving dehydration or dehydrohalogenation of norbornyl derivatives, are shown to have led instead to mixtures containing nortricyclene (II) as the major component. The same acid catalyst did not isomerize norbornadiene (IV). Norbornane (III) was almost entirely unaffected by prolonged heating with aluminum chloride and aluminum bromide. The theoretical implications of these results are discussed.

The heat of isomerization of cyclopropane to propene has been estimated to be  $-7.86$  kcal. per mole.<sup>2</sup> Three-membered rings, when present in more complicated molecules, generally are unstable relative to olefinic isomers with the same sequence of carbon atoms; conversion usually can be accomplished by heat or by suitable catalysts.<sup>3a,3b</sup>

Among the most interesting of these cyclopropane-olefin transformations are those involving homoallylic rearrangement.<sup>3b,6,9,11,12</sup> When, in such rearrangements, interconversion between the cyclic and acyclic forms is possible, it is often observed that the formation of cyclopropyl derivatives is favored in reactions governed by kinetic control, while conditions permitting thermodynamic control of the reaction course lead to production of olefinic products. However, it has been pointed out by Roberts,<sup>11</sup> that certain transfor-

mations in the bicyclo[2.2.1]heptane ring system furnish exceptions to this generalization. Thus, in reactions presumably involving free radical, anionic and cationic intermediates, derivatives of nortricyclene (II) predominated over those related to norbornene (I) to a considerable extent.

Many additional examples are now available to lend support to this initial conclusion. For instance, the solvolysis of 5-norbornen-2-*endo*- and *exo*-yl (dehydronorbornyl) (Ia and Ib) and 3-nortri-



- (1) Paper I of a series on Bridged Ring Systems.
- (2) J. W. Knowlton and F. D. Rossini, *J. Research Natl. Bur. Standards*, **43**, 113 (1949). The value for the free energy of isomerization does not appear to be available.
- (3) (a) *Cf.*, for example, the isomerization of cyclopropane<sup>4,5</sup> and of simple substituted cyclopropanes,<sup>4,6,7</sup> rearrangements in the thujane and carane series,<sup>8</sup> and the conversion of 3,5-cyclosteroids into cholestene derivatives.<sup>9,10</sup> A discussion, extremely pertinent to points raised in the present paper, has been presented by Roberts and co-workers.<sup>11</sup> (b) A comprehensive review of the chemistry of small ring compounds is available; E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955).
- (4) G. Egloff, G. Hulla and V. I. Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942.
- (5) R. H. Lindquist and G. K. Rollefson, *J. Chem. Phys.*, **24**, 725 (1956); J. R. McNesby and A. S. Gordon, *ibid.*, **25**, 582 (1956).
- (6) J. D. Roberts and R. H. Mazur, *THIS JOURNAL*, **73**, 2509, 3542 (1951).
- (7) R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).
- (8) J. Simonsen and L. N. Owen, "The Terpenes," Vol. II, Cambridge University Press, Cambridge, 1949.
- (9) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Third Ed., Reinhold Publishing Corp., New York, N. Y., 1949, pp. 256 ff.; E. M. Kosower and S. Winstein, *THIS JOURNAL*, **78**, 4347, 4354 (1956).
- (10) For an additional steroid example, see A. R. H. Cole, *J. Chem. Soc.*, 3810 (1954), and references therein cited.
- (11) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *THIS JOURNAL*, **72**, 3116 (1950); *cf.* also J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954); S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950).
- (12) For a discussion with leading references, see M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

cyclyl (IIa) derivatives,<sup>11,13</sup> as well as the nitrous acid deamination of 5-norbornene-2-*endo*-yl amine (Ia, X' = NH<sub>2</sub>),<sup>13,14</sup> gave mixtures of Ib and IIa consisting chiefly (83–96%) of nortricyclic products (IIa). Furthermore, several groups of workers<sup>15–17</sup> have studied the addition of one mole of various reagents to norbornadiene (IV) under a variety of experimental conditions. In strong acid-catalyzed carboxylic acid media, *e.g.*, acetic acid-toluenesulfonic acid<sup>16</sup> and formic acid-boron trifluoride,<sup>15</sup> which would be expected to give largely thermodynamic control of the product ratios, only 10–15% of olefinic esters (Ib, X = OAc or OOC) were present in the product. It appears, therefore, in these instances, that derivatives containing a cyclopropane ring are favored at equilibrium. However, there has been no successful attempt to ascertain the exact position of such equilibria. Such a study appeared to be particularly desirable

- (13) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **77**, 3034 (1955).
- (14) W. E. Parham, W. T. Hunter and R. Hanson, *ibid.*, **73**, 5068 (1951).
- (15) L. Schmerling, J. P. Luvisi and R. W. Welch, *ibid.*, **78**, 2819 (1956).
- (16) S. Winstein and M. Shatavsky, *Chemistry & Industry*, 16 (1956); *THIS JOURNAL*, **78**, 592 (1956).
- (17) S. J. Cristol and G. D. Brindell, Abstracts of Papers, Cincinnati Meeting, Am. Chem. Soc., March, 1955, p. 35N.

in view of the fact that other tricyclic compounds in the bicyclo[2.2.1]heptane series are known to be less stable than certain of their olefinic isomers.<sup>18</sup>

### Results

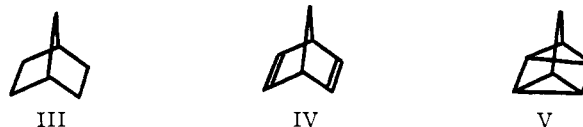
**Norbornene (I) and Nortricyclene (II).**—Pure norbornene was prepared by the Diels-Alder reaction of ethylene with cyclopentadiene.<sup>19</sup> The homogeneity of this material was shown by the following observations: (1) Oxidation with sodium permanganate gave *cis*-1,3-cyclopentanedicarboxylic acid in 95% yield<sup>20</sup> (nortricyclene was reported to be unaffected by potassium permanganate).<sup>11</sup> (2) Quantitative microhydrogenation under mild conditions resulted in the uptake of 97.3 and 98.8% of the theoretical quantity of hydrogen.<sup>21</sup> (3) Fractional distillation through an efficient column gave substance of constant boiling point (96.0° at 760 mm.) and of constant melting point (46.0–46.5°), which represented over 80% of the material collected. (4) Gas chromatography, employing three different column materials, failed to reveal the presence of impurities.

Earlier methods reported for the preparation of norbornene, involving acid-catalyzed dehydration (m.p. 52–54°)<sup>22</sup> and quinoline dehydrohalogenation (m.p. 51–53°, 50–52°),<sup>23</sup> gave material of higher melting point, but these products apparently consisted mainly of nortricyclene (m.p. 57.5–57.8°), a compound isomorphous with norbornene.<sup>24</sup> Thus, the quinoline dehydrobromination of 2-*exo*-norbornyl bromide gave a poor yield of a mixture of norbornene (I) (35%) and nortricyclene (II) (65%), melting at 50.7–52.2° after sublimation. The action of phosphoric anhydride upon 2-*exo*-norbornanol gave a mixture of 30% I and 70% II, m.p. 55.0–56.2°, when purified similarly.<sup>25</sup> There are many instances in the bicyclo[2.2.1]heptane series of the formation of tricyclic byproducts during the course of reactions which normally lead to olefins.<sup>8</sup>

Isomerization of norbornene was effected with a silica-alumina catalyst at the reflux temperature. The course of the reaction was followed by gas chromatography. In the later stages considerable quantities of polymer formed and the temperature of the boiling liquid rose. At equilibrium, 22.9 ± 1.3% of I and 77.1 ± 1.3% of II were present. A repetition of this experiment gave the following values: 22.4 ± 0.8% I and 77.6 ± 0.8% II. For purposes of preparation of II, it was advantageous to stop the reaction before isomeriza-

tion was complete; in this way losses due to polymerization were minimized. In this manner 80% of a mixture containing 71% of II could be obtained from I. Purification of II, by fractional distillation, gave product of b.p. 101.8–102.0° (760 mm.) m.p. 57.5–57.8°, which contained only 1% of I as impurity. The intermediate fractions of this distillation, containing appreciable quantities of both I and II, had melting points intermediate between those of pure I and II.

Isomerization of nortricyclene (II) by the same procedure gave a mixture which analyzed for 22.9 ± 0.9% I and 77.1 ± 0.9% II. In none of these experiments was any monomeric material other than I or II formed, as far as could be detected.



**Norbornane (III).**—The action of aluminum halide catalysts upon saturated hydrocarbons is capable of giving rise to very deep-seated rearrangements, even under mild conditions of temperature.<sup>4,26</sup> In addition, such reactions are often accompanied by extensive fragmentation and degradation. Such catalysts are often used in order to obtain experimentally an estimate of the relative stability of two or more isomers. However, norbornane, b.p. 105.7° (760 mm.), m.p. 87.8–88.3°, was recovered essentially unchanged after prolonged refluxing with either aluminum chloride or aluminum bromide.

**Norbornadiene (IV).**—The preparation of a dicarboxylic acid derivative of the interesting hydrocarbon, tetracyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (V) has been reported recently.<sup>27</sup> It can be seen that compound V is related to IV as II is to I. Attempted isomerization of IV, by methods which were successful for I, failed; the major amount of material could be recovered unchanged. Only a small amount of polymeric material formed, even after refluxing for several days. The known thermal isomerization of IV into cycloheptatriene<sup>28</sup> was, therefore, also not observed under these conditions.

### Discussion

Norbornane (III), the parent compound of the bicyclo[2.2.1]heptane ring system, is quite strained, perhaps to the extent of 20 kcal. per mole.<sup>29</sup> Although this value is quite large, other bicycloheptanes, such as bicyclo[3.1.1]heptane and bicyclo[3.2.0]heptane, easily derivable from III by simple carbonium ion shifts, must be strained even to a greater extent, since they contain four-membered rings.<sup>30</sup> Furthermore, while rearrangements from

(26) H. Pines and J. Mavity in B. T. Brooks, *et al.*, eds., "The Chemistry of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1955, Chap. 39, pp. 9–58.

(27) S. J. Cristol and R. L. Snell, *THIS JOURNAL*, **76**, 5000 (1954).

(28) Shell Chemical Corporation, Technical Information Bulletin, June, 1956; W. G. Woods, *J. Org. Chem.* **23**, 110 (1958).

(29) For the derivation of this figure, see ref. 21. Earlier, lower estimates were based upon a poor choice for a strain-free model compound. See R. P. Linstead, *Ann. Reports (Chem. Soc. London)*, **32**, 305 (1935), and refs. therein cited.

(30) From the heat of combustion of cyclobutane (S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952)) one can estimate the strain in that molecule to be 24 kcal.

(18) For example, only 17% of tricyclene is present at equilibrium with camphene and traces of bornylene (G. Swann and F. J. Cripwell, *Ind. Chemist*, **24**, 373 (1948)). 1,3,3-Trimethylnortricyclene (cyclofenchene)<sup>9</sup> and 1-methylnortricyclene (unpublished observation of the author) are similarly isomerized, for the most part, to olefinic products.

(19) (a) L. M. Joshel and L. W. Butz, *THIS JOURNAL*, **63**, 3350 (1941); (b) C. L. Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944).

(20) S. F. Birch, W. J. Oldham and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

(21) Ph.D. Thesis of the author, Harvard University, 1956.

(22) G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

(23) K. Alder and H. F. Rickert, *ibid.*, **543**, 1 (1940).

(24) This phenomenon is common with compounds in this series (J. Pirsch, *Angew. Chem.*, **57**, 40 (1944)).

(25) Professor J. D. Roberts, private communication, has indicated that similar observations have been made in his laboratories. E. Pulkkinen (*Suomi. Kemistilehti*, **27A**, 26 (1954)) has reported that the aluminum isopropoxide dehydration of 2-*endo*-norbornanol led to a mixture of I and II, but no details have yet appeared.

the bicyclo[3.1.1]heptane to the bicyclo[2.2.1]-heptane ring system occur with ease,<sup>8</sup> there is not a single case of the reverse transformation occurring, except, perhaps, as an intermediate step in a complex reaction sequence.<sup>21</sup> Similarly, hydration of bicyclo[3.2.0]hept-2-ene gave 7-hydroxybicyclo[2.2.1]heptane (7-norbornanol).<sup>31</sup> The inertness of III to aluminum halide rearrangement, is, therefore, somewhat understandable.<sup>32</sup>

The double bond present in norbornene (I) is strained to an unusual extent. Physical data support this statement; e.g., the high degree of complexation with silver nitrate,<sup>33</sup> the abnormally large heat of hydrogenation<sup>34</sup> and the position of C=C and C-H stretching bands in the infrared spectrum, comparable with those of cyclobutene<sup>35</sup> (Table I).

TABLE I

COMPARISON OF NORBORNENE WITH CYCLIC OLEFINS	C=C stretch., <sup>a</sup> cm. <sup>-1</sup>	C-H stretch., <sup>b</sup> cm. <sup>-1</sup>	Ag <sup>+</sup> complex., <sup>c</sup> K <sub>eq.</sub> , l./m.	Heat of hydrogen., <sup>d</sup> kcal./m.
Cyclohexene	1646	3017	0.0188	27.1
Cyclopentene	1611	3045	.114	(25.4) <sup>e</sup>
Cyclobutene	1571	3070	...	..
Norbornene	1568	3070 <sup>b</sup>	.270	33.1
Bicyclo[2.2.2]-octene	1614	..	.098	28.3

<sup>a</sup> Infrared bands; data, unless otherwise indicated, were taken from ref. 35a. <sup>b</sup> Average of the values given for four norbornenes substituted in the 5-position; ref. 35b. <sup>c</sup> Ref. 33. <sup>d</sup> Ref. 34; values in solution at 25°. <sup>e</sup> Estimated roughly from the value in the gas phase at 82°; M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *THIS JOURNAL*, 59, 831 (1937).

The high degree of strain in norbornene is particularly surprising in view of the fact that incorporation of a double bond into the bicyclo[2.2.1]-heptane ring system would *relieve* a number of non-bonded interactions between hydrogen atoms; notably the eclipsed methylene groups at C<sub>2</sub>-C<sub>3</sub> and the 1,3 boat-axial interactions between the *endo*-hydrogens at C<sub>2</sub>-C<sub>6</sub> and C<sub>3</sub>-C<sub>5</sub>. From this point of view, the strain, as measured by the heat of hydrogenation, should be less than that of cyclohexene, by analogy with the similar situation pertaining in cyclopentene. The very much higher (6 kcal.) heat of hydrogenation of norbornene must be attributed to a considerable amount of angle strain in the rigid bicyclic molecule,<sup>34</sup> a conclusion which is supported by the other data cited.<sup>33,35</sup> A further factor, probably minor, is the impossibility of hyperconjugative-type stabilization in norbornene.<sup>11</sup>

In view of the very high degree of strain in I, the greater stability of the cyclopropane derivative, nortricyclene (II), no longer can be considered to be

(31) E. F. Baxter, Jr., unpublished observation.

(32) The similar inertness of cyclopentane may be cited as a precedent.<sup>12</sup>

(33) J. C. Traynham and M. F. Sehnert, *THIS JOURNAL*, 78, 4024 (1956).

(34) R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, 79, 4116 (1957); for an earlier estimate see K. Alder and G. Stein, *Ber.*, 67, 613 (1934).

(35) (a) R. C. Lord and R. W. Walker, *THIS JOURNAL*, 76, 2518 (1954), and refs. therein cited; R. C. Lord, quoted by R. N. Jones and C. Sandorfy in W. West, ed., "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 371 (b) H. B. Henbest, G. D. Meakins, B. Nicholls and R. A. L. Wilson, *J. Chem. Soc.*, 997 (1957).

unexpected. The angle strain in I and II must be very nearly comparable; the free energy difference between the two isomers is only 0.91 kcal/mole.<sup>36</sup> Furthermore, the symmetry of II is particularly favorable from a conformational point of view, since non-bonded interactions have been minimized. This would further favor II over I at equilibrium.

The experimentally determined value for the percentage of I at equilibrium, 23%, appears to be somewhat higher than that obtained for the (presumed) equilibrium between compounds of type Ib and IIa (*vide supra*). This difference easily can be rationalized on conformational grounds. In Ib, the substituent, X, is held in an eclipsed conformation relative to the *exo*-hydrogen atom at C<sub>3</sub>. This results in rendering Ib less stable relative to the unsubstituted parent compound, I. No such interactions are present in either IIa or II, since the hydrogen upon C<sub>2</sub> is perfectly skewed with regard to the substituents upon C<sub>3</sub>. For substituted compounds of the type under discussion, then, the position of equilibrium would be expected to be even more in favor of the tricyclic isomers than in the unsubstituted case.

Recently, a rearrangement of a norbornene derivative into a substituted bicyclo[3.2.0]hept-2-ene has been observed.<sup>37</sup> The driving force for this transformation was attributed to factors other than the decrease of ring strain.<sup>37</sup> However, the possibility that the bicyclo[3.2.0]hept-2-ene ring system is more stable than that present in norbornene cannot be ruled out quite so easily. The incorporation of a cyclopentene-type double bond into the former ring system should result in a net stabilization, relative to norbornene, of roughly 8 kcal. (see Table I). This may be sufficient to reverse the stability order of the parent saturated ring systems, which undoubtedly is: norbornane > bicyclo[3.2.0]heptane. The failure to observe the formation of bicyclo[3.2.0]hept-2-ene by rearrangement from norbornene unfortunately casts no light upon this question, since there may be no energetically feasible path by which these molecules can be interconverted into one another.

Although the strain in IV is probably proportionately greater than in I,<sup>34</sup> V with its collection of three- and four-membered rings is undoubtedly even less stable.<sup>27</sup>

**Acknowledgments.**—The author wishes to acknowledge the assistance of Mr. R. A. Horkitz, who made a number of preliminary observations and prepared several of the compounds used in this research. The gas chromatography apparatus was purchased with a grant from the Food Machinery and Chemical Corporation.

### Experimental<sup>38</sup>

**Norbornene (I).**—Norbornene<sup>19</sup> was purified by fractional distillation. Over 80% of the material collected boiled at 96.0° (const.) (760 mm.) and melted in the range between

(36) Calculated from the relationship,  $\Delta F = -RT \ln K$ ;  $T = 378^\circ$  abs.,  $K = 3.37$ .

(37) S. Winstein and E. T. Stafford, *THIS JOURNAL*, 79, 505 (1957).

(38) M.p.'s and b.p.'s are corrected. Gas chromatographic studies were made upon a Perkin-Elmer model 154-B vapor fractometer, using for the most part, a silicone oil column. Fractional distillations were carried out in a 100 × 1.3-cm. column, filled with Podbielniak Heli-Pak packing.

46.0 and 46.5°. The remainder was only slightly less pure; reported<sup>19b</sup> b.p. 96.1° (cor.), m.p. 46°. Gas chromatography failed to reveal the presence of impurities, either with a silicone oil column, a column employing didecyl phthalate as the liquid phase, or one with silver nitrate-diethylene glycol.<sup>39</sup> The latter column is particularly effective in separating olefins in this series (see ref. 33).

**Dehydrohalogenation of *exo*-Norbornyl Bromide.**<sup>22</sup>—*exo*-Norbornyl bromide, prepared by the addition of HBr to norbornene,<sup>11</sup> was treated with quinoline according to the published procedure.<sup>22</sup> From 15 g. of starting material, only 1.1 g. (14%) of hydrocarbon was isolated. Sublimation gave substance which melted at 50.7–52.2° (lit.<sup>22</sup> 51–53°). Gas chromatography showed the composition of the combined material to be 35% norbornene (I) and 65% nortricycylene (II).

**Dehydration of 2-*exo*-Norbornanol.**<sup>22</sup>—The dehydration of 4 g. of 2-*exo*-norbornanol with 7 g. of P<sub>2</sub>O<sub>5</sub> was performed as reported in the literature.<sup>22</sup> About 1.05 g. of product formed; this contained, however, some polymeric material. After sublimation, 0.8 g. (24%) of hydrocarbon melting at 55.0–56.0° (lit.<sup>22</sup> m.p. 52–54°) was obtained. The composition was 30% I and 70% II.

**Isomerization of Norbornene (I).**—Hydrated titanium dioxide,<sup>40</sup> a catalyst which effectively isomerizes methyl substituted norbornene derivatives (ref. 40 and unpublished observations), failed to cause isomerization of norbornene at the reflux temperature of the latter. Isolation of unchanged material by distillation followed by treatment with fresh catalyst as before also was not successful.

A silica-alumina catalyst<sup>41</sup> effected isomerization, but not without some difficulty. After three hours of refluxing with the catalyst used in the proportion of about 1 g. to 30 g. of the hydrocarbon, the product was distilled from the reaction flask. By this preliminary process, only about 10% isomerization to II had occurred. Treatment of the recovered material with fresh catalyst resulted in ready isomerization, which could be followed conveniently by the increasing temperature of the refluxing liquid. At intermittent times, refluxing was stopped briefly and samples were taken for gas chromatographic analysis. After 12 minutes the pot temperature had risen to 104° and 50% nortricycylene had formed. After 90 minutes, the pot temperature, which was rising more rapidly, was 111°. Only one-half to two-thirds of the amount of sample initially used in the experiment could be distilled from the reaction vessel after this length of time. The analysis showed 22.9 ± 1.3% I and 77.1 ± 1.3% II to be present. About half of the residue could be distilled at 20 mm. pressure between 125 and 150° to give a viscous oil, *n*<sub>D</sub><sup>20</sup> 1.52671, without distinguishing features in the infrared spectrum. This polymeric material was not investigated further.

A second isomerization yielded a mixture which contained 22.4 ± 0.8% I and 77.6 ± 0.8% II.

**Preparation of Nortricycylene (II).**—Norbornene (100 g.) (freshly distilled over sodium) was refluxed with 1.1 g. of silica-alumina catalyst for two hours, and then distilled directly from the reaction flask. A total of 95.5 g. of hydrocarbon was recovered, containing 89% I and 11% II. There remained 3.6 g. in the pot. The hydrocarbon was added to 2.0 g. of titanium oxide catalyst, and refluxed for 790 minutes. At the end of this time only an additional 2–3% of II had formed, since analysis showed the material to contain 13.7% II. Silica-alumina catalyst (1.0 g.) was now added and refluxing continued. After 200 minutes the temperature of the refluxing liquid had reached 103.4° and the material now contained only 31% I. After 70 additional minutes the product (79 g.) was distilled; it contained 71% of II. The pot residue was 12.5 g. Part of the material unaccounted for after both operations (9.0 g.) represented samples taken for analysis; the rest represented operational losses of the volatile material.

A total of 139.8 g. of mixed hydrocarbon from several isomerization reactions, which analyzed for about 25% I,

was fractionally distilled over 1.5 g. of sodium. A summary is presented below.

Fraction	B.p., <sup>a</sup> °C.	M.p., °C.	I, <sup>b</sup> %	II, <sup>b</sup> %	Wt., g.
Forerun	To 96.4	(Wet)	..	..	1.9
1	96.4–97.4	46.8–47.2	86	14	7.1
2	97.4–97.5	48.0–48.7	80	20	6.5
3	97.5–98.9	49.0–49.6	64	36	13.8
4	98.9–100.5	51.8–52.2	38	62	10.8
5	100.5–101.0	52.9–53.9	26	74	13.8
6	101.0–101.6	55.2–55.7	15	85	10.2
7	101.6–101.8	56.8–57.5	6	94	8.9
8	101.8–102.0	57.0–57.7	3	97	8.8
9	102.0–101.9	57.5–57.8	1	99	9.9
10	<sup>c</sup>	56.4–56.9	1	99	38.6
				Residue	6.1
				Distillation loss	4.9

<sup>a</sup> Corrected to 760 mm. <sup>b</sup> Analysis by gas chromatography. <sup>c</sup> Material collected rapidly by overheating the column jacket.

From the individual analysis of the various fractions it was estimated that a total of 32.6 g. or 25.2% of norbornene (I) was present in the 129.7 g. of material collected. The previously reported constants for nortricycylene were: m.p. 56°<sup>11,42</sup>; b.p. 106–107°<sup>11</sup> 106°.<sup>42a</sup> The infrared spectrum of fraction 9 was identical with the spectra of II reproduced in the literature.<sup>11,42</sup>

There was no evidence, in any of the isomerization reactions, of the formation of isomers other than I or II. Gas chromatography revealed the presence of trace amounts of low-boiling materials in some of the samples, but it was felt that these may have been present in the starting material.

**Isomerization of Nortricycylene (II).**—Nortricycylene, 30 g. (taken from fraction 10), was refluxed with 1.0 g. of silica-alumina catalyst. After 35 minutes, the product was distilled, weight 17.2 g. There remained 11.2 g. in the pot. Analysis showed the volatile material to contain 22.9 ± 0.9% I and 77.1 ± 0.9% II.

**Attempted Isomerization of Norbornane (III).** (a) With AlCl<sub>3</sub>.—To 24.7 g. of norbornane (III) was added 3.0 g. of AlCl<sub>3</sub>; the mixture was heated sufficiently to cause very gentle boiling. An air condenser was employed because of the high melting point of the hydrocarbon. The starting material, m.p. 84.7–85.6°, did not contain any lower boiling material, but did give a peak, indicative of a small amount of higher boiling material, when analyzed by gas chromatography. After refluxing 15 minutes, this peak had disappeared, but a new one, appearing at a position before that of norbornane, was present in addition to a few trace compounds. The amount of this impurity, 0.8%, had not changed after 770 minutes of reflux, when the product, m.p. 81.8–85.8°, was distilled from the reaction flask. It was concluded, therefore, that the impurity, originally present in the starting material, had been degraded, but that norbornane had been largely unaffected.

In order to test this postulate, 84.4 g. of III was fractionally distilled from 11.9 g. of AlCl<sub>3</sub>. It was reasoned that, were the lower boiling substance formed from III but present only to a small extent at equilibrium, then removal of the more volatile component by means of the efficient column would allow the conversion of a considerable fraction of the starting material into the new compound. This was not found to be the case. After prolonged reflux, the first fractions (2.1 g.) were found to contain seven components. After an additional period under total reflux, the head temperature did not fall. Continuation of the distillation yielded samples of norbornane, b.p. 105.7° (760 mm.) (const.), m.p. 87.8–88.3°, which were free from impurities detectable by gas chromatography. The reported constants for pure norbornane were: m.p. 86–87°<sup>19b,22</sup> b.p. 105.3–105.5° (cor.)<sup>19b</sup>. At the end of the distillation, when the temperature of the heaters was increased in an effort to recover the remaining quantities of material, HCl gas was evolved and the collected hydrocarbon again was contaminated with 5

(39) B. W. Bradford, D. Harvey and D. E. Chalkley, *J. Inst. Petrol.*, **41**, 80 (1955).

(40) Kindly supplied by Dr. O. Stallmann, Organic Chemicals Department, E. I. du Pont de Nemours and Co. Cf. J. D. Roberts and J. A. Yancey, *THIS JOURNAL*, **75**, 3165 (1953), refs. therein cited, and ref. 18.

(41) Houdry S-90; kindly supplied by Dr. J. W. Lynn, Research Department, Union Carbide Chemicals Co.

(42) (a) E. R. Lippincott, *THIS JOURNAL*, **73**, 2001 (1951); (b) K. Alder, *et al.*, *Ann.*, **593**, 23 (1955).

or 6 impurities amounting to a total of 1-2%. The total amount of hydrocarbon recovered was 75.1 g.

(b) With  $\text{AlBr}_3$ .—A 20.4-g. sample of norbornane of m.p. 87.5-88.0° was refluxed with 4 g. of  $\text{AlBr}_3$  and one drop of *sec*-butyl bromide.<sup>28</sup> Hydrogen bromide gas<sup>26</sup> was admitted to the reaction flask. After refluxing for 25 minutes a lower boiling substance, amounting to 0.3%, was present. After 60 hours, the product, 14.1 g., m.p. 84.0-85.8°, was distilled from the reaction flask. A residue of 5.8 g. remained behind. The product contained 0.4% of the impurity and traces of 2 or 3 other components.

It was concluded from these experiments that norbornane was quite stable to the action of the aluminum halides at the reflux temperature. At most, a very small amount of fragmentation and isomerization was observed, but it is possible that some or all of the new substances present in the product arose from impurities in the starting material.

**Attempted Isomerization of Norbornadiene (IV).**—A commercial sample of norbornadiene,<sup>28</sup> 46 g.,  $n_D^{20}$  1.4705, was refluxed with 1.0 g. of silica-alumina catalyst for 1090 minutes. The starting material contained a large number of impurities present in very small amounts. Neither these impurities nor IV were altered by the acidic catalyst. The infrared spectra of the material before and after treatment were identical. After distillation there remained only a small amount of residue in the reaction flask.

To 17.5 g. of norbornadiene from the above attempted isomerization was added 0.6 g. of the silica-alumina catalyst. Refluxing was continued for 1280 minutes and then the product, 12.5 g., was distilled. The pot residue, a mobile oil, weighed 2.5 g. The product,  $n_D^{20}$  1.4709, was identical with the starting material employed initially, as determined by gas chromatography and infrared spectroscopy.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

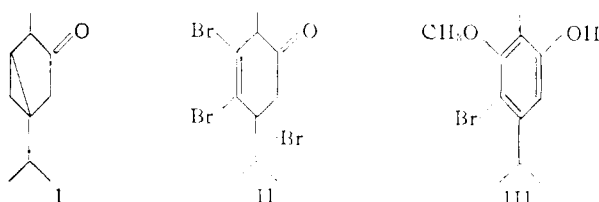
## The Structure of Thujone Tribromide<sup>1</sup>

BY RICHARD H. EASTMAN, PHILLIP M. ILOFF, JR.,<sup>2</sup> AND HART ISAACS, JR.

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Structures are proposed for thujone tribromide and its congeners on the basis of spectroscopic and chemical data.

In a continuation of the study<sup>3</sup> of cleavage reactions of the bicyclo[3.1.0]hexane system we have turned our attention to the action of bromine on thujone (I) which was reported by Wallach<sup>4</sup> to produce a tribromide for which he proposed the structure II, and from which he obtained a substituted carvacrol, assigned the structure III, on treatment with sodium methoxide in methyl alcohol. We have repeated and confirmed his experimental observations, and extended the study to include ultraviolet and infrared spectroscopic examination of the tribromide and the carvacrol, as well as a chemical investigation of the latter.



The tribromide shows  $\lambda_{\text{max}}^{\text{alc}}$  243  $m\mu$  ( $\epsilon$  11,700), 337  $m\mu$  ( $\epsilon$  185) and bands at 5.93 and 6.17  $\mu$  in the infrared, which rule out II as a structural possibility and reveal the tribromide as a conjugated cyclohexenone carrying a single carbon substituent on the  $\beta$ -carbon atom of the olefinic linkage.<sup>5</sup> The phenolic character of the product of sodium methox-

ide treatment of the tribromide is confirmed by bands at 2.97  $\mu$  (OH) and 6.17, 6.32, 6.63  $\mu$  (benzenoid)<sup>6a</sup> in the infrared, and  $\lambda_{\text{max}}^{\text{alc}}$  283  $m\mu$  ( $\epsilon$  2030)<sup>6</sup> in the ultraviolet absorption spectra. The structural problem was thus reduced to locating the bromine and the methoxyl substituents in the carvacrol, and the distribution of three bromine atom substituents about a properly substituted cyclohexenone in the case of the tribromide itself.

Attachment of the methoxyl group to an *aliphatic* carbon atom in the carvacrol was evident when an attempted hydrobromic acid cleavage of the O-CH<sub>3</sub> bond presumed to be present resulted instead in the elimination of the elements of methyl alcohol and the formation of a dimeric species,  $\text{C}_{20}\text{H}_{22}\text{Br}_2\text{O}_2$  (see below). The ease with which the elimination proceeded<sup>7</sup> indicated attachment of the methoxyl group to the benzylic carbon atom of the isopropyl substituent, and that such was the case was established by a proton nuclear magnetic resonance determination<sup>8</sup> on the methoxybromocarvacrol which showed three major peaks, A, B and C, exclusive of the aromatic proton signal. Peaks A and B were of equal area, A being assigned to the protons of the methoxyl group, and B to those of the single methyl group attached to the aromatic ring. The area of the third peak, C, was twice that of either A or B, and C is assigned to the six identical protons of the *gem*-dimethyl unit.

The infrared absorption (10% solution in chloroform, 1.0 mm.) of the methoxybromocarvacrol showed the pattern in the 5-6  $\mu$  region which is characteristic of the benzenoid system with substituents in the 1-, 2-, 3- and 5-positions,<sup>9</sup> thus lending weight

(6) L. Doub and J. Vandenbelt, *THIS JOURNAL*, **69**, 2714 (1947); **71**, 2414 (1949).

(7) The dimer,  $\text{C}_{20}\text{H}_{22}\text{Br}_2\text{O}_2$ , was the only product recovered from an attempted bromination of the methoxybromocarvacrol at -5°.

(8) By James N. Shoolery, Varian Associates, Palo Alto, Calif.

(9) C. W. Young, R. B. Duvall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

(1) From the Doctoral Dissertation of P. M. Iloff, Jr., and the Senior Research Thesis of H. Isaacs, Jr., in the Department of Chemistry at Stanford University. Presented at the American Chemical Society Meeting in New York, N. Y., Sept. 13, 1957.

(2) Shell Fellowship recipient, 1949-1950.

(3) R. H. Eastman and A. Oken, *THIS JOURNAL*, **75**, 1029 (1953).

(4) O. Wallach, *Ann.*, **275**, 179 (1893); O. Wallach and J. T. Conroy, *ibid.*, **286**, 109 (1895).

(5) (a) Infrared assignments are from L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954. (b) The ultraviolet absorption is interpreted according to Woodward's rules as expressed by L. F. and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, pp. 190 ff.