The ultraviolet spectrum resembled that of phenylcyclopropane.[2] The infrared spectrum had no band in the double bond region. The n.m.r. spectrum showed signals at 249, 241 and 208 c.p.s.[19] (cyclopropyl), 181 c.p.s. (methyl) and −6 c.p.s. (phenyl) in the ratio expected for *o*-tolylcyclopropane. Gas phase chromatography, carried out at 150° using a 2 m. × 0.25-in. column containing silicone oil (Dow–Corning 200) on diatomaceous earth gave chromatograms having a single symetrical peak.

Reaction of 3-Mesitylpropyltrimethylammonium Iodide (VIII) with Potassium Amide.—Treatment of 3-mesitylpropyldimethylamine with methyl iodide in ether gave methiodide VIII, m.p. 193–194°, in essentially quantitative yield.

Anal. Calcd. for $C_{15}H_{26}NI$: C, 51.87; H, 7.49; N, 4.03. Found: C, 51.83; H, 7.42; N, 3.76.

Compound VIII (66.0 g.) was added during 35 min. to 400 ml. of liquid ammonia containing potassium amide (0.21 mole). The mixture became yellow then yellow-green during addition. After the mixture was stirred for 8.5 hr., 20 g. of ammonium chloride was added carefully during 10 min. Ether (200 ml.) then was introduced dropwise and the Dry Ice condenser was replaced by a water condenser to permit the ammonia to evaporate. The solid mass which remained was dissolved in 300 ml. of water and, after additional ether (100 ml.) was added, the liquid layers were separated. The ether solution was washed with 10% hydrochloric acid solution, water, 5% sodium bicarbonate solution, water, and dried over magnesium sulfate. After the solvent was removed by distilling through a Vigreux column, the residue was distilled through a semimicro column, yielding 8.70 g. (29%) of *trans*-1-mesitylpropene, b.p. 72–74° (3–4 mm.), $n^{20}D$ 1.5262–1.5280.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.95; H, 10.27.

The n.m.r. spectrum showed signals at 212 c.p.s.[19] (methyl attached to double bond), 191 c.p.s. (methyl attached to benzene ring), 32 c.p.s. (vinyl) and 8 c.p.s. (phenyl). The infrared spectrum had a strong band at 970 cm.$^{-1}$ (*trans*-double bond). Gas phase chromatography at 165° using the Apiezon L column described above indicated that the product contained trace amounts of two impurities. A sample of *trans*-1-mesitylpropene purified by chromatography under the preceding conditions had λ_{max} 242mμ, ε 9,600 (in 95% ethanol) indicating that the olefin was conjugated.[20] About 50% of the starting material was recovered.

From similar treatment of methiodide VIII with sodium amide, the quaternary salt was recovered in high yield.

Acknowledgments.—I wish to thank Mr. Kirt Keller for technical assistance and Mrs. Carolyn Haney for the n.m.r. spectra.

(19) Referred to external benzene; positive values indicate resonance at higher field than the standard. Neat liquids at 25° were analyzed.

(20) W. F. Forbes, *Helv. Chim. Acta*, **41**, 310 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

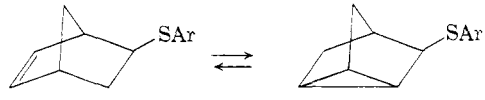
Bridged Polycyclic Compounds. XV. Reactions of Dehydronorcamphor with Some Basic Reagents[1]

BY STANLEY J. CRISTOL AND PETER K. FREEMAN

RECEIVED APRIL 1, 1961

Dehydronorcamphor undergoes an interesting ring-opening rearrangement when treated with sodium amide and benzyl chloride to give N-benzyl-Δ^3-cyclopentenylacetamide. When treated with sodium amide alone, dehydronorcamphor yields Δ^3-cyclopentenylacetamide. The reaction of dehydronorcamphor with potassium *t*-butoxide results in a 3-dehydronorbornylidenedehydronorcamphor and Δ^3-cyclopentenylacetic acid. No rearrangement or ring-opening reaction was observed when dehydronorcamphor was treated with ethanolic sodium ethoxide. Possible mechanisms for the formation of these reaction products are discussed.

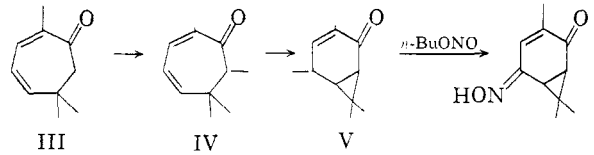
In recent years there has been an active interest in homoallylic carbonium ions, such as the allylcarbinyl,[2] cholesteryl,[3] B-norcholesteryl,[4] 7-norbornenyl[5] and the 5-norbornenyl.[6] Homoallylic free radicals such as the rearranging free radicals I and II have recently received attention in this Laboratory.[7] In addition, an interesting study by Corey and co-workers[8] has shown that enolate



Ar: C_6H_5 or *p*-$CH_3C_6H_4$–

I II

reactions of eucarvone (III) involve a homoallylic rearrangement of anion IV to a bicyclic enolate (V).



III IV V

Therefore, in the light of this interest in homoallylic carbonium ions, free radicals and carbanions, reactions of dehydronorcamphor (VI) with base were studied in order to see if analogous rearrangement or mesomerism would occur.

(1) Previous paper in series: S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2-82 (1961).

(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951). For the most recent discussions of intermediates which may be involved in reactions of allylcarbinyl derivatives see R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959); M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(3) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **78**, 4354 (1956); S. Winstein and E. M. Kowoser, *ibid.*, **81**, 4399 (1959).

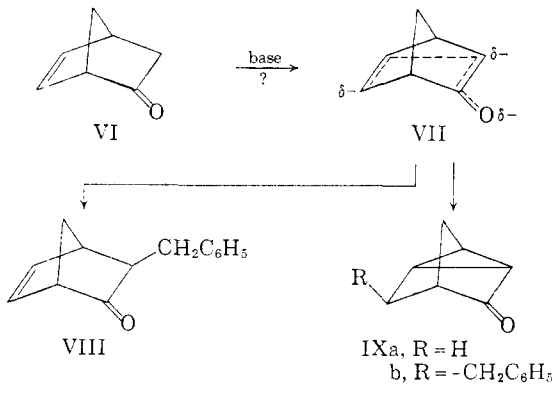
(4) W. G. Dauben and G. L. Fonken, *ibid.*, **78**, 4736 (1956).

(5) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(6) 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); J. D. Roberts, C. C. Lee and W. H. Saunders, *ibid.*, **77**, 3034 (1955); S. Winstein and M. Shatavsky, *Chem. & Ind.* (London), 56 (1956).

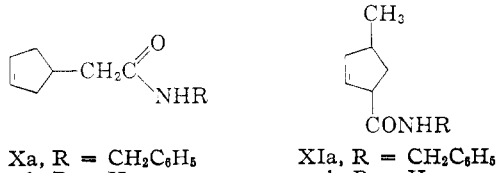
(7) S. J. Cristol, G. D. Brindell and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

(8) E. J. Corey and H. J. Burke, *ibid.*, **78**, 174 (1956); E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **78**, 180 (1956).



The possibility of dehydronorcamphor rearranging, in the presence of base by way of an intermediate such as VII, to nortricyclanone (IXa) was tested by heating dehydronorcamphor (3.00 g.) in an ethanolic solution of sodium ethoxide at reflux for four hours. Acidification and distillation yielded a 47% recovery of dehydronorcamphor. As the infrared spectrum of nortricyclanone has strong absorptions at 12.0 and 12.5 μ, the absence of these peaks in the infrared spectrum of the dehydronorcamphor recovered demonstrates that there was no rearrangement.

Since an intermediate such as VII might be alkylated at either C-3 or C-6 giving structures VIII and IXb, dehydronorcamphor was treated with sodium amide in refluxing dioxane, followed by the addition of benzyl chloride. This reaction gave, instead of the expected alkylation products, a compound which analyzed for $C_{14}H_{17}NO$. The infrared spectrum showed peaks at 3.26, 6.26 and 6.66 μ indicating a benzene ring.[9a] A secondary amide was indicated by the single sharp absorption at 3.03 μ, the amide I band at 6.08 μ and the amide II band at 6.44μ.[9b] The possibilities for this compound were structures Xa (or a double bond isomer of Xa), resulting from cleavage of the C-1, C-2 bond and XIa (or a double bond isomer of XIa) resulting from cleavage of the C-2, C-3 carbon–carbon bond.



Xa, R = $CH_2C_6H_5$
b, R = H

XIa, R = $CH_2C_6H_5$
b, R = H

In order to simplify the question of structure and of the reaction course, the reaction of dehydronorcamphor with sodium amide alone was investigated. This reaction gave a 33% yield of a compound which analyzed for $C_7H_{11}NO$. The infrared absorption at 2.96, 3.13, 5.99, 6.10 μ (primary amide), and 3.26 μ (vinylic hydrogen) was consistent with structures Xb, XIb, or double-bond isomers of these two types.[9c] As the melting point of the pure amide was 132.5–133.5°, Δ^1-cyclopentenylacetamide and the α,β-unsaturated amide, cyclopentylidenacetamide, may be ruled out, since they are known compounds and have melting points of 144°[10,11] and 138°,[11] respectively. Possibility XIb was eliminated as the hydrogenation product was identical with authentic cyclopentylacetamide. Thus the choice is narrowed to either Δ^3-cyclopentenylacetamide (Xb) or Δ^2-cyclopentenylacetamide. In the cleavage reaction with sodium amide and benzyl chloride, one may assume that the choice of structure for the reaction product is also limited to the Δ^3 and Δ^2-isomers.

Synthesis of Δ^2 - cyclopentenylacetamide, N-benzyl-Δ^2-cyclopentenylacetamide and their epoxides, as well as the epoxides of the Δ^3-isomers Xa and Xb, served as an aid in demonstrating that the products of these ring cleavage reactions actually were the Δ^3-isomers Xa and Xb.

Δ^2-Cyclopentenylacetamide was synthesized from Δ^2-cyclopentenylacetic acid, which was prepared according to the procedure of Noller and Adams.[12] The Δ^2-isomer had a melting point of 131.5–132.5°, and the mixed melting point determination with the dehydronorcamphor–sodium amide cleavage product showed no depression. Although the mixed melting point of the 9-acylamidoxanthene of Δ^2-cyclopentenylacetamide, m.p. 199.0–200.0°, and the 9-acylamidoxanthene of the cleavage product, m.p. 190.0–191.5°, appeared to give no depression, the 9° difference in melting points gave an indication that the derivatives were different compounds. The infrared spectra of the two cyclopentenylacetamides supported this distinction by exhibiting differences in the fingerprint region.

Similar results were obtained by comparison of N-benzyl-Δ^2-cyclopentenylacetamide (synthesized from Δ^2-cyclopentenylacetyl chloride and benzylamine) with the corresponding cleavage product, Xa. The melting point of the Δ^2-derivative was 79.0–79.5° and gave no depression in melting point when mixed with Xa (m.p. 78.5–80.0°). The infrared spectra of these two derivatives were very similar, but still slightly different in the fingerprint region.

In order to gain further evidence on the similarity or difference of Δ^2-cyclopentenylacetamide and the cyclopentenylacetamide resulting from the ring opening, epoxides of these two compounds were synthesized. Treatment of Δ^2-cyclopentenylacetamide with peroxybenzoic acid gave a 50% yield of the Δ^2-epoxide (m.p. 116.5–117.0°). Similarly, the epoxide of the cleavage product was prepared in a 50% yield and exhibited a melting point of 106.5–107.5°. The mixed melting point of these two derivatives was depressed to 104.0–105.5°. The infrared spectra are strikingly different, and they indicate there is none of the Δ^2-epoxide in the epoxide obtained from the dehydronorcamphor sodium amide reaction. The possibility that the cleavage reaction product is actually the Δ^2-isomer and that the two epoxides are *cis-trans* isomers seems unlikely since both epoxides were prepared in the same manner.

(9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., second edition, 1958; (a) pp. 65, 71–72; (b) pp. 206, 211, 217; (c) pp. 206, 210, 216.

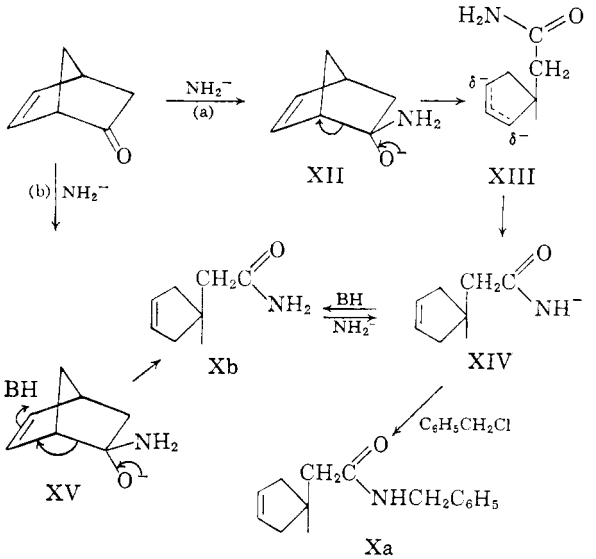
(10) O. Wallach and N. Speransky, *Ann.*, **323**, 159 (1902).

(11) A. Kandiah and R. P. Linstead, *J. Chem. Soc.*, 2139 (1929).

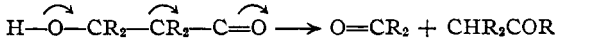
(12) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 2444 (1926). More recently, ozonolysis experiments have verified that the double bond is clearly in the Δ^2-position: K. Mislow and I. V. Steinberg, *ibid.*, **77**, 3807 (1955).

Additional evidence was obtained by comparison of the epoxides of the two N-benzylcyclopentenylacetamides. Epoxidation of the Δ^2-isomer gave a 47% yield of the Δ^2-epoxide. Epoxidation of Xa gave a crude yield of epoxide in 89% yield. The infrared spectra of pure epoxide from Xa (m.p. 97.5–98.5°) and crude epoxide from Xa showed that these two epoxide samples were essentially the same. Comparison with the infrared spectrum of the epoxide of the Δ^2-isomer (m.p. 101.5–102.5°) indicated that these two compounds had different structures. The mixed melting point of a mixture of the two epoxides was 93–101°. Thus it appears that the correct structures for the cleavage reaction products are Xa and Xb.

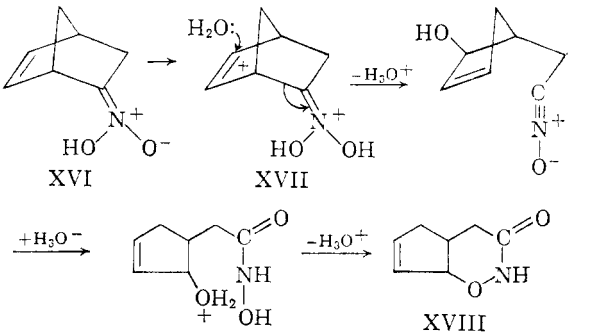
It is interesting to consider the possible mechanism for the formation of Xa and Xb. Two reasonable routes (a and b) may be suggested. In route a, the amide ion adds to the carbonyl carbon atom from the *exo* side to give intermediate XII. The *exo* approach is to be expected on the basis of the *exo* addition of Grignard reagents to dehydronorcamphor.[13] Intermediate XII then cleaves



to form the mesomeric anion XIII. Immediately upon being formed, a proton on the amide group neutralizes the mesomeric carbanion intramolecularly to give XIV. Intermediate XIII can explain the production of the Δ^3-isomer as it would be geometrically easier for a proton of the amide group to neutralize the carbanion at the γ-position (forming a 6-membered ring) than at the δ-position forming a 7-membered ring.[14] The reaction may proceed, instead, by route b, which explains the formation of Xa and Xb by the concerted shift of an electron pair on oxygen, fission of the C_1–C_2 bond, formation of a double bond at C_1–C_6, and protonation of the developing anion at C_5, as shown in intermediate XV. This concerted mechanism and the two-step mechanism of route a are both analogous to a reverse aldol condensation reaction.[15] It is interesting to compare this



ring-opening reaction with the ring-opening reaction occurring during the acidification of the sodium salt of 5-nitronorbornene, which was recently reported by Noland, Cooley and McVeigh.[16] These workers postulate a concerted rearrangement



and bond fission to explain the cleavage reaction of the *aci* form of 5-nitronorbornene (XVI), which yields rearrangement product XVIII. The flow of electrons in transition state XVII is just the reverse of the electron flow which occurs in the bond fission pictured in XV.

The possibility that dehydronorcamphor ring opens to give Δ^2-cyclopentenylacetamide, which is then converted to Xb by the action of sodium amide, was ruled out. Treatment of Δ^2-cyclopentenylacetamide with sodium amide using the reaction conditions of the dehydronorcamphor–sodium amide reaction did not isomerize the Δ^2-amide to the Δ^3-amide.

The stability of nortricyclanone (IXa) to sodium amide in refluxing dioxane[17] is an additional indication that under these reaction conditions there is no formation of a resonance-stabilized intermediate VII. If such intermediates were formed, they would lead to isomerization and ring opening with formation of Δ^3-cyclopentenylacetamide. The greater stability of nortricyclanone to a ring-opening reaction, as compared with dehydronorcamphor, may probably be ascribed to the fact that nortricyclanone cannot undergo cleavage to form a resonance-stabilized anion.

The fact that dehydronorcamphor undergoes cleavage with benzyl chloride and sodium amide rather than alkylation was unexpected, as Haller–Bauer cleavage of ketones is ordinarily observed only with non-enolizable ketones, with but a few exceptions being recorded.[18] The unexpected re-

(13) (a) S. J. Cristol and P. K. Freeman, Abstracts of Papers, 133rd Meeting of the American Chemical Society, April, 1958, p. 6N. (b) P. Malkönen and N. J. Toivonen, *Suom. Kem.*, **31B**, 146 (1958).

(14) ω-Bromo-*n*-pentylamine undergoes ring closure to form piperidine hydrobromide 500 times as fast as ω-bromo-*n*-hexylamine forms hexamethylenimine hydrobromide. For a discussion of this reaction and other ring closure reactions see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 114–121.

(15) C. A. Grob, *Experientia*, **13**, 126 (1957), has summarized bond-breaking reactions of the type, a—C—C—C—X, in which a is an electron-donating group and X a group which can assume electrons of the C–X bond (which may be a single or multiple bond). The mechanisms a and b are additional examples of this type of bond fission.

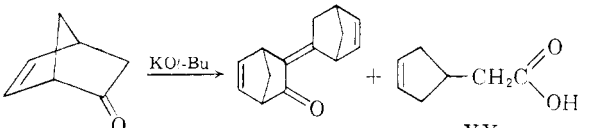
(16) W. E. Noland, J. H. Cooley and P. A. McVeigh, *J. Am. Chem. Soc.*, **81**, 1209 (1959).

(17) P. K. Freeman, Thesis, University of Colorado, 1957.

(18) K. E. Hamlin and A. W. Weston, *Org. Reactions*, **9**, 1 (1957).

sult could obviously be caused by exceptionally facile cleavage in this system or by inability to form an enolate ion rapidly. It has been shown[19] that norcamphor undergoes sodium acetate-catalyzed bromination in acetic acid at about 1/50 the rate shown by acetone. This value is consistent with the predicted stabilities of the enolate ions, based upon the data available for the heats of hydrogenation of norbornene (−33.1 kcal./mole[20]) and propylene (−30.1 kcal./mole[21]). Turner's work[20] on the heat of hydrogenation of norbornene and norbornadiene suggests that ionization of dehydronorcamphor should not be much less rapid than that of norcamphor, and it appears likely therefore that the cleavage cannot be ascribed principally to inability to form an enolate ion. On the other hand, if cleavage does in fact form a mesomeric anion such as XIII or if XV represents a particularly stable system, it would appear that the unanticipated cleavage is best interpreted in terms of its own facile nature.

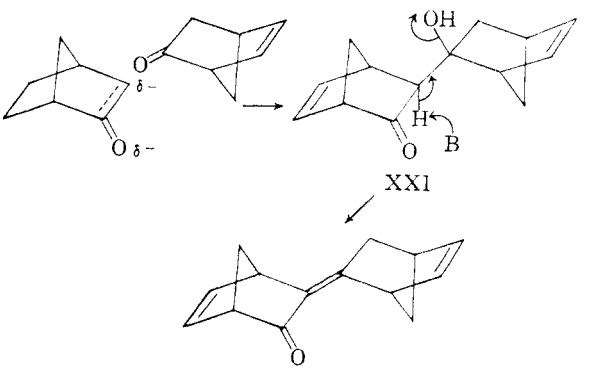
In order to see if a more bulky base might be unable to attack the carbon of the carbonyl, and thus be forced to react with an α-hydrogen atom, dehydronorcamphor was allowed to react with a *t*-butyl alcohol solution of potassium *t*-butoxide. This reaction was carried out at reflux temperature for 9.5 hours and gave 31% of the condensation product 3-dehydronorbornylidenedehydronorcamphor (XIX) and 19% of Δ^3-cyclopentenylacetic acid (XX). Structure XIX for the condensation



VI XIX XX

product was based on its empirical formula, $C_{14}H_{14}O$, and its infrared and ultraviolet spectra. Peaks at 5.75 and 5.93 μ suggest the conjugated system, and the characteristic absorption for the norbornene double bond was present at 6.36 and 14.01 μ.[22] The ultraviolet absorption (λ_{max} 262 mμ, log ϵ 4.00) gives convincing evidence for the conjugated carbonyl structure.

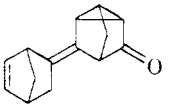
A guess at the complete steric representation of XIX can be made, since it is logical to assume that *exo* addition during the condensation reaction would give intermediate XXI, which then would be attacked at the α-hydrogen atom by the *t*-butoxide ion, giving the favored *trans* bimolecular elimination[23] and producing XXII. The condensation product was isolated by vapor-phase chromatography from a higher boiling product, which was not successfully identified. Although this less volatile product was not identified, its carbon and hydrogen analysis indicated that it was not isomer



XXI

XXII

XXIII, which was necessary for the postulation of an intermediate such as VII. The structure of



XXIII

the acid XX was verified by converting the acid, with thionyl chloride and benzylamine, to the known compound Xa. It seems probable that Δ^3-cyclopentenylacetic acid was formed by an attack of potassium hydroxide, produced from the water generated in the dehydration reaction, on dehydronorcamphor.

Acknowledgment.—The authors are indebted to the Shell Development Co. for support of this work.

Experimental[24]

Dehydronorcamphor.—The synthesis of dehydronorcamphor was accomplished according to the procedure of Bartlett and Tate.[25] A redistilled sample of the product showed the following absorptions in the infrared (film cell): λ max 5.70s, 6.37w, 11.70w, 12.18w, 13.05w, 13.62w and 14.14 mμ. Two additional procedures were developed for the synthesis of dehydronorcamphor by oxidation of dehydronorborneol.

A. Chromium Trioxide–Pyridine Oxidation of Dehydronorborneol.—A slurry of 131 g. (1.31 moles) of chromium trioxide in dry pyridine was prepared according to the directions of Poos, Arth, Beyler and Sarett.[26] A solution of 50.0 g. (0.454 mole) of dehydronorborneol in 500 ml. of pyridine was added to the chromium trioxide–pyridine complex in one portion, with stirring. The oxidation was mildly exothermic during 1 hour. The stirring was continued overnight. Then the reaction mixture was filtered through a 10-inch Buchner funnel containing a pad of Celite 512. The residue in the funnel was washed with ether. The filtrate was acidified with 330 ml. of concentrated sulfuric acid dissolved in 1 liter of water. This solution was then continuously extracted with ether in a 6-liter continuous extraction apparatus for 2.5 days. The ether extract was washed with 6 *N* sulfuric acid, 5% sodium bicarbonate, and finally with water until neutral. The ether solution was dried over magnesium sulfate and then distilled *in vacuo*. The distillation yielded 19.3 g., b.p. 62–65° (18.0 mm.), and 7.34 g., b.p. 70–71° (18.5 mm.) (a total of 26.6 g., 54.1%),

The dinitrophenylhydrazone had m.p. 172–173°. Roberts, Trumbull, Bennett and Armstrong[27] report m.p. 173.8–175.0°.

(19) W. G. Woods and J. D. Roberts, *J. Org. Chem.*, **22**, 1124 (1957).

(20) R. B. Turner, W. R. Meador and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

(21) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 876 (1935).

(22) P. v. R. Schleyer, paper presented at the 130th A.C.S. Meeting, Atlantic City, N. J., September, 1956.

(23) S. J. Cristol, N. L. Hause and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 674 (1951).

(24) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(25) P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).

(26) G. I. Poos, R. E. Beyler, G. E. Arth and L. H. Sarett, *ibid.*, **75**, 422 (1953).

(27) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

B. Oppenauer Oxidation of Dehydronorborneol.—The procedure of Adkins and Franklin[28] was adapted to the needs of the following reaction.

Dehydronorborneol (10.0 g., 0.0910 mole) and *p*-benzoquinone (50.5 g., 0.468 mole) were dissolved in 1300 ml. of benzene; 400 ml. of benzene was distilled from the solution, which was then allowed to cool to room temperature. Aluminum *t*-butoxide (17.3 g., 0.0703 mole) in 150 ml. of dry benzene was added, with stirring, during 1 hour. The reaction mixture was then stirred at room temperature for 7 days. The aluminum alkoxides were decomposed by adding 4 ml. of water and warming the reaction mixture on a steam-bath. The aluminum hydroxide was removed by centrifuging and then washed three times with ether. The ether was evaporated on a steam-bath, and then the remaining solution was washed with two 100-ml. and one 50-ml. portions of 5% sodium hydroxide solution, and 50 ml. of water. Fractionation of the solution through a Vigreux column, using 3 g. of biphenyl as a chaser, yielded 7.40 g. (75.5%), b.p. 95–97° (93 mm.).

Dehydronorcamphor and Sodium Ethoxide.—Three grams (0.028 mole) of dehydronorcamphor was added to a solution of 0.64 g. (0.028 g.-atom) of sodium in 50 ml. of absolute ethanol, and the solution was heated at reflux for 4 hours. After neutralization with acetic acid, ether extraction and distillation gave 1.47 g. (47%) recovery of dehydronorcamphor, b.p. 58–60° (13.5 mm.) The infrared spectrum had no absorption at 12.0 and 12.5 μ proving that there was no nortricyclanone present, since the infrared spectrum of nortricyclanone[17] (film cell) showed the absorptions: λ_{max} 5.64s, 11.60w, 12.00s, 12.50m and 12.88w μ.

Reaction of Dehydronorcamphor with Sodium Amide and Benzyl Chloride.—A solution of sodium amide in 40 ml. of dry, purified dioxane was prepared according to the procedure of Hauser, Swamer and Adams[29] from 1.40 g. (0.0609 g. atom) of sodium. This mixture was warmed to 50°. Dehydronorcamphor (5.00 g., 0.0463 mole) in 20 ml. of dry, purified dioxane was then added. The reaction mixture was heated at reflux for 1.5 hours and then cooled in an ice–water bath. Benzyl chloride (7.34 g., 0.0578 mole) was added to the cooled reaction mixture, with stirring. This reaction mixture was warmed to reflux and then heated at reflux for 1.5 hours. At this point the reaction mixture was allowed to cool and then poured into 500 ml. of a saturated sodium chloride solution. The resultant mixture was extracted with three 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate and the solvents were removed by flash distillation. Distillation of the residue gave 4.19 g. (45.6%) of N-benzyl-Δ^3-cyclopentenylacetamide, b.p. 160–180° (0.40 mm.). Two recrystallizations from benzene gave 1.80 g., m.p. 71–75°. An analytical sample had m.p. 78.5–80.0°, λ_{max}^{KBr} 3.03s, 3.26w, 6.08s, 6.26w, 6.44s, 6.66m, 7.40m, 7.60w, 7.82w, 8.17m, 8.65w, 9.30w, 9.70w, 9.86w, 10.55w, 11.17w, and 13.42 μ.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.20; H, 7.96. Found: C, 78.59; H, 7.86.

Epoxidation of N-Benzyl-Δ^3-cyclopentenylacetamide.—To 9.4 ml. of 0.497 *M* peroxybenzoic acid in chloroform, 1.00 g. (0.00465 mole) of N-benzyl-Δ^3-cyclopentenylacetamide was added, with swirling and cooling in an ice–water bath. The reaction mixture was cooled and shaken in an ice–water bath for 1 hr. It was then placed in a refrigerator and kept at 8° for 2 days. The reaction mixture was diluted with chloroform and extracted with 10 ml. of 5% sodium hydroxide solution and two 10-ml. portions of water. The chloroform layer was dried over sodium sulfate. Filtration and evaporation yielded 0.95 g. (89%) of crude epoxide, m.p. 60–82°. Two recrystallizations from ethanol–petroleum ether (b.p. 60–70°) gave 0.10 g., m.p. 94–97°. An analytical sample had m.p. 97.5–98.5°; λ_{max}^{KBr} 6.07s, 6.44s, 11.94m, 13.41m and 14.41m μ; mixed m.p. with the epoxide of the Δ^2-isomer described below was 93–101°.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found: C, 72.57; H, 7.26.

The infrared spectra of the crude epoxide and the analytical sample demonstrated that the two fractions were essentially the same. Comparison of the above spectra with the spectrum of the epoxide of the Δ^2-isomer indicated that these compounds had different structures.

Reaction of Dehydronorcamphor with Sodium Amide.—Ten grams (0.0926 mole) of dehydronorcamphor in 15 ml. of dried and purified dioxane was added to 7.5 g. (0.19 mole) of sodium amide in 50 ml. of dried and purified dioxane, with stirring, under nitrogen. This addition was complete in 10 min. with no evolution of ammonia. Then the reaction mixture was heated in an oil bath for 20 minutes; during this time, the oil-bath rose to a temperature of 75°. At this temperature ammonia was evolved so rapidly that the oil bath had to be removed for a few minutes. After the evolution of ammonia subsided somewhat, the reaction mixture was heated to the reflux temperature and allowed to reflux for 1 hour. The oil bath was then removed and the reaction mixture was allowed to stand overnight at room temperature. The reaction mixture was then acidified with 10 ml. of glacial acetic acid and poured into 100 ml. of a saturated sodium chloride solution. This mixture was extracted with three 100-ml. portions of ether. The combined ether extracts were washed with 30 ml. of water and then dried over anhydrous magnesium sulfate. The ether was evaporated leaving a dioxane solution, which was concentrated with simultaneous addition of benzene. The benzene–dioxane solution, upon cooling to room temperature, yielded 5.84 g. (50.3%) of crude Δ^3-cyclopentenylacetamide, m.p. 95–118°. One recrystallization from benzene gave 3.83 g. (33.1%), m.p. 126–129°. An analytical sample had m.p. 132.5–133.5° after several recrystallizations from ethanol and water λ_{max}^{KBr} 2.96s, 3.13s, 3.26m, 5.99s, 6.10s, 7.44m, 7.71m, 7.92m, 8.07m, 8.58w, 8.84w, 10.51w and 11.17w μ.

Anal. Calcd. for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.33; H, 8.61; N, 11.41.

The 9-(Δ^3-cyclopentenylacetamido)-xanthene was prepared according to procedure II of Phillips and Pitt[30] and had a melting point of 190.0–191.5°.

Anal. Calcd. for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27. Found: C, 78.43; H, 6.12.

Reduction of 0.335 g. (0.00268 mole) of Δ^3-cyclopentenylacetamide in a low pressure, quantitative hydrogenator, using 27 mg. of 10% palladium-on-carbon catalyst, led to the uptake of 0.960 mole of hydrogen per mole of compound and yielded 0.341 g. (100%) of cyclopentylacetamide, m.p. 144.5–146.0° (lit.[31] m.p. 145.5–146.5°). The mixed melting point determination with an authentic sample of cyclopentylacetamide showed no depression, and the infrared spectra of the reduction product and cyclopentylacetamide were identical.

Epoxidation of Δ^3-Cyclopentenylacetamide.—To 5.5 ml. of 0.458 *M* peroxybenzoic acid in chloroform, 0.30 g. (0.0024 mole) of Δ^3-cyclopentenylacetamide was added, in portions, with cooling and swirling of the reaction mixture in an ice–water bath. The reaction mixture was cooled in an ice–water bath for 1 hour and then was placed in a refrigerator and kept at 8° for 4 days. The reaction mixture was then diluted with chloroform and extracted with three 10-ml. portions of water. The combined aqueous extracts were saturated with potassium carbonate and extracted with four 15-ml. portions of methylene chloride. The combined methylene chloride extracts were dried over sodium sulfate. Crystallization of the epoxide from methylene chloride–carbon tetrachloride solution gave 0.17g. (50%), m.p. 102–105°. An analytical sample had m.p. 106.5–107.5°; λ_{max}^{KBr} 2.95s, 3.11m, 5.98s, 6.09s, 6.96m, 7.04s, 11.57w, 11.89m and 14.05m μ.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85. Found: C, 59.37; H, 8.03.

Synthesis of Δ^2-Cyclopentenylacetamide.—Δ^2-Cyclopentenylacetic acid was synthesized according to the directions of Noller and Adams.[12] This was converted in 88% yield to Δ^2-cyclopentenylacetyl chloride, b.p. 65–75° (13 mm.), which in turn was converted in 44% yield to Δ^2-cyclopentenylacetamide, m.p. 128–132°, by procedures described earlier.[32]

Recrystallization of the amide from benzene and from ethanol–water gave material, which, when carefully ground

(28) H. Adkins and R. C. Franklin, *J. Am. Chem. Soc.*, **63**, 2381 (1941).

(29) C. R. Hauser, F. W. Swamer and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).

(30) R. F. Phillips and B. M. Pitt, *J. Am. Chem. Soc.*, **65**, 1355 (1943).

(31) F. H. Seubold, Jr., *ibid.*, **76**, 3732 (1954).

(32) N. P. Buu-Hoi and P. Cagniant, *Bull. soc. chim.*, **12**, 978 (1945).

with an agate mortar and pestle, had m.p. 131.6–132.5° (lit.[32] m.p. 133°); λ_{max}^{KBr} 2.96s, 3.13s, 3.26m, 5.99s, 6.10s, 7.36w, 7.55m, 7.66m, 7.80w, 8.08m, 8.27m, 8.64w, and 8.72w μ. A mixed melting point determination with Δ^3-cyclopentenylacetamide gave no depression.

The 9-(Δ^2-cyclopentenylacetamido)-xanthene was prepared using the same procedure as the one described above for the Δ^3-isomer. A derivative with m.p. 199.0–200.2° was obtained. A mixed melting point determination with 9-(Δ^3-cyclopentenylacetamido)-xanthene gave a melting point of 197.0–199.0°.

Anal. Calcd. for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27. Found: C, 78.74; H, 6.38.

Epoxidation of Δ^2-Cyclopentenylacetamide.—To 5.8 ml. of 0.44 *M* peroxybenzoic acid in chloroform, 0.30 g. (0.0024 mole) of Δ^2-cyclopentenylacetamide was added, in portions, with cooling and swirling of the reaction mixture in an ice–water bath. The remaining procedure was the same as the epoxidation of the Δ^3-isomer described above. Crystallization from methylene chloride–carbon tetrachloride solution yielded 0.17 g. (50%), m.p. 103–113°. One recrystallization from methylene chloride–petroleum ether (b.p. 60–70°) gave 0.12 g., m.p. 116.0–116.5°; λ_{max}^{KBr} 2.92s, 3.09w, 5.96s, 6.16m, 6.93w, 7.06m, 11.70w and 11.93 mμ. A mixed melting point determination with the Δ^3-epoxide gave a melting point of 104.0–105.5°. An analytical sample had m.p. 116.5–117.0°.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85. Found: C, 59.50; H, 7.76.

Δ^2-Cyclopentenylacetamide with Sodium Amide.—Δ^2-Cyclopentenylacetamide (0.80 g., 0.0064 mole) in 10 ml. of dry, purified dioxane was added in one portion to a mixture of 0.5 g. (0.013 mole) of sodium amide in 25 ml. of dry, purified dioxane, with stirring, under nitrogen. The reaction mixture was warmed to reflux during 15 minutes and then heated at reflux for 1 hour. The reaction mixture was allowed to cool and then a few milliliters of iced water was added, with stirring. The resulting mixture was extracted with two 50-ml. portions of ether. The combined ether extracts were washed with 10 ml. of water and then dried over anhydrous sodium sulfate. The ether solution was concentrated to about 10 ml. and then the amide was precipitated by the addition of petroleum ether (b.p. 60–70°). Filtration yielded 0.51 g. (64%) of cyclopentenylacetamide. The infrared spectrum of the product was identical with Δ^2-cyclopentenylacetamide and showed that none of it had rearranged to Δ^3-cyclopentenylacetamide.

N-Benzyl-Δ^2-cyclopentenylacetamide.—Δ^2-Cyclopentenylacetyl chloride (8.4 g., 0.058 mole) was added, with stirring, to a solution of 18.7 g. (0.175 mole) of benzylamine in 100 ml. of benzene. The addition was accomplished during 10 minutes; stirring and cooling in an ice-water bath kept the reaction temperature below 20°. After the addition was complete, the reaction mixture was stirred for an additional 0.5 hour at room temperature, and for 15 minutes at reflux. Upon cooling, the reaction mixture was extracted with 20 ml. of water, one 20-ml. and two 10-ml. portions of 5% hydrochloric acid, 10 ml. of 5% sodium hydroxide and 25 ml. of water. The benzene solution was then concentrated on a hot plate and 8.09 g. (64.7%) of substituted amide, m.p. 77.5–79.0°, crystallized from the solution upon cooling to room temperature. Two recrystallizations from benzene–petroleum ether (b.p. 60–70°) and one from ethanol–water gave 4.24 g., m.p. 79.0–79.5°; λ_{max}^{KBr} 3.02s, 3.27w, 6.08s, 6.28w, 6.44s, 6.66m, 7.42m, 7.76w, 7.87w, 8.17m, 8.36w, 8.67w, 9.29w, 9.51w, 9.70w, 9.85w, 10.80w, 11.04w, 11.69w, and 13.44m μ. A mixed melting point determination with N-benzyl-Δ^3-cyclopentenylacetamide gave no depression. An analytical sample had m.p. 79.0–79.5°.

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.20; H, 7.96. Found: C, 78.01; H, 7.88.

Epoxidation of N-Benzyl-Δ^2-cyclopentenylacetamide.—To 5.0 ml. of 0.479 *M* peroxybenzoic acid in chloroform, 0.50 g. (0.0023 mole) of N-benzyl-Δ^2-cyclopentenylacetamide was added, with swirling and cooling in an ice–water bath. The remaining details of the reaction were the same as in the epoxidation of the Δ^3-isomer described above. The first crop of crystals from chloroform–carbon tetrachloride weighed 0.13 g., m.p. 98–100°; the second crop from chloroform–petroleum ether (b.p. 60–70°) weighed 0.12 g., m.p. 97–99° (a total yield of 47%). An analytical sample was prepared by recrystallization from ethanol–petroleum ether (b.p. 60–70°), m.p. 101.5–102.5°; λ_{max}^{KBr} 6.08s, 6.49s, 11.91m, 13.38m and 14.34m μ.

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found: C, 72.90; H, 7.26.

Reaction of Dehydronorcamphor with Potassium *t*-Butoxide.—Potassium *t*-butoxide was prepared by dissolving 7.28 g. (0.186 g. atom) of potassium in 160 ml. of anhydrous *t*-butyl alcohol as described by Johnson and Daub.[33] Dehydronorcamphor (20.02 g., 0.186 mole) was added to the refluxing solution of potassium *t*-butoxide, with stirring under nitrogen, in one portion. The reaction mixture was stirred at reflux for 9.5 hours and then allowed to stand overnight at room temperature. The reaction mixture was poured onto 100 ml. of ice and water, 70 ml. of ether was added and the layers were separated, aided by 10 ml. of a saturated sodium chloride solution. The aqueous layer was extracted with two 50-ml. portions of ether and the combined ether extracts were washed with 15 ml. of a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. The ether was removed by flash distillation. Distillation of the residue yielded 5.79 g., b.p. 113–119° (1.5 mm.), and 2.02 g., b.p. 119–125° (1.5 mm.) Vapor-phase chromatography on a silicone oil-impregnated, crushed firebrick column was used to separate the same two components that were in each of the fractions. Analytical samples were prepared by several runs through the column. The higher boiling material was not successfully identified (*Anal.* Found: C, 77.86; H, 8.43).

The lower boiling material was 3-dehydronorbornylidene-dehydronorcamphor, λ_{max}^{EtOH} 262 mμ (log ϵ 4.00); λ_{max} (film cell) 5.75s, 5.93s, 6.36w and 14.01s μ.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.83; H, 7.11. Found: C, 84.75; H, 7.30.

Since the molecular weight of the higher boiling compound was unknown, it was assumed that the molecular weight of the higher boiling compound was between 199 and 400. In fraction 1 (b.p. 113–119°), the vapor-phase chromatogram showed areas under the peaks of 135 and 27 for the lower boiling component and the higher boiling component, respectively. In fraction 2, the areas were 106 and 69, respectively. Then using Eastman's formula[34]

$$\frac{m_i}{w} = \frac{A_i\sqrt{M_i}}{\Sigma_i A_i\sqrt{M_i}}$$

where m_i/w is the fraction by weight of the ith component, A_i, the area under the peak on the chromatogram and M_i the molecular weight; the yield of the lower boiling condensation product is 31.3 ± 1.3%.

The aqueous layer was acidified with 6 *N* hydrochloric acid and extracted with one 100-ml. and two 50-ml. portions of ether. The combined ether layers were washed with 15 ml. of water and then dried over anhydrous sodium sulfate. After the ether had been evaporated, the residue was distilled *in vacuo*, giving 4.35 g. (18.6%) of Δ^3-cyclopentenylacetic acid, b.p. 76–78° (0.80 mm.); the infrared spectrum (film cell) showed absorptions at 3.22m, 3.41m, 3.72w, 5.80s and 6.15w μ. Vapor-phase chromatography, on a silicone oil–fire brick column, indicated that there was only one compound present. An analytical sample had b.p. 97.5–98.0° (3.5 mm.).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.93; H, 8.23.

The N-benzyl-Δ^3-cyclopentenylacetamide derivative was synthesized in 88.5% yield as described above for the Δ^2-isomer; m.p. 78.0–79.5°. The infrared spectrum was identical with that of the N-benzyl-Δ^3-cyclopentenylacetamide prepared directly from dehydronorcamphor with sodium amide and benzyl chloride.

(33) W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 42 (1951).

(34) R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 4243 (1957).