and 0.3 mole of ketone was added at such a rate that the temperature did not exceed 120°. After the addition of the ketone was complete, the temperature was maintained at 120–130° for 1 hr., then raised slowly to 140° over a period of 0 5 hr. The total reaction time should never be allowed to exceed two hours. After cooling, the reaction mixture was poured on ice and made alkaline with potassium hydroxide. The (usually tarry) residue was filtered from the solution, and both the solution and the residue were extracted with hot benzene. The benzene was removed by distillation, and the residue was crystallized from a suitable solvent (Table I).

The Preparation of 4-Substituted 8-Aminoquinolines.—To a solution of 1.5 moles of stannous chloride dihydrate in 700 ml. of absolute ethanol was added 0.5 mole of the 4-substituted 8-nitroquinoline. The mixture was refluxed on a steam bath for 4 hr., after which most of the ethanol was removed by distillation. The residual solution was made alkaline with sodium hydroxide and filtered. Both the filtrate and the residue were extracted with ether, and the combined ether extracts were dried over anhydrous sodium sulfate. After removal of the solvent, the residue was crystallized from a suitable solvent (Table II).

General Procedure for the Synthesis of 1,10-Phenanthrolines.—To a well stirred solution of 0.05 mole of the appropriate amine, 0.1 mole of arsenic acid, and 50 ml. of 85% phosphoric acid heated to 100° was added 0.07 mole of the appropriate ketone at such a rate that the temperature did not exceed 120°. When the addition of the ketone was complete, the temperature was raised slowly to 140°, and maintained there for 1 hr. The reaction mixture was then cooled, poured on ice, made alkaline with a solution of concd. potassium hydroxide, and the precipitate which formed was extracted with hot benzene. After removal of the solvent, the residue was purified by crystallizing from a suitable solvent (Table III).

In the case of 4,7-bis(*p*-ethylphenyl)-1,10-phenanthroline, the crude residue was purified by precipitating the hydrochloride from the benzene solution, making alkaline, and then proceeding as before.

β-(*o*-Nitroanilino)ethyl Mesityl Ketone.—Twenty-six grams (0.13 mole) of vinyl mesityl ketone was added slowly to a well stirred solution of 13.8 g. (0.1 mole) of *o*-nitroaniline, 11.5 g. (0.08 mole) of arsenic acid, 10 g. (0.07 mole) of anhydrous zinc chloride, and 200 ml. of concd. hydrochloric acid heated on a steam bath. After the addition of the ketone was complete, the mixture was refluxed for 3 hr., then poured on ice, and finally made alkaline with potassium hydroxide. The resulting precipitate was removed by filtration, dried, and extracted with hot benzene. Removal of benzene and crystallization from petroleum ether yielded 20 g. of product which melted at 100–101°. Infrared absorption bands were found at 2.96, 6.35, 11.59, 13.33 μ.

Anal. Calcd. for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.46; N, 8.94. Found: C, 69.61; H, 6.46; N, 8.88.

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Some Aspects of the Chemistry of the Bicyclo[5.4.0]undecane Ring System. Synthesis of Several Tetrahydrobenzosuberones[1]

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The synthesis of bicyclo[5.4.0]undec-4-en-5-one and bicyclo[5.4.0]undec-10-en-5-one by the polyphosphoric acid cyclization of 5-(1′-cyclohexenyl)valeric acid is described. The ultraviolet spectral properties and other physical properties were found to be identical in all respects with the properties reported for the products of the selenium dioxide dehydrogenation of *cis*- and *trans*-bicyclo[5.4.0]undecan-5-one. The selenium dioxide dehydrogenation reaction and structural assignments are re-interpreted in light of this study.

Recently, Ginsberg and Rosenfelder[2] reported the formation of several bicyclo[5.4.0]undecenones (tetrahydrobenzosuberones) by the selenium dioxide dehydrogenation of *cis*- and *trans*-bicyclo[5.4.0]undecan-5-one (I and II, respectively, Fig. 1). The assignment of the position of the olefinic linkage in the dehydrogenated species was based upon the ultraviolet spectral characteristics of the α,β-unsaturated ketones and their derivatives as well as upon the further reactivity of these products with *N*-bromosuccinimide followed by treatment with lutidine to form doubly unsaturated ketones. The selenium dioxide dehydrogenation of *cis*-bicyclo[5.4.0]undecan-5-one (I) was presumed to take place at C-6 rather than at the ring junction, tertiary carbon, C-11 adjacent to the carbonyl group to yield *cis*-bicyclo[5.4.0]undec-6-en-5-one (III). It was reasoned that the molecular geometry of the *cis* ring system does not permit attack of the reagent at the ring junction. However, treatment of the *trans* ketone (II) in a like manner yielded bicyclo[5.4.0]undec-10-en-5-one (IV). In the latter reaction, attack of the reagent undoubtedly took place at the ring junction.

It was surprising indeed that the attack of selenium dioxide took place in the *cis* ring system at a position other than at the tertiary carbon at the ring junction. Although Mel'nikov and Rokitskaya[3] have postulated the initial reaction of selenium dioxide is through the formation of the enol ester, it was later proposed by Duke[4] that the

(1) This work was supported, in part, by a Frederick Gardner Cottrell Grant from the Research Corp. and Grants B-2239 and B-3628 from the Department of Health, Education, and Welfare, Public Health Service.

(2) D. Ginsberg and W. J. Rosenfelder, *Tetrahedron*, **1**, 3 (1957).

(3) N. N. Mel'nikov and M. S. Rokitskaya, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2738 (1937).

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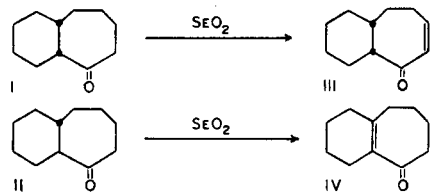

Figure 1

reaction does not proceed through the enol ester, but, more probably, through a coordination complex which is stereochemically situated for further reaction at an alpha carbon. In the *cis* ketone, acid-catalyzed conversion to the enol was not observed. Enolization was only catalyzed by basic reagents.[2] Therefore, under the acidic conditions, it could be argued that the selenium dioxide dehydrogenation would proceed at a position other than the ring junction. However, if the reaction proceeds *via* a coordination complex, the necessity of enol formation is obviated. The hindrance due to the molecular geometry at both alpha carbons as well as the acidity of the tertiary hydrogen at C-11 as contrasted to the secondary hydrogens at C-6 will govern the initial hydroxylation by the reagent. On examination of molecular models of this system, geometric blocking of C-11 could not be visualized. In addition, the ultraviolet spectral evidence reported for the establishment of the position of the olefinic linkage in *cis*-bicyclo[5.4.0]-undec-6-en-5-one does not agree with dehydrogenation at positions other than C-11. The ultraviolet maxima reported for *cis*-bicyclo[5.4.0]undec-6-en-5-one, 241 mμ, is not in agreement with the absorption maxima which would be calculated for a structure of the type proposed assuming a rough correlation of this ring system with those previously studied[5] (the calculated ultraviolet maxima would be expected to be about 227 mμ). The ultraviolet absorption maxima of the dinitrophenylhydrazone derivative of the dienone isolated from the reaction of *cis*-bicyclo[5.4.0]undec-6-en-5-one with *N*-bromosuccinimide followed by dehydrobromination with lutidine could not have the extended conjugative structure as originally reported. The ultraviolet absorption maxima of this ketone is in closer agreement with a cross conjugated system in which the most substituted conjugate chromophore gives rise to the observed absorption.[6]

Recently, the synthesis of bicyclo[5.4.0]undec-10-en-5-one was undertaken as an independent route to the structure proof of a ketone suspected of being the same as ketone IV obtained by Ginsberg and Rosenfelder.[2] However, this compound was isolated as one of the products in the abnormal Schmidt reaction of spiro[5.5]undecan-1-one in polyphosphoric acid.[7] The unsaturated ketone had a completely different set of spectral and physical properties for the ketone as well as its dinitrophenylhydrazone derivative. The synthetic route followed is summarized in Figure 2.

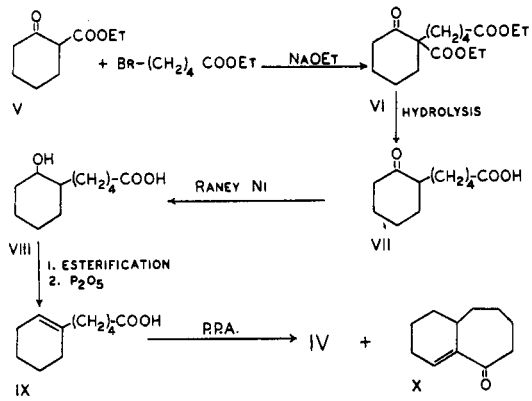

Figure 2

Condensation of 2-carboethoxycyclohexanone (V) with ethyl 5-bromovalerate yielded the keto diester (VI), which after hydrolysis and decarboxylation gave 5-(2′-oxocyclohexyl)valeric acid (VII). The keto acid VII was reduced with hydrogen using a Raney nickel catalyst to the corresponding hydroxy acid VIII. After esterification with methyl alcohol, the hydroxy ester was dehydrated with phosphorus pentoxide, then hydrolyzed to yield 5-(1′-cyclohexenyl)valeric acid (IX). Cyclization of the unsaturated acid IX with polyphosphoric acid at 80° yielded a mixture of two ketones, bicyclo-[5.4.0]undec-4-en-5-one (X) and bicyclo[5.4.0]-undec-10-en-5-one (IV). The ketonic mixture was separated by fractional distillation into two impure fractions which were purified further by column chromatography over activated alumina in 1:1 ether–petroleum ether.

The spectral properties and physical constants of bicyclo[5.4.0]undec-4-en-5-one were found to be identical in all respects with the compound formulated as *cis*-bicyclo[5.4.0]undec-6-en-5-one (III) by Ginsberg and Rosenfelder.[2] The mixed melting points of the 2,4-dinitrophenylhydrazone and semicarbazone derivatives of the synthetic ketone prepared in this study and the ketone prepared by the selenium dioxide dehydrogenation of *cis*-bicyclo[5.4.0]undecan-5-one showed no depression. Treatment of ketone X with *N*-bromosuccinimide followed by lutidine converted the α,β-unsaturated ketone to a dienone XI also identical in all respects with the dienone from the reported *cis*-bicyclo-[5.4.0]undec-6-en-5-one. Allylic bromination with this reagent might be expected to give any one or all

(5) (a) R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); (b) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 76 (1942); (c) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Co., New York, 1959, pp. 15–22.

(6) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy in Organic Chemistry," 2nd ed., E. Arnold, London, England, 1957 pp. 93–125.

(7) (a) R. T. Conley and B. E. Nowak, Abstracts of Papers, American Chemical Society, 134th Meeting, 1958, p. 11-P; (b) R. T. Conley and B. E. Nowak, *Chem. Ind.* (London), 1161 (1959); (c) R. T. Conley and B. E. Nowak, *J. Org. Chem.*, **26**, 692 (1961).

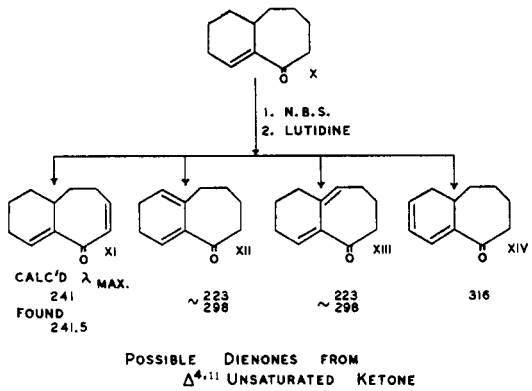

Figure 3

of the possible ketones indicated in Figure 3. Only dienone XI would be expected to exhibit the observed ultraviolet maxima of 241 mμ. Compounds XII and XIII would be expected to give rise to a complex ultraviolet spectrum having at least two ultraviolet absorptions due to the introduction of the second double bond in cross conjugation with the initial olefinic group and the carbonyl group.[5c] The last dienone XIV has the homoannular extended conjugation which normally shifts the wave length of absorption to approximately 316 mμ. It can be concluded, therefore, that only a compound having the structure XI adequately satisfies the ultraviolet data.

In similar experiments with bicyclo[5.4.0]undec-10-en-5-one the dienone obtained had an absorption maxima at 247.5 mμ. As indicated in Figure 4 only compound XV agrees with the wave length

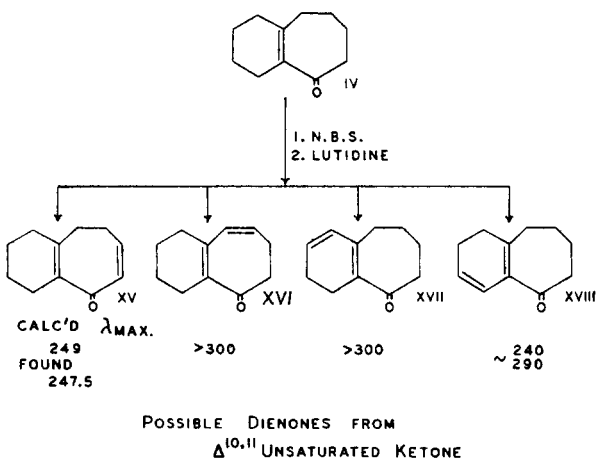

Figure 4

maxima anticipated on the basis of existing correlations. Structures XVI, XVII, and XVIII can be eliminated on the observed fact that no absorption bands were present in the high wavelength region of the ultraviolet spectrum.

Therefore, from this study, it must be concluded that the selenium dioxide dehydrogenation proceeds at the ring junction in both *cis*- and *trans*-bicyclo[5.40]undecan-5-one and that the structure formulated as III should be revised to structure X. In addition the assignments of the doubly unsaturated ketones obtained from the dehydrohalogenation experiments should be structures XI and XV rather than those originally formulated.[2]

Of further interest is the apparent stereospecific introduction of the double bond hinged at C-11. It must be concluded that this specificity further supports a course of reaction which does not necessitate the formation of the enol. Further studies concerning the stereochemical ramifications in this and related systems will be reported at a later time.

Recently, Hill and Conley[3] reported the formation of bicyclo[5.4.0]undec-10-en-5-one (IV) among the products of the Beckmann rearrangement of spiro[5.5]undecanone-1-oxime (XIX) in polyphosphoric acid. The structure was established by reduction of the unsaturated ketone to the saturated alcohol followed by oxidation to the saturated *cis*-bicyclo[5.4.0]undecan-5-one (I). However, the melting point of the 2,4-dinitrophenylhydrazone derivative is not in agreement with that observed in this investigation. The Schmidt reaction[7] of spiro[5.5]undecan-1-one (XX) in polyphosphoric acid has been reported to yield 2-cyclohexylidenecyclopentanone (XXI). The physical constants for the derivatives of XXI are in good agreement with the corresponding oxime rearrangement product. Since both IV and XXI can be formed by recyclization of olefinic, unsaturated nitrile intermediates which are simply double bond positional isomers, the possibility exists that the Beckmann rearrangement because of the experimental conditions employed yielded a mixture of the two possible ketones. Since the two ketones may not have been separated by the chromatographic techniques employed, it is most probable that the high-melting dinitrophenylhydrazone derivative was obtained by fractional crystallization from the ketonic mixture and assigned an incorrect structure.

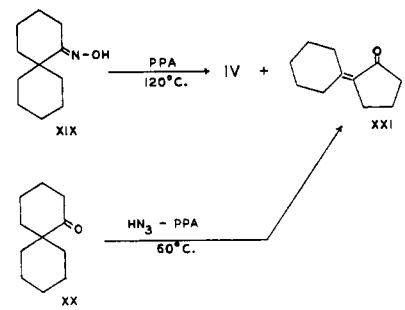

Figure 5

Experimental

All melting points were determined using a Hoover-Thomas Unimelt apparatus and are corrected. The ultra-

(8) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).

violet spectra were determined using a Cary, Model 11 or a Beckman DK2-A recording spectrophotometer. The infrared spectra used for sample comparison purposes and functional group identification were determined using a Baird, Model AB-2, double beam recording spectrophotometer equipped with sodium chloride optics.

Reactants.—Ethyl 5-bromovalerate was prepared according to the method used by Merchant, Wickert, and Marvel.[9] 2-Carboethoxycyclohexanone was obtained by the method outlined by Snyder, Brooks, and Shapiro.[10]

Samples for Comparison.—*cis*-Bicyclo[5.4.0]undecan-5-one was prepared as described by Gutsche and Peters.[11] Samples of bicyclo[5.4.0]undec-4-en-5-one (X) and bicyclo[5.4.0]undec-10-en-5-one (IV) and their corresponding dienones were prepared according to the methods outlined by Ginsberg and Rosenfelder.[2]

Diethyl 5-(1′-carboxy-2′-oxocyclohexyl)valerate (VI).—To a mixture of 11.0 g. of 50% sodium dispersion diluted to 300 ml. with dry xylene 40.0 g. of 2-carboethoxycyclohexanone was added as rapidly as possible with vigorous agitation. After 20 min., 50 g. of ethyl 5-bromovalerate dissolved in 50 ml. of xylene was rapidly added. The reaction mixture was slowly brought to reflux. After refluxing for 48 hr., the reaction mixture was cooled and poured over 2000 ml. of crushed ice and water. The xylene layer was separated and the aqueous layer extracted six times with 400-ml. portions of benzene. The benzene extracts and the xylene layer were combined and evaporated. The residue was distilled *in vacuo* to yield 36 g. of crude diethyl 5-(1′-carboxy-2′-oxocyclohexyl)valerate, b.p. 158–166°/2 mm.

5-(2′-Oxocyclohexyl)valeric Acid (VII).—A mixture of 36.0 g. of crude diethyl 5-(1′-carboxy-2′-oxocyclohexyl)-valerate, 100 g. of barium hydroxide, and 350 ml. of methanol was heated at reflux for 24 hr. After cooling, the hydrolysis mixture was acidified with cold, 10% hydrochloric acid. After thorough extraction with chloroform, the extracts were combined, dried over anhydrous magnesium sulfate, and evaporated. The residue was vacuum distilled to yield 25.4 g. of 5-(2′-oxocyclohexyl)valeric acid, b.p. 176–177.5°/0.5 mm.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.57; H, 9.03.

5-(2′-Hydroxycyclohexyl)valeric Acid (VIII).—A sodium hydroxide solution of 12.5 g. of 5-(2′-oxocyclohexyl)valeric acid was hydrogenated with Raney nickel and hydrogen at 60 p.s.i.g. After 7 days, the solution was filtered, acidified with dilute hydrochloric acid, and extracted with chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by chromatography over activated alumina in chloroform.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.78; H, 9.90.

Methyl 5-(2′-Hydroxycyclohexyl)valerate.—A mixture of 15.3 g. of 5-(2′-hydroxycyclohexyl)valeric acid, 150 ml. of methanol, and 2 ml. of concd. sulfuric acid was refluxed for 5 hr. After cooling, an equal volume of water was added and the methanol evaporated. The solution was extracted five times with 75-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified by chromatography over activated alumina in petroleum ether. The product on evaporation of the solvent weighed 12 g.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.14; H, 10.59.

Methyl 5-(1′-Cyclohexenyl)valerate.—A mixture of 10.0 g. of methyl 5-(2′-hydroxycyclohexyl)valerate, 12.0 g. of phosphorus pentoxide, and 250 ml. of anhydrous benzene was shaken together at room temperature for 24 hr. The reaction mixture was poured over 1000 ml. of crushed ice and water. The benzene layer was separated and the aqueous layer extracted four times with 250-ml. portions of benzene. The benzene layer and extracts were combined and evaporated. The residue was distilled *in vacuo* to yield 7.2 g. of methyl 5-(1′-cyclohexenyl)valerate, b.p. 100–103°/0.5 mm.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.42; H, 10.27. Found: C, 73.31; H, 10.10.

5-(1′-Cyclohexenyl)valeric Acid (IX).—A solution of 7.2 g. of methyl 5-(1′-cyclohexenyl)valerate, 10 g. of potassium hydroxide, 100 ml. of ethyl alcohol, and 100 ml. of water was refluxed for 24 hr. The ethyl alcohol was evaporated and the aqueous solution once extracted with 40 ml. of ether. The aqueous solution was acidified with cold, 10% hydrochloric acid and extracted three times with 100-ml. portions of chloroform. The chloroform extracts were combined, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 6.0 g. of 5-(1′-cyclohexenyl)valeric acid, b.p. 138°/0.8 mm.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.34; H, 9.89.

The amide was prepared by refluxing 1 g. of the purified acid with 1 g. of oxalyl chloride in 25 ml. of anhydrous benzene for 2 hr., followed by bubbling anhydrous ammonia through the ice-cold solution of the acid chloride in benzene. The product, 5-(1′-cyclohexenyl)valeramide was obtained in high yield (0.9 g.) m.p. 106–107° (lit.,[8] m.p. 106–107°). Mixed melting point determination with an authentic sample[8] showed no depression, m.p. 106–107°.

Polyphosphoric Acid Cyclization.—A mixture of 9.0 g. of 5-(1′-cyclohexenyl)valeric acid and 165 g. of polyphosphoric acid was heated together with stirring at 80° for 2.5 hr. The reaction mixture was hydrolyzed over 1000 ml. of crushed ice and water. The aqueous solution was extracted four times with 200-ml. portions of chloroform. The chloroform extracts were washed with 200 ml. of a saturated sodium carbonate solution, dried over sodium sulfate, filtered, and evaporated. The crude residue (5.6 g.) was vacuum fractionated through a micro column to yield two ketonic fractions, 2.1 g. of bicyclo[5.4.0]undec-10-en-5-one (IV), b.p. 129–131.5°/20 mm. and 1.9 g. of bicyclo[5.4.0]-undec-4-en-5-one (X), b.p. 136–139°/20 mm. Each fraction was chromatographed over activated alumina in 1:1 petroleum ether–ether mixture to effect further purification. The center fractions in each chromatograph were used in further study. Each fraction after column chromatography showed only one component when subjected to vapor phase chromatography using a Perkin-Elmer Vapor Fractometer, Model 154C equipped with a standard R type column. At 196°, 30 p.s.i.g. of helium pressure and 52 ml./min. helium flow, the retention time of bicyclo[5.4.0]undec-10-en-5-one (IV) was 15.6 min. Bicyclo[5.4.0]undec-4-en-5-one (X) under the same conditions had a retention time of of 16.9 min. An equivolume mixture of the two components separated satisfactorily, although not completely under these instrument parameters, a small amount of overlap of the two eluent bands was observed.

Bicyclo[5.4.0]undec-10-en-5-one (IV).—*Anal.* Calcd. for $C_{11}H_{14}O$: C, 80.44; H, 9.81. Found: C, 80.37; H, 9.80. Ultraviolet absorption (ethanol) λ_{max} 250.5 mμ, ϵ_{max} 14,200.

The infrared spectrum of the synthetic product was identical with an authentic sample prepared by the selenium dioxide dehydrogenation of *trans*-bicyclo[5.4.0]undecan-5-one.

The 2,4-dinitrophenylhydrazone derivative was prepared by standard procedure.[12] After recrystallization from

(9) R. Merchant, J. N. Wickert, and C. S. Marvel, *J. Am. Chem. Soc.*, **49**, 1829 (1927).

(10) H. R. Snyder, L. A. Brooks, and S. H. Shapiro, *Org. Syntheses*, Coll. Vol. II, 531 (1953).

(11) C. D. Gutsche and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5971 (1955).

(12) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., J. Wiley and Sons, New York, 1956.

chloroform–petroleum ether, a bright red crystalline solid was obtained, m.p. 170–171° (lit.,[2] m.p. 170–171°). Mixed melting point determination with an authentic sample[2] showed no depression, m.p. 170–171.5°.

Anal. Calcd. for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.11; H, 5.71; N, 16.05. Ultraviolet absorption (ethanol) λ_{max} 386.5 mμ, ϵ_{max} 27,700.

The semicarbazone derivative prepared by standard procedure[12] formed colorless crystals from methanol, m.p. 183–184.5°. No depression was observed on mixed melting point with a sample prepared from the ketone obtained from the selenium dioxide dehydrogenation of *trans*-bicyclo[5.4.0]undecan-5-one, m.p. 183–184°.

Anal. Calcd. for $C_{12}H_{19}N_3O$: C, 65.13; H, 8.65; N, 18.99. Found: C, 65.01; H, 8.50; N, 18.71.

Conversion to the Dienone (XV).—0.5 g. of Bicyclo-[5.4.0]undec-10-en-5-one, 0.5 g. of *N*-bromosuccinimide, and 25 ml. of anhydrous carbon tetrachloride were refluxed for 2 hr. The solution was filtered and evaporated. The residue was treated with lutidine to effect debromination. After the usual work-up, the residual ketone was chromatographed over activated alumina in 1:1 ether–petroleum ether to yield a small amount of colorless oil, assigned to structure XV on the basis of the ultraviolet absorption (ethanol) λ_{max} 247.5 mμ, ϵ_{max} 8700.

The dinitrophenylhydrazone derivative was recrystallized from chloroform–petroleum ether, m.p. 192–193° (lit.,[2] m.p. 191–192°).

The semicarbazone derivative was recrystallized from methanol, m.p. 204.5–205° (lit.,[2] m.p. 205–206°).

Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.73; H, 7.82; N, 19.16. Found: C, 65.98; H, 8.08; N, 18.91.

Bicyclo[5.4.0]undec-4-en-5-one (X).—*Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.81. Found: C, 80.29; H, 9.65. Ultraviolet absorption (ethanol) λ_{max} 241.5 mμ, ϵ_{max} 9300.

The dinitrophenylhydrazone derivative was prepared by standard procedure.[12] After recrystallization from chloroform–petroleum ether, a red crystalline solid was obtained, m.p. 177–178°. Mixed melting point with bicyclo[5.4.0]-undec-6-en-5-one from selenium dioxide dehydrogenation showed no depression, m.p. 177–178°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 59.29; H, 5.85; N, 17.27. Found: C, 59.24; H, 5.92; N, 16.23. Ultraviolet absorption (ethanol) λ_{max} 388.5 mμ, ϵ_{max} 24,200.

The semicarbazone derivative formed colorless crystals from methanol, m.p. 190–191°. Mixed melting point with bicyclo[5.4.0]undec-6-en-5-one from selenium dioxide dehydrogenation showed no depression, m.p. 190–191°.

Anal. Calcd. for $C_{12}H_{19}N_3O$: C, 65.13; H, 8.65; N, 18.99. Found: C, 65.27; H, 8.91; N, 19.20.

Conversion to the Dienone XI.—Conversion to the dienone was carried out by the same procedure as described above for bicyclo[5.4.0]undec-10-en-5-one. Ultraviolet absorption (ethanol) λ_{max} 241.5 mμ, ϵ_{max} 5300.

The dinitrophenylhydrazone derivative was recrystallized from chloroform–petroleum ether, m.p. 200–202° (lit.,[2] 201–202°). Ultraviolet absorption (ethanol) λ_{max} 383 mμ, ϵ_{max} 22,000.

The semicarbazone was recrystallized from methanol, m.p. 224–225° (lit.,[2] 224–225°).

Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.73; H, 7.82; N, 19.16. Found: C, 65.79; H, 7.91; N, 19.36.

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3-Phenylcyclobutylamine. II

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Alkylation of diethyl malonate with 2-phenylpropane-1,3-diol di-*p*-toluenesulfonate followed by saponification gave 3-phenylcyclobutane-1,1-dicarboxylic acid which was decarboxylated to *cis*- and *trans*-3-phenylcyclobutanecarboxylic acids. These acids were degraded to *cis*- and *trans*-3-phenylcyclobutylamine, respectively. The dicarboxylic acid was degraded to 3-phenylcyclobutanone, the oxime of which gave *cis*-3-phenylcyclobutylamine[1] on reduction. This configurational assignment is based on the conversion of *cis*-3-phenylcyclobutanol,[3] via its tosylate ester, to *trans*-3-phenylcyclobutyl azide and hence to *trans*-3-phenylcyclobutylamine.

One of the two geometrical isomers of 3-phenylcyclobutylamine has been prepared[1] by reduction of 3-phenylcyclobutanone oxime with lithium aluminum hydride, but its configuration was not known. In an attempt to determine the configuration of this amine, and to provide the other isomer for pharmacological comparison, alternative synthetic routes to the amine have been investigated. These methods were also to provide access to an intermediate, 3-phenylcyclobutanone (V), by a potentially less hazardous route than that using dichlorodifluoroethylene previously employed.[2]

Diethyl phenylmalonate (I) was reduced to 2-phenylpropane-1,3-diol (II) with lithium aluminum hydride.[3] The di-*p*-toluenesulfonate (III) of II, on alkylating diethyl malonate, gave diethyl 3-phenylcyclobutane-1,1-dicarboxylate, which was saponified to 3-phenylcyclobutane-1,1-dicarboxylic acid (IV). This acid was degraded to 3-phenyl-

(1) A. Burger and R. Bennett, *J. Med. Pharm. Chem.*, **2**, 1269 (1960).

(2) J. D. Roberts, A. Bruce Kline, and H. E. Simmons, *J. Am. Chem. Soc.*, **75**, 4765 (1953).

(3) This method is more convenient than the high pressure hydrogenolysis described by H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 3131 (1948).