The Acetolysis of 1,5-Diphenyl-cis-3-bicyclo[3.1.0]hexyl p-Toluenesulfonate

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Relative to hydrogen, phenyl substituents at C(1) and C(5) have been shown not to enhance the rate of ionization in the cis-3-bicyclo[3.1.0]hexyl p-toluenesulfonate system in dry acetic acid. The chief products from acetolysis are the rearranged olefins IX and X and the rearranged acetate VIII. These results would seem to weigh against the proposition that ionization in this system leads directly to a stabilized, tris-homocyclopropenyl cation.

It has been observed recently that the nitrous acid deamination of cis- and trans-3-bicyclo[3.1.0]hexyl-amines (I) in water proceeds without significant rearrangement[2] of the type observed in the acetolysis of the cis-3-toluenesulfonate,[3] which has been ascribed[3] to the intervention of a unique, stable structure, the tris-homocyclopropenyl cation II. The results of the amine deamination studies are, in fact, highly surprising if the thesis of "homoaromaticity" advanced by Winstein, et al., and the assignment of considerable stability for the ion II are accepted in the spirit with which they were proposed.[3b] Consequently, it seemed of some importance to put the hypothesis of the tris-homocyclopropenyl intermediate to a test using the same reaction, toluenesulfonate acetolysis, and the same ring system for which this idea was developed. Experiments along these lines are reported herein.

We have synthesized cis-1,5-diphenylbicyclo[3.1.0]-hexan-3-ol (VI) by the route indicated in Fig. 1 and have measured the kinetics of acetolysis of the p-toluenesulfonate ester. It was our expectation that two phenyl substituents placed 1,5 would stabilize a tris-homocyclopropenyl structure considerably[4] relative to the starting toluenesulfonate or the classical, unrearranged 3-cation since phenyl conjugation is absent in these bond-localized structures.[4a]
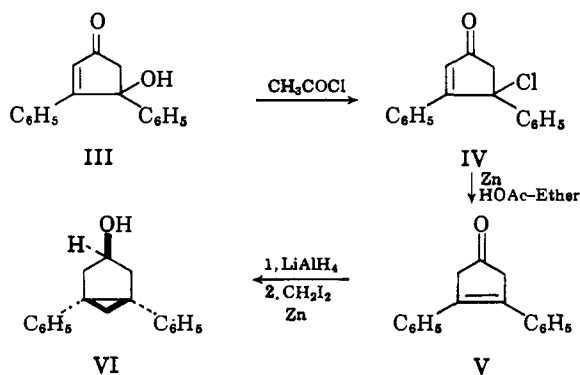
If, then, the acetolysis of cis-3-bicyclo[3.1.0]hexyl toluenesulfonates involves direct formation of the

tris-homocyclopropenyl cation with corresponding anchimeric assistance, phenyl substitution at C(1) and C(5) should produce a marked increase in acetolysis rates relative to the parent system. Rates of acetolysis of 1,5-diphenyl-cis-3-bicyclo[3.1.0]hexyl toluenesulfonate were measured under essentially the same conditions used previously[3c] by the titrimetric method,[5] and the results are presented in Table I together with data[3c] for the unsubstituted toluenesulfonate. It is clear from inspection of rate constants and activation parameters given in this table that phenyl substitution does not facilitate ionization as expected on the basis of the interpretation of Winstein, et al., for the 3-bicyclo[3.1.0]hexyl cation system and the expectation of stabilization by phenyl. In fact, a small rate-retarding effect of phenyl is evident, the magnitude of which is about as expected for an inductive effect.[6] Thus, these results argue strongly against the idea of anchimerically assisted ionization of the cis-3-bicyclo-[3.1.0]hexyl toluenesulfonates to give directly the tris-homocyclopropenyl[3] structure.
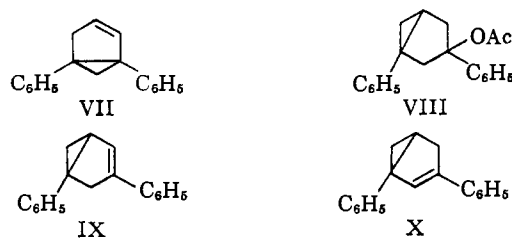
TABLE I

Kinetic Data on Acetolysis of cis-3-Bicyclo[3.1.0]hexyl Toluenesulfonates (Titrimetric Method)

[ROTs], 10^2M	Temp., °C.	[NaOAc], 10^2M	10^5k. sec.$^{-1}$
1,5-Diphenyl substituted[a]			
1.95	80.0	3.27	31.3
1.95	65.0	3.27	6.00
1.95	55.0	3.27	1.87

At 55.0°, $\Delta H^{\ddagger} = 25.4$ kcal./mole, $\Delta S^{\ddagger} = -2.75$ e.u.

Unsubstituted[b]			
1.26	75.0	3.05	69
1.26	50.0	3.05	4.6

At 50.0°, $\Delta H^{\ddagger} = 23.7$ kcal./mole, $\Delta S^{\ddagger} = -5.2$ e.u.

[a] Calculated 10^5k at 75° = 18.6 and at 50° = 1.0. [b] Data taken from Table II, ref. 3c.

Despite the absence of rate enhancement in the acetolysis of the toluenesulfonate of VI, a heavy predominance of rearrangement is noted in the products of reaction. Neither the acetate corresponding to VI nor the product of 1,2-elimination without rearrangement (VII) could be detected. Instead the acetate

(1) Postdoctoral research associate under a grant (No. 7672) from the National Science Foundation.

(2) E. J. Corey and R. L. Dawson, J. Am. Chem. Soc., 85, 1782 (1963).

(3) (a) S. Winstein, J. Sonnenberg and L. DeVries, ibid., 81, 6523 (1959); (b) S. Winstein, ibid., 81, 6524 (1959); (c) S. Winstein and J. Sonnenberg, ibid., 83, 3235 (1961); (d) ibid., 83, 3244 (1961).

(4) Compare the discussion of R. Breslow, J. Lockhart and H. W. Chang for the phenyl-substituted cyclopropenyl cations, ibid., 83, 2375 (1961).

(4a) The hybridization change at the phenyl-substituted carbon atoms should also favor the tris-homocyclopropenyl cation relative to the classical 1,5-diphenylbicyclo[3.1.0]hexyl-3-cation. See M. J. S. Dewar and H. N. Schmeising, Tetrahedron, 11, 96 (1960); C. J. McGinn, J. Chem. Phys., 35, 1511 (1961).

(5) S. Winstein, E. Greenwald and L. L. Ingraham, J. Am. Chem. Soc., 70, 821 (1948).

(6) For example, the rate constant for formolysis (50°) of 3-phenyl-1-propyl toluenesulfonate is ca. 60% that for 5-phenyl-1-pentyl or n-hexyl toluenesulfonate: C. K. Sauers, Ph.D. Thesis, University of Illinois, 1957.

VIII (ca. 9%) and a mixture of the olefins IX and X (ca. 81%) were obtained at 65° in acetic acid–sodium acetate. The olefin VII was synthesized from the toluenesulfonate of VI by reaction with potassium t-butoxide in dimethyl sulfoxide under mild conditions; by n.m.r. analysis it was shown that this olefin is not a significant component of the olefinic mixture isolated from solvolysis. The tertiary acetate VIII was identified by elemental analysis and by its infrared and n.m.r. spectra.

It is pertinent to note that the olefin VII rearranged with extraordinary ease to the olefinic isomer IX; at reflux temperature in cyclohexane solution the half-life for rearrangement was roughly one-half hour. It is likely that if VII is formed directly in solvolysis of the toluenesulfonate of VI, it would undergo essentially complete rearrangement under the conditions of our preparative acetolysis experiments.[7]

The rates of formation of the phenyl-conjugated olefinic components in acetolysis were measured directly in separate experiments involving determination of ultraviolet absorption as a function of time. Good first-order kinetics was observed using [ROTs] = ca. 10^{-3} M and [NaOAc] = ca. 10^{-2} to 10^{-4} M. The rate constants determined in this way were less than those measured titrimetrically as expected, since only a fraction of starting tosylate (ca. $^3/_4$) is converted to conjugated olefin. Thus, spectroscopically determined constants for olefin formation at 80°, 65° and 50° were 24.0, 4.30 and 0.64, respectively, $\times$ 10^{-5}.

The oily mixture of conjugated olefins from solvolysis could not be separated chromatographically; however, an analysis was possible from the n.m.r. spectrum since the spectra of the pure olefins VII and IX were available and were quite characteristic. The ratio IX/X in the mixture was roughly 1.1. The ultraviolet absorption of the mixture, λ_{max} 268 mμ (ϵ 15,000) was essentially the same as for pure IX which shows λ_{max} 268 mμ (ϵ 15,500).

The results described above concerning the products of acetolysis of VI toluenesulfonate differ sharply from those found[3] for cis-3-bicyclo[3.1.0]hexyl toluenesulfonate, in which case only cis-3-acetate is formed. However, both reactions involve extensive rearrangement; in the latter case this is discernible in the solvolysis of the 3-deuterio analog. Since our results would seem to exclude a primary intermediate of type II in the acetolysis, the question of formulating this primary cation must be reopened. It is possible, as indicated previously,[2] that this cation is essentially a classical ion with weak interaction involving the vacant orbital at C(3) and the loose electrons of the three-membered ring. Such a structure, which might be formulated as


XI, could be invoked to explain the stereospecific formation of cis-3-acetate from cis-3-bicyclo[3.1.0]hexyl toluenesulfonate, if the interaction is presumed to involve that part of the C(3)–p orbital trans to the cyclopropyl CH₂ and the loose electrons of the cyclopropyl ring; this geometry seems reasonable on the basis of present theoretical knowledge of the cyclopropyl system.[8] To the ion XI must be ascribed the property

of rapid interconversion with the isomeric ions formed by 1,3-rearrangement of the cross-ring bond; e.g., XIa. This would seem to be a tolerable assumption in view of remarkably facile rearrangement of the olefin VII to its isomer IX. However, it should be stated explicitly that a detailed and completely acceptable formulation of the cations in the 3-bicyclo[3.1.0]-hexyl system is beyond our present knowledge.

At this point a few remarks regarding the synthetic work are appropriate. The structures of the intermediates IV and V used for the synthesis of VI were verified beyond doubt by n.m.r., infrared and ultraviolet spectroscopy; relevant details are recorded in the Experimental section. An alternative approach to VI involved the intermediate transformations XII → XIV; however, this sequence was found to be unsatisfactory because of low yields in the reaction forming XIV. The faster and more efficient conversion of the
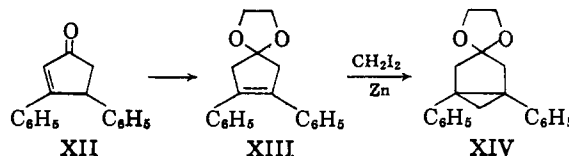
alcohol derived from V to cyclopropane using methylene iodide–zinc[9] as compared to the case of the ketal XIII is in accord with a recent discussion of this reaction.[3c]

Finally, mention might be made of an attempt to detect a stable ion as a product from the carbinol XV in acidic media. The carbinol was obtained from VI by oxidation to the corresponding ketone and reaction with phenyllithium. Treatment of XV with acidic
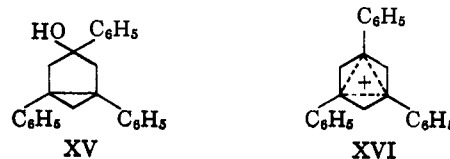
reagents under mild conditions produced no change (and no color); under more forcing conditions, e.g., boron trifluoride etherate or thionyl chloride–ether, 1,3,5-triphenylbenzene was formed rapidly. There was no evidence for an exceptionally stable or long-lived ionic species such as XVI.

Experimental[10]

4-Chloro-3,4-diphenyl-Δ²-cyclopentenone (IV).—According to Allen and Spanagel's procedure,[11] 5 g. of anhydroacetone benzil[12] was treated with 15 ml. of acetyl chloride at room temperature. Pure 4-chloro-3,4-diphenyl-Δ²-cyclopentenone, 2.7 g., colorless rods, m.p. 118–119°, recrystallized twice from n-pentane-benzene, was obtained; $\lambda_{max}^{CHCl_3}$ 5.80 μ (1724 cm.⁻¹) and 5.89 μ (1698 cm.⁻¹); n.m.r. (CDCl₃): δ = 3.27 p.p.m. (quartet, two methylene protons) and δ = 6.85 p.p.m. (singlet, olefinic proton).

3,4-Diphenyl-Δ³-cyclopentenone (V).—To a mixture of 40 g. of zinc dust and 8 ml. of glacial acetic acid in 350 ml. of ether, 5 g. of 4-chloro-3,4-diphenyl-Δ²-cyclopentenone in 150 ml. of ether was added at room temperature under vigorous stirring (magnetically), and stirring was continued for 25 minutes. Inorganic material was filtered and thoroughly washed with ether. The ether solution was washed successively with water, 5% sodium carbonate solution and water, and then evaporated to dryness. Recrystallization of the residual solid from n-pentane–benzene gave 3,4-diphenyl-Δ³-cyclopentenone, colorless needles, m.p. 146–147°, in 97% yield (4.2 g.). Mixture melting point with the specimen described below, obtained as the minor product from the Δ²-isomer during ketalization, showed no depression, and the

(7) Pyrolysis of the xanthate of VI at 180–200° or base-catalyzed decomposition of the benzenesulfonylhydrazone of 1,5-diphenyl-3-bicyclo-[3.1.0]hexanone at 160° afforded mainly the conjugated olefin IX, as expected because of the thermal instability of VII, the probable intermediate.

(8) C. A. Coulson and W. E. Moffitt, Phil. Mag., 40, 1 (1949).

(9) H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 81, 4256 (1959).

(10) Microanalyses were performed by Scandanavian Microanalytical Laboratory. Infrared data were obtained using a Perkin-Elmer Infracord. The n.m.r. data were obtained at 60 Mc. and are expressed as shift downfield from tetramethylsilane in parts per million.

(11) C. F. H. Allen and E. W. Spanagel, J. Am. Chem. Soc., 54, 4338 (1932).

(12) F. R. Japp and J. Knox, J. Chem. Soc., 87, 673 (1905).

infrared spectrum (5.70 μ (1754 cm.$^{-1}$) and n.m.r. (δ = 3.43 p.p.m. (singlet, two equiv. methylene groups) and δ = 7.18 p.p.m. (phenyl protons)) were also completely identical.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.07; H, 6.09.

3,4-Diphenyl-Δ^3-cyclopentenol.—To a mixture of 3.32 g. of lithium aluminum hydride in 250 ml. of anhydrous ether was added a solution of 10 g. of 3,4-diphenyl-Δ^3-cyclopentenone (V) in 150 ml. of anhydrous benzene dropwise with stirring and cooling (1 hour), and stirring was continued for 1 hour at room temperature. The reaction mixture was heated to reflux 0.5 hour. To the cooled reaction mixture ethyl acetate was added followed by water and dilute hydrochloric acid. The organic layer was washed twice with water and evaporated to dryness, giving a yellow oil which solidified. The crude product was dissolved in a small amount of benzene and colorless crystals were obtained by addition of *n*-pentane. Recrystallization from *n*-pentane–benzene gave pure 3,4-diphenyl-Δ^3-cyclopentenol, m.p. 102.5–103.5°, yield 9.6 g. (95%), $λ_{max}^{CHCl_3}$ 2.72 μ (3676 cm.$^{-1}$) and 2.87 μ (3484 cm.$^{-1}$).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.41; H, 6.83.

1,5-Diphenyl-bicyclo[3.1.0]hexan-3-ol (VI).—A mixture of 21.6 g. (0.08 mole) of methylene iodide, 6.5 g. (0.1 mole) of zinc–copper couple and 0.07 g. of iodine in 60 ml. of anhydrous ether was refluxed for 1 hour. To this reagent 9.44 g. (0.04 mole) of 3,4-diphenyl-Δ^3-cyclopentenol in 30 ml. of anhydrous ether was added, the reaction mixture turned to gray and then gradually dark. After refluxing for 44 hours with efficient magnetic stirring, inorganic material was filtered through a Super Cel pad and washed thoroughly with ether. The ether solution was washed successively with 5% dilute hydrochloric acid (60 ml. × 3), 5% sodium bicarbonate solution (60 ml. × 3) and saturated sodium chloride solution (60 ml. × 3) and evaporated to dryness. Recrystallization of residual crystalline product from ethanol gave 1,5-diphenyl-bicyclo[3.1.0]hexan-3-ol (VI), colorless needles, m.p. 155.5–156.5°, yield 6.1 g. (61%); $λ_{max}^{CHCl_3}$ 2.72 μ (3676 cm.$^{-1}$) 2.86 μ (3497 cm.$^{-1}$). From the mother liquors about 1.2 g. of the starting material was recovered.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.46; H, 7.33.

1,5-Diphenyl-3-bicyclo[3.1.0]hexyl Acetate.—To a solution of 150 mg. of 1,5-diphenyl-3-bicyclo[3.1.0]hexanol in 1 ml. of anhydrous pyridine was added 0.5 ml. of acetic anhydride with ice-cooling, the mixture was allowed to stand at room temperature for 3 days, then poured into ice-water to give an oil which gradually crystallized. Recrystallization from methanol gave 145 mg. of the acetate, m.p. 83.5–84.5°, colorless blocks; $λ_{max}^{CHCl_3}$ 5.75, 7.94 μ.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.15; H, 6.92.

1,5-Diphenyl-3-bicyclo[3.1.0]hexyl *p*-Toluenesulfonate.—About 1 g. of *p*-toluenesulfonyl chloride was added to a solution of 500 mg. of 1,5-diphenyl-3-bicyclo[3.1.0]hexanol in 5 ml. of dry pyridine with cooling. After standing at room temperature for 29 hours, a few drops of water was added and the mixture stored for 30 minutes and poured into a mixture of ether and water in a separatory funnel. The ether layer was washed with dilute sodium bisulfate and water. Evaporation of the ether and recrystallization from methanol gave 700 mg. (88%) of *p*-toluenesulfonate of VI, m.p. 106–107°.

Anal. Calcd. for $C_{25}H_{24}O_3S$: C, 74.24; H, 5.98; S, 7.91. Found: C, 74.13; H, 5.98; S, 7.87.

Preparation Acetolysis of 1,5-Diphenyl-3-bicyclo[3.1.0]hexyl *p*-Toluenesulfonate.—A solution of 542 mg. of *p*-toluenesulfonate in 50 ml. of glacial acetic acid containing 0.05 mole of sodium acetate and 0.01 mole of acetic anhydride was heated at 65° for 67 hours. The mixture was poured into 50 ml. of methylene chloride and 100 ml. of water in a separatory funnel (no grease) and the water layer was extracted four times with additional methylene chloride. The combined extracts (*ca.* 150 ml.) were successively washed with water, 5% sodium bicarbonate (100 ml. × 2) and water and then dried over anhydrous sodium sulfate. After filtration of inorganic material, the solvent was distilled under reduced pressure and then carbon tetrachloride was added and evaporated. The addition and evaporation of carbon tetrachloride was repeated four times without heating and the residual pale brown liquid was kept in a desiccator. The infrared spectrum (CCl$_4$) showed the presence of an acetate (5.76 μ) and in comparison of the intensities of C–H stretching band and acetate band of this product with those of pure acetate (below) the content of the acetate was approximately 10%.

The mixture was dissolved in *n*-pentane–benzene (4:1) and chromatographed on neutral alumina activity III eluting with the same solvent. From the rapidly eluted portion (*ca.* 50 ml.), 252 mg. (81%) of colorless oil was obtained and from the next elution (60 ml.) 21 mg. (7.7%) the crystalline tertiary acetate was

isolated. Further elution gave a small amount of blue semicrystalline material which was not investigated. The tertiary acetate VIII, after recrystallization from a small amount of methanol, had m.p. 90.5–91.0°, $λ_{max}^{CCl_4}$ 5.76 μ. The infrared spectrum of this acetate was different from that of 1,5-diphenyl-3-bicyclo[3.1.0]hexyl acetate and the melting point of an admixture was depressed.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.20; H, 6.95.

The oily product was purified by distillation twice at 130–135° (bath temperature) at 0.03 mm. On distillation a very small amount of crystalline material was obtained, but was not investigated further. The ultraviolet spectrum (95% EtOH) of the oily product showed absorption bands at 203 mμ (ε 28,000), 217 mμ (shoulder, ε 16,800) and 268 mμ (ε 15,000). The last band could be attributed to a phenyl conjugated double bond. The n.m.r. spectrum indicated that this material is a mixture of olefinic compounds possessing a cyclopropane ring, IX and X in a ratio of *ca.* 1:1.

Attempts to separate these components by v.p.c. using 1% or 3% silicone oil DC 550 or Apiezon columns were unsuccessful.

A sample, freshly distilled and chromatographed on neutral alumina activity III with pentane, was used for analysis.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.16; H, 6.88.

The same result was obtained from an acetolysis run carried out at 50° for 113 hours. The ultraviolet, infrared and n.m.r. spectra of the hydrocarbon fraction before distillation were essentially the same as those of distilled material.

1,5-Diphenyl-3-bicyclo[3.1.0]hexyl S-Methyl Xanthate.—A solution of sodium methylsulfinyl carbanion in dimethyl sulfoxide[13] was prepared as follows: 200 mg. of sodium hydride in mineral oil dispersion was placed in three-necked round-bottomed flask and washed with light petroleum ether three times. The flask, which was fitted with a reflux condenser, the top of which was connected to a three-way stopcock, was evacuated to remove traces of petroleum ether and then the system was placed under nitrogen. Then 15 ml. of dry dimethyl sulfoxide (distilled over calcium hydride) was added and the resulting mixture was heated at 65° for 30 minutes. The concentration of the resulting sodium methylsulfinyl carbanion was determined by means of titration with 0.1 N hydrochloric acid. A 5-ml. portion of this solution of sodium methylsulfinyl carbanion (corresponding to 31 mg. of sodium hydride) was added to a solution of 250 mg. of 1,5-diphenyl-3-bicyclo[3.1.0]hexanol in 5 ml. of dimethyl sulfoxide and the mixture (turned immediately to yellow) was stirred for 30 minutes. Then 100 mg. of carbon disulfide was added with the aid of anhydrous ether and the resulting red solution was stirred for 30 minutes. A solution of 184 mg. of methyl iodide in ether was added and stirring continued for 2.5 hours; during this period a further 2 drops of methyl iodide was added. All of these operations were carried out at room temperature under nitrogen. Finally, 10 ml. of cold water and 15 ml. of ether was added and the ether layer was washed with water three times and once with saturated salt solution. Evaporation of ether gave pale yellow crystals; 2 ml. of methanol was added and the insoluble solid was collected and recrystallized from ethanol–ethyl acetate to give S-methyl xanthate, m.p. 123.5–124.5°, in 97% (330 mg.) yield.

Anal. Calcd. for $C_{20}H_{20}OS_2$: C, 70.57; H, 5.92; S, 18.80. Found: C, 70.49; H, 5.93; S, 18.90.

The attempted preparation of S-methyl xanthate according to the usual methods using sodium hydride in ether or benzene at its boiling point resulted into the recovery of the starting material or non-crystalline material.

1,3-Diphenylbicyclo[3.1.0]hexene-3 (IX) by Xanthate Pyrolysis.—A sample of VI-S-methyl xanthate (80 mg.), placed in a small round-bottomed flask equipped with a reflux condenser, the top of which was connected to an aspirator, was heated in an oil-bath under ordinary atmosphere. At about 180° decomposition occurred and the bath temperature was gradually raised to 205° and maintained at this temperature for 10 minutes; during this period the flask was evacuated for 3 minutes to remove methyl mercaptan and carbon oxysulfide. Distillation of the resulting brown oil at 130° (bath temp.) under 0.05 mm. gave rise to 35 mg. of pale yellow oil, 1,3-diphenylbicyclo[3.1.0]hexene-3 (IX); $λ_{max}^{95\%\ EtOH}$ 202 mμ (ε 26,100), 217 mμ (shoulder, ε 16,100) and 268 mμ (ε 15,600); $λ_{max}^{cyclohexane}$ 268 mμ (ε 15,200).

Further purification by distillation, followed by chromatography on neutral alumina activity III with *n*-pentane, afforded crystalline material, m.p. 45–50°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.29; H, 6.92.

1,5-Diphenyl-3-bicyclo[3.1.0]hexanone Benzenesulfonylhydrazone and its Decomposition.—A mixture of 280 mg. of 1,5-diphenyl-3-bicyclo[3.1.0]hexanone (below) and 220 mg. of

(13) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

benzenesulfonylhydrazide in 6 ml. of ethanol containing 2 drops of acetic acid was heated under reflux for 1 hour, after solution of the starting material and the reagent, silky needles separated. Collection and recrystallization from ethanol gave 431 mg. (95%) of benzene–sulfonylhydrazone, m.p. 179° dec.

Anal. Calcd. for $C_{24}H_{22}O_2N_2S$: C, 71.62; H, 5.51; N, 6.96; S, 7.95. Found: C, 71.77; H, 5.53; N, 7.03; S, 7.98.

A small sample, 58 mg., of the above benzenesulfonylhydrazone and 58 mg. (7.4 equivalent) of sodium methoxide were dissolved in 2 ml. of diglyme and the resulting solution was refluxed for 30 minutes; the mixture turned immediately to yellow. After cooling, 5 ml. of water was added and the separated oil was extracted with ether. The extract was washed with water and evaporated to dryness, giving rise to brown oily residue the infrared and ultraviolet spectra of which were identical with those of 1,3-diphenylbicyclo[3.1.0]hexene-3 from VI-S-methyl xanthate.

Treatment of VI *p*-Toluenesulfonate with Potassium *tert*-Butoxide.—A small sample (50 mg.) of VI *p*-toluenesulfonate was added to a solution of potassium *tert*-butoxide, prepared from 30 mg. of potassium, 1 ml. of dry *t*-butyl alcohol and 1 ml. of anhydrous benzene, and the mixture was stirred at room temperature for 20 hours and then at 50° for 7 hours under nitrogen. The mixture was poured into a mixture of water and ether and the ether layer was washed thoroughly with water and finally with saturated salt solution. Removal of solvent gave a crystalline residue which was found to be the starting material by infrared.

Recovered *p*-toluenesulfonate was again dissolved in a solution of 1 ml. of benzene and 1 ml. of *t*-butyl alcohol containing 40 mg. of potassium and heated under reflux for 24 hours in a nitrogen atmosphere. The mixture was worked up in the manner described above to give a pale brown oil, the infrared and ultraviolet spectra of which were identical with those of 1,3-diphenyl-bicyclo[3.1.0]hexene-3 (IX) except for slightly weaker ultraviolet absorption (found, ε 14,900).

1,5-Diphenylbicyclo[3.1.0]hexene-2 (VII).—Sodium *t*-butoxide in dimethyl sulfoxide was prepared from 40 mg. of sodium hydride with mineral oil dispersion, 2 ml. of dimethyl sulfoxide and 0.5 ml. of *t*-butyl alcohol using a procedure similar to that described for the preparation of the S-methyl xanthate of VI. To this solution 50 mg. of *p*-toluenesulfonate of VI was added and resulting pale yellow solution was stirred at room temperature for 26 hours under nitrogen. Water was added and the resulting milky solution was extracted twice with ether, and then extracts were thoroughly washed with water (twice) and saturated salt solution (twice). Evaporation of the ether gave 34 mg. of crystalline product.

Approximately 110 mg. of crude product, which had been obtained from another run using 100 mg. of *p*-toluenesulfonate of VI, was chromatographed on neutral alumina activity III with *n*-pentane to yield 83 mg. of crystals from the rapidly eluted portion. Rechromatography, followed by recrystallization from ether–ethanol (dissolving in a small amount of ether, followed by addition of ethanol) at −20° without heating, gave 46 mg. of pure 1,5-diphenylbicyclo[3.1.0]hexene-2 (VII), m.p. 98.5–99.5°, no absorption maximum at 268 mμ in the ultraviolet; $\lambda_{max}^{95\%\ EtOH}$ 205 mμ (ε 25,600) and 225 mμ (shoulder, ε 13,700); $\lambda_{max}^{cyclohexane}$ 236 mμ (ε 10,450).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.94; H, 6.95.

The infrared spectrum (CCl₄) of the sample before recrystallization differs from that of both of acetolysis product and 1,3-diphenylbicyclo[3.1.0]hexene-3 (IX). The n.m.r. spectrum showed the peaks for cyclopropyl methylene as a pair of doublets centered at δ = 0.88, 2.18. two protons (cyclopentene ring methylene at δ = 2.93 (quartet) and two olefinic proton multiplets centered at 5.75 and 6.25 δ.

A small sample was heated at 100–110° for 1.5 hours; the resulting solid showed an absorption maximum at 268 mμ (ε 15,200). The infrared spectrum was identical with that of crystalline IX obtained above for analysis.

Isomerization from 1,5-Diphenylbicyclo[1.3.0]hexene-2 (VII) to 1,3-Diphenylbicyclo[3.1.0]hexene-3 (IX).—A solution of 1.564 mg. of 1,5-diphenylbicyclo[3.1.0]hexene-2 (VII) in 50 ml. of cyclohexane was gently refluxed under nitrogen. At suitable times about 4-ml. portions of the solution were taken out by syringe and then subjected to ultraviolet measurements. By measurement of absorption at 268 mμ the half-life for the isomerization to IX (ε 15,200 at 268 mμ) was found to be roughly 30 minutes under these conditions.

Kinetics of Acetolysis of VI Toluenesulfonate. A. Titrimetric Rates.—The excellent procedure of Winstein, Greenwald and Ingraham[6] was followed in detail using the sealed ampoule reactor technique with a thermostated bath in which temperature control was ±0.05° or better. The solvent was anhydrous acetic acid containing a small amount of acetic anhydride; brom phenol blue was used as the indicator in the titrations of excess sodium acetate against 0.0497 *N* *p*-toluenesulfonic acid in dry acetic acid.

B. Spectrophotometric Rates.—The same acetolysis conditions were employed as described above. For assay, a sample was removed from a cooled reactor ampoule and carefully measured into 5-ml. volumetric flask (0.300 ml. being delivered). After dilution to 5 ml. with 95% ethanol, ultraviolet absorption at 268 mμ was measured using a 1-cm. cell and a Cary model 15 ultraviolet spectrometer. Rate constants and activation parameters were calculated by standard methods (*cf.* ref. 5).

Excellent first-order reaction kinetics was observed by both titrimetric and spectrophotometric methods, out to 80% reaction and beyond.

3,4-Diphenyl-Δ²-cyclopentenone (XII).—3,4-Diphenyl-Δ²-cyclopentenone (XII) was prepared by reduction of anhydroacetone benzil with hydroiodic acid and red phosphorus in glacial acetic acid by Geissman and Koelsch's procedure[14]; m.p. 110.5–111.5°, pale yellow needles from ethanol, colorless needles from benzene; $\lambda_{max}^{CHCl_3}$ 5.85 μ (1709 cm.⁻¹) 5.95 μ (1681 cm.⁻¹). The n.m.r. spectrum (CDCl₃) showed an olefinic proton at 6.75 p.p.m. (doublet) and other peaks consistent with the Δ²-structure.

3,4-Diphenyl-Δ³-cyclopentenone Ethylene Ketal (XIII) and 3,4-Diphenyl-Δ²-cyclopentenone (V).—A mixture of 5 g. of 3,4-diphenyl-Δ²-cyclopentenone, 20 g. of ethylene glycol, 0.15 g. of *p*-toluenesulfonic acid and 200 ml. of benzene was heated in a round-bottomed flask equipped with Soxhlet extractor containing calcium carbide in an extractor thimble for 50 hours at reflux. To the cooled reaction mixture powdered potassium hydroxide and then ice-water were added. The organic layer was washed twice with water and dried over anhydrous sodium sulfate. After removal of solvent under reduced pressure the dark brown residue gradually crystallized. A small amount of benzene was added and the crystals were collected. Recrystallization from ethanol afforded 3,4-diphenyl-Δ³-cyclopentenone ethylene ketal (XII), m.p. 93–94°, yield 1.63 g. (27%). The structure of this compound was confirmed by spectral data. $\lambda_{max}^{CHCl_3}$ 8.93 μ (1120 cm.⁻¹) and 9.81 μ (1019 cm.⁻¹) (ketal) and no carbonyl; n.m.r. spectrum (CCl₄) two equal, intense singlet peaks at δ = 3.15 p.p.m. (two methylene groups on cyclopentene ring), at δ = 4.91 p.p.m. (two methylene groups of ketal), no peak in the olefinic proton region.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.84; H, 6.59.

The crude crystalline material obtained from the mother liquors was recrystallized fractionally from ethanol to give, in addition to the recovered starting material (*ca.* 0.1 g.), another product, 3,4-diphenyl-Δ³-cyclopentenone (V), pale yellow needles, m.p. 145–146°, $\lambda_{max}^{CHCl_3}$: 5.71 μ (1751 cm.⁻¹). N.m.r. (CDCl₃): δ = 3.43 p.p.m. (singlet) (equivalent four methylene protons) and δ = 7.22 p.p.m. (phenyl protons), yield 0.14 g. Mixture melting point with the reduction product of 4-chloro-3,4-diphenyl-Δ²-cyclopentenone (IV) (above) showed no depression; the infrared and n.m.r. spectra were completely identical.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.21; H, 6.18.

In other runs using a larger excess of ethylene glycol (20 equivalents) and refluxing for 24–35 hours, much more of the ketal XIII was obtained (37–42% yield), and no 3,4-diphenyl-Δ²-cyclopentenone was isolated.

1,5-Diphenylbicyclo[3.1.0]hexan-3-one Ethylene Ketal (XIV). —A mixture of 1.365 g. of zinc–copper couple, 3.78 g. of methylene iodide and 0.015 g. of iodine in 10 ml. of anhydrous ether was refluxed for 1 hour. The reagent turned dark and there was a gentle exothermic reaction. Then, 0.278 g. of 3,4-diphenyl-Δ³-cyclopentenone ethylene ketal XIII was added and refluxing was continued for 84 hours with magnetic stirring; during reaction 5 ml. of anhydrous ether was added. The cooled reaction mixture was filtered through a Hyflo Super Cel pad on a buchner funnel and the residue was washed thoroughly with ether. The ether solution was successively washed with 5% hydrochloric acid (8 ml. × 3), 5% sodium bicarbonate solution (8 ml. × 3) and saturated sodium chloride solution (8 ml. × 3). Removal of ether under reduced pressure afforded a brown viscous residue, which was chromatographed on Florisil using *n*-pentane–benzene (1:1) mixture to give 40 mg. of crystalline product. Recrystallization from *n*-hexane or *n*-pentane–*n*-hexane (1:1) gave pure 1,5-diphenylbicyclo[3.1.0]hexan-3-one ethylene ketal (XIV), m.p. 109–110°; $\lambda_{max}^{CHCl_3}$ 3.29 μ (3040 cm.⁻¹) (cyclopropane ring?), 8.94 and 9.79 μ (1119 and 1021 cm.⁻¹) (ketal).

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.01; H, 6.98.

1,5-Diphenylbicyclo[3.1.0]hexan-3 one.—To the chromium trioxide–pyridine complex, prepared from 4.03 g. of chromium trioxide and 45 ml. of pyridine, 2.4 g. of 1,5-diphenylbicyclo-[3.1.0]hexan-3-ol (VI) in 20 ml. of pyridine was added with cooling and stirring. The resulting mixture was stirred for 12 hours at room temperature and stored for an additional 12 hours. During the first half-hour, the mixture turned from yellow to

(14) T. A. Geissman and C. F. Koelsch, *J. Org. Chem.*, **3**, 489 (1938).

dark brown. Then, the mixture was poured into a mixture of 100 ml. of ether, 150 ml. of benzene and 150 ml. of water in a separatory funnel. After separation of the organic layer, the water layer was extracted with 100 ml. of an ether-benzene mixture. The combined organic extracts were thoroughly washed with dilute sulfuric acid and then water, sodium bicarbonate solution and water. Removal of solvent, followed by recrystallization of the residual crystalline material from n-pentane-benzene, gave 1,5-diphenylbicyclo[3.1.0]hexan-3-one in quantitative yield, colorless blocks, m.p. 135.0–135.5°, $\lambda_{max}^{CCl_4}$ 5.72 μ (1748 cm.$^{-1}$).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.18; H, 6.52.

1,3,5-Triphenylbicyclo[3.1.0]hexan-3-ol (XV).—To a solution of phenyllithium in 20 ml. of absolute ether, prepared from 0.148 g. of lithium metal and 1.28 g. of bromobenzene, 0.5 g. of 1,5-diphenylbicyclo[3.1.0]hexan-3-one in 25 ml. of anhydrous benzene and ether (1:2) was added dropwise at room temperature under nitrogen and with stirring. After heating at reflux for 2 hours, 20 ml. of water was added and organic layer was washed with water. Removal of the solvent and recrystallization of the resulting crystals from n-pentane-benzene or cyclohexane gave colorless crystals of 1,3,5-triphenylbicyclo[3.1.0]hexan-3-ol, m.p.

150.5–151.5° (the first crop of crystals, recrystallized twice from n-pentane-benzene, showed m.p. 102.5–103.5°, but after one more recrystallization it melted at 150.5–151.5°), yield 0.35 g. (53%), $\lambda_{max}^{CHCl_3}$ 2.75 (3636 cm.$^{-1}$) and 2.89 μ (3460 cm.$^{-1}$). In a subsequent run on larger scale a 76% yield of XV, m.p. 150–151.5°, was obtained.

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.49; H, 6.81.

The carbinol XV gave no color with 1% sufuric acid in glacial acetic acid or with trifluoroacetic acid. With boron fluoride etherate a rose-red color developed immediately and a crystalline precipitate rapidly separated, m.p. 177.5–178.5° (43% yield), which was identified as 1,3,5-triphenylbenzene by m.p., infrared absorption, n.m.r. spectrum and elemental analysis. Reaction of the carbinol XV with thionyl chloride in ether at reflux for 1 hour also produced 1,3,5-triphenylbenzene. At higher concentrations of sulfuric acid in acetic acid, triphenylbenzene was formed rapidly. The carbinol could be recovered unchanged after treatment (in solution) with acetyl chloride (excess) in benzene at reflux for 40 minutes, conditions which convert triphenylcarbinol to the corresponding chloride.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

Reactions of Benzyne Intermediates in Non-basic Media[1]

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Diazotization of anthranilic acid or variously substituted anthranilic acids leads to crystalline inner salts, the diazonium-2-carboxylates. Mild pyrolysis (35–60°) of these substances causes the elimination of nitrogen and carbon dioxide and formation of benzyne intermediates. The nature of the intermediates was revealed by trapping with furan, with anthracene, with carboxylic acids and with *tert*-butyl alcohol. The mixture of products obtained from each of the latter two reactions indicated that carbon atoms 1 and 2 of the inner salt III become equivalent during the reaction. Certain aspects of the mechanism of addition to the benzyne intermediate are discussed.

Introduction

Evidence presented in 1953[3] established that the reaction of chlorobenzene with potassium amide in liquid ammonia was not a simple displacement reaction. The amino group in the product had become attached with nearly equal probability to the carbon atom which had borne the chlorine and to one of the *ortho* carbons. This discovery placed rigid requirements upon any attempt to write a mechanism for the reaction, and led Roberts[3] to propose, as the simplest explanation, that chlorobenzene first undergoes an elimination reaction to form benzyne (I). This intermediate resembled one which Wittig,[4] on the basis of very different evidence, had envisioned some years earlier, and it was almost simultaneously advanced[5] to account for the rearrangements which accompany the reaction of phenyllithium with fluoronaphthalenes and fluoroanisoles. Research activity on a broad front was stimulated by these startling proposals.

$$(1)$$

I
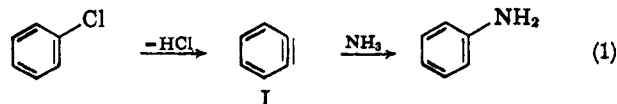
Several recent reviews[6] summarize research during the past decade which has defined the benzyne concept

more fully and greatly extended its scope. The use of reactive dienes to trap a C_6H_4 fragment, generated from *o*-fluorobromobenzene and lithium amalgam, provided very satisfying evidence for the existence of benzyne.[7] Various alternatives to the elimination-addition mechanism for the reaction of eq. 1 have now been eliminated,[8] and the mechanism of the elimination step has been clarified by kinetic[9] and deuterium exchange studies.[10] Some progress has also been made in understanding the mechanism of the addition step.[11] Experiments with 9,10-phenanthryne and 1,2-naphthyne have suggested that these two substances are more stable than benzyne, as reflected by their greater discrimination between phenyllithium and lithium piperidide.[12] On the practical side, the benzyne concept has stimulated the development of new, potentially important methods for effecting cyclization to an aromatic ring under alkaline conditions.[13,14]

At the outset of the present research, benzyne was within the province of the metallo-organic chemist. The only reactions in which it had been discovered were those of aryl halides, ethers or sulfonates with

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