of aldehydes in one run with naphthalene, and one with furan. In neither of these two cases could the presence of an aldehyde be corroborated by other tests, and when the runs were repeated the positive indications failed to reappear.

Acknowledgment.—The authors are grateful for a research grant from the Esso Standard Oil Company, Baton Rouge, Louisiana. They also acknowledge their indebtedness to V. F. Farrugia, who contributed useful empirical information on the preparation and use of mixed anhydrides, and who also performed part of the work with formic acetic anhydride which is summarized here.

The Stereochemistry of the Nucleophilic Addition of *p*-Toluenethiol to 1-*p*-Tolylsulfonylcyclopentene[1]

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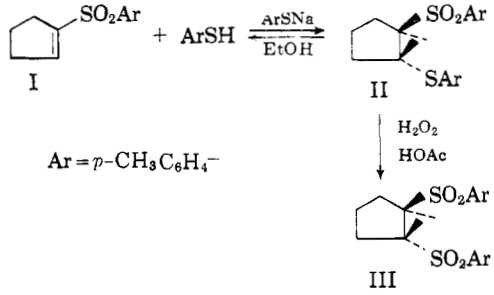
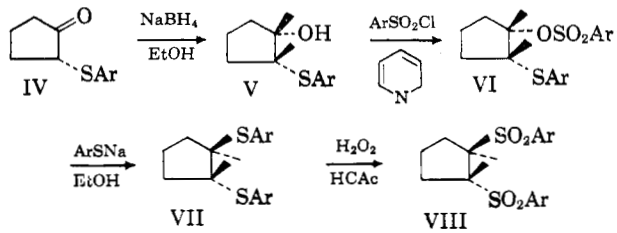
Under mildly basic conditions *p*-toluenethiol adds to 1-*p*-tolylsulfonylcyclopentene to give *trans*-2-*p*-tolylmercapto-1-*p*-tolylsulfonylcyclopentane. The stereochemistry of the adduct was proved by an independent synthesis. An explanation, together with supporting evidence, for the stereoselectivity involved is given.

Having demonstrated[2] that *p*-toluenethiol adds to 1-*p*-tolylsulfonylcyclohexene under mildly basic conditions to give, *via* a *trans* addition, *cis*-2-*p*-tolylmercapto-1-*p*-tolylsulfonylcyclohexane, it was decided to study the stereochemistry of like additions to other activated cyclic olefins. Accordingly, *p*-toluenethiol was added to 1-*p*-tolylsulfonylcyclopentene (I)[3] in the presence of a 0.1 molar equivalent of sodium ethoxide in ethanol. The resulting adduct (II) was oxidized to its respective disulfone (III).

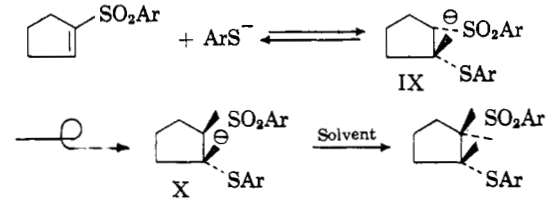


trans-1,2-Bis-*p*-tolylsulfonylcyclopentane was independently synthesized in the following manner:



Reduction of the keto sulfide (IV) by sodium borohydride in ethanol gave the *cis*-hydroxy sulfide (V) which was converted to its tosylate (VI). The tosylate was shown to have a *cis* configuration by demonstrating that it could be oxidized to the known[3] *cis*-2-(*p*-tolylsulfonyl)cyclopentyl *p*-toluenesulfonate. The S$_N$2 displacement by thiolate upon *cis*-2-(*p*-tolylmercapto)cyclopentyl *p*-toluenesulfonate (VI) would be expected to lead to inversion even if the unlikely possibilities of isomerization or anchimeric assistance are taken into consideration. Elimination of *p*-toluenesulfonic acid from VI followed by addition of thiolate to the resulting vinyl sulfide to give a dithioether with a *cis* configuration was discredited by a demonstration that thiolate does not add to vinyl sulfides under these reaction conditions. The independently prepared *trans*-disulfone (VIII) was shown to be identical to III. Thus III and therefore the adduct (II) have a *trans* configuration.[4]

These *over-all* results are opposite to those in the cyclohexyl system in which an adduct of *cis* configuration is obtained under identical conditions. This difference can be explained by greater steric strain in the *cis*-cyclopentyl system relative to the *cis*-cyclohexyl system. The addition is presumed to proceed through the following mechanistic path:



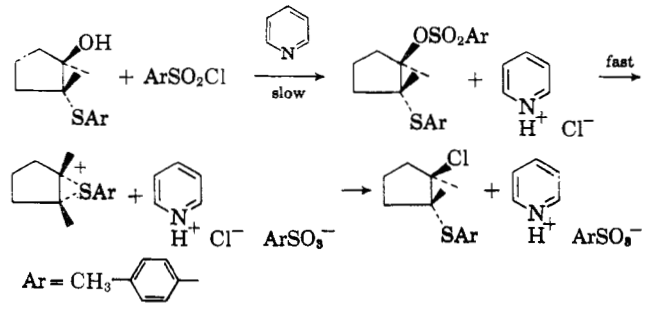
Presumably there is more steric strain in the anion intermediate (IX) due to interaction between an arylsulfonyl group and an arylmercapto group than in the corresponding *cis*-cyclohexyl anion (XI), in which the

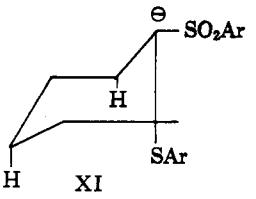
(1) Abstracted from the Ph.D. thesis of A. J. Levy, Purdue University, 1962.

(2) W. E. Truce and A. J. Levy, *J. Am. Chem. Soc.*, **83**, 4641 (1961).

(3) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1951).

(4) An attempt was made to prepare *trans*-2-(*p*-tolylmercapto)cyclopentyl *p*-toluenesulfonate (from its respective alcohol, *p*-toluenesulfonyl chloride and pyridine) as an intermediate toward the preparation of *cis*-1,2-bis-*p*-tolylmercaptocyclopentane. The only products isolated, however, were pyridinium *p*-toluenesulfonate and *trans*-2-*p*-tolylmercapto-1-chlorocyclopentane. This reaction is an excellent example of neighboring group participation by bivalent sulfur.





XI

strain is due to steric interactions of an arylmercapto group with two axial hydrogens. Thus, steric acceleration causes IX to isomerize at a greater rate than either protonation or elimination back to olefin (I) and thiolate, whereas, in the cyclohexyl system, isomerization is too slow to compete with protonation or elimination.

Evidence in support of this explanation was obtained from a study of the relative rates of isomerization of analogous compounds. Both *cis*-2-phenylsulfonyl-1-methylcyclohexane and *cis*-2-phenylsulfonyl-1-methylcyclopentane were prepared and their relative rates of isomerization under basic conditions were determined. The five-membered ring sulfone was found to isomerize fifteen times faster than the six-membered ring sulfone, presumably a consequence of more steric interference between an arylsulfonyl group and a methyl group (in the five-ring) than between a methyl group and two axial hydrogens (in the six-ring).

It is unlikely that this rate enhancement is due simply to a greater rate of anion formation in a five-membered ring (as is the case with the comparable esters and nitro compounds) caused by the greater stability of a double bond *exo* to a five-membered ring.[5] Weinstock and co-workers[6] found that *p*-tolylsulfonylcyclopentane and *p*-tolylsulfonylcyclohexane undergo base-catalyzed deuterium exchange of their alpha protons with solvent at approximately the same rate. In addition, the bulk of the available evidence suggests that double bond formation between sulfur and carbon in sulfones is not pronounced.[6,7a-e]

An attempt was made to isomerize *cis*-2-phenylsulfonyl-1-methylcyclopentane with thiolate as base (the base present during the course of the addition reaction); however, no isomerization occurred. This strongly indicates that the *cis* adduct is not an intermediate in the reaction (*i.e.*, losing a proton to form its anion followed by isomerization to the *trans* anion), for the results indicate that if formed it would remain and not isomerize. This is also borne out by the fact that employing various reaction modifications (*e.g.*, lower temperature, shorter time, etc.), it was never possible to isolate any *cis* adduct.

In the cyclohexyl system the *trans* isomer was the predominant product when the addition reaction was run in a dioxane solvent; the dearth of available protons afforded the *cis* anion an opportunity to isomerize to the more stable *trans* form by inhibiting the protonation step. It was not surprising therefore that in the cyclopentyl system we obtained the same more stable *trans* adduct in dioxane as we obtained in ethanol.

(5) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

(6) J. Weinstock, J. Bernardi, and R. G. Pearson, *ibid.*, **80**, 4961 (1958).

(7) (a) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961); (b) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960); (c) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, **83**, 3696 (1961); (d) H. L. Goering, D. L. Towns, and B. Dittmar, *J. Org. Chem.*, **27**, 736 (1962); (e) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 384.

Our mechanistic proposal that there is initial formation of anion IX, followed by rapid isomerization to X is based upon coulombic repulsion in the transition state, *i.e.*, the negative charges would tend to be as far from one another as possible in the developing anion. However, there is also the unlikely possibility, that in this system steric effects so outweigh coulombic effects, that reaction proceeds directly to X. But, the question of how fleeting is the existence of IX[7a-e,8] is largely academic.

Experimental[9,10]

Addition of *p*-Toluenethiol to 1-*p*-Tolylsulfonylcyclopentene in Ethanol.—A solution of 4.44 g. (20.0 mmoles) of 1-*p*-tolylsulfonylcyclopentene in 40 ml. of ethanol was placed in a 200-ml. three-necked flask equipped with a mechanical stirrer, reflux condenser and a bypass addition funnel. To this was slowly added a mixture prepared from 2.48 g. (20.0 mmoles) of *p*-toluenethiol, 0.05 g. (0.0020 g.-atom) of sodium, and 60 ml. of ethanol; the resulting solution was refluxed under nitrogen for 15 hr.

The cooled solution was evaporated to dryness, the residue added to 200 ml. of chilled 10% sodium hydroxide solution, and the mixture extracted with chloroform. The chloroform layer was dried over anhydrous magnesium sulfate and the chloroform removed under reduced pressure. The residual oil was chromatographed on a column of activated alumina using hexane as the solvent. The column was eluted with hexane-benzene mixtures to give 5.11 g. (73.8%) of adduct, m.p. 64–65°, and 0.96 g. (21.6%) of recovered olefin, m.p. 112–114°.

From the sodium hydroxide layer, 0.32 g. (12.9%) of *p*-toluenethiol was recovered.

Preparation of *trans*-1,2-Bis-*p*-tolylsulfonylcyclopentane.—To a solution of 2.40 g. (7.00 mmoles) of the above adduct, in 80 ml. of glacial acetic acid, 40 ml. of 30% hydrogen peroxide was slowly added and the solution refluxed for 1 hr. The mixture was poured into cold water and a white solid separated. The solid was collected by filtration and recrystallized several times from methanol to give an essentially quantitative yield of a white crystalline solid, m.p. 189–190°. A mixed melting point with independently synthesized *trans* disulfone showed no depression.

Anal. Calcd. for $C_{19}H_{22}O_4S_2$: C, 60.35; H, 5.85. Found: C, 60.29; H, 6.00.

Preparation of *cis*-2-*p*-Tolylmercapto-1-hydroxycyclopentane.—In a 3-l. flask cooled in an ice bath was placed 11.4 g. (0.30 mole) of sodium borohydride in 1500 ml. of ethanol. To the cooled solution 123.6 g. (0.60 mole) of 2-*p*-tolylmercaptocyclopentanone[11] in 300 ml. of ethanol was slowly added. The solution was stirred for 1 hr. at 0° and for 4 hr. at room temperature; at the end of this time it had changed from bright yellow to very pale yellow. The solution was poured into 2500 ml. of ice–water, extracted with ether, and dried over anhydrous calcium sulfate. Solvent was removed under reduced pressure and vacuum distillation gave 109.9 g. (88.0%) of a pale yellow liquid, b.p. 118–121°/0.7 mm., $n^{27}D$ 1.5731. The infrared spectrum showed no carbonyl band at 5.75 μ but a strong alcohol band at 3.0 μ.

Preparation of *cis*-2-*p*-(Tolylmercapto)cyclopentyl *p*-Toluenesulfonate.—To a solution of 109.9 g. (0.528 mole) of *cis*-2-*p*-tolymercapto-1-hydroxycyclopentane in 540 ml. of dry pyridine cooled to 0° in an ice bath, 154.3 g. (0.81 mole) of *p*-toluenesulfonyl chloride was slowly added. The solution was stirred at 0° for 12 hr., after which time 50 ml. of water was slowly added, never letting the temperature rise above 5°.

The mixture was poured into 1 l. of cold water and extracted with chloroform. The chloroform solution was washed with 3 l. of 10% sulfuric acid, then with water, saturated sodium bicarbonate, and finally with water. The solution was dried over anhydrous magnesium sulfate and solvent removed to leave an off-white solid. The solid was recrystallized several times from

(8) It is assumed in this discussion that the bonds about the carbon atom bearing the negative charge are tetrahedral: G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(9) All melting points are uncorrected.

(10) Microanalyses were performed by C. S. Yeh and V. Keblys.

(11) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 3468 (1956).

ethanol to give 94.0 g. (49.2%) of a white solid, m.p. 101.5–102.5°.

Anal. Calcd. for $C_{19}H_{22}O_3S_2$: C, 62.98; H, 6.08. Found: C, 63.07; H, 6.26.

The *cis* configuration was shown by oxidation to the known *cis*-2-(*p*-tolylsulfonyl)cyclopentyl *p*-toluenesulfonate.

In a 100-ml. round-bottom flask cooled in an ice bath was placed 2.80 g. (7.70 mmole) of *cis*-2-(*p*-tolylmercapto)cyclopentyl *p*-toluenesulfonate in 40 ml. of glacial acetic acid. To this was slowly added 20 ml. of 30% hydrogen peroxide. The solution was refluxed for 2 hr., poured into water and the solid collected by filtration. Crystallization from methanol gave a quantitative yield of *cis*-2-(*p*-tolylsulfonyl)cyclopentyl *p*-toluenesulfonate, m.p. 133–135° (lit.,[3] m.p. 134–137°), and no melting point depression when admixed with an authentic sample.

Preparation of *trans*-1,2-Bis-*p*-tolylsulfonylcyclopentane.—In a 500-ml. round-bottom flask was placed 10.0 g. (28.0 mmoles) of *cis*-2-(*p*-tolylmercapto)cyclopentyl *p*-toluenesulfonate in 150 ml. of ethanol. To this was slowly added, with stirring, a solution of 0.644 g. (0.0280 g.-atom) of sodium and 3.47 g. (28.0 mmoles) of *p*-toluenethiol in 100 ml. of ethanol. The mixture was then refluxed for 30 min. under nitrogen. The solution was evaporated to one half its original volume, water was added, and the milky solution extracted with chloroform. The chloroform solution was washed with two 50-ml. portions of chilled 5% aqueous sodium hydroxide solution and then dried over anhydrous calcium sulfate.

From the water layer and basic extracts a trace amount of *p*-toluenethiol was recovered.

The chloroform layer was evaporated to dryness to give a residual yellowish oil which was chromatographed on a column of activated alumina using pentane as solvent and eluent. There was obtained 8.01 g. (91.1%) of *trans*-1,2-bis-*p*-tolylmercaptocyclopentane $n^{25}D$ 1.6061 and 0.24 g. (2.4%) of recovered tosylate.

The dithioether was oxidized in the usual manner to give a quantitative yield of *trans*-1,2-bis-*p*-tolylsulfonylcyclopentane, m.p. 189–190°.

Attempted Preparation of *trans*-2-(*p*-Tolymercapto)cyclopentyl *p*-Toluenesulfonate.—A solution prepared from 33.0 g. (0.16 mole) of *trans*-2-*p*-tolylmercapto-1-hydroxycyclopentane[3] in 140 ml. of dry pyridine in a 500-ml. three-neck flask was cooled to 0° and 66.7 g. (0.35 mole) of *p*-toluenesulfonyl chloride was added slowly with stirring. The reaction was stirred for 4 hr. at 0° and then allowed to stand at 0° for an additional 8 hr. A white solid separated and was filtered away from the now brownish liquid. The solid was washed free of pyridine with dry ether. It was dissolved in water and treated with aqueous sodium hydroxide whereupon the odor of pyridine became quite evident. Evaporation of the aqueous solution to dryness gave a solid that was shown to be sodium *p*-toluenesulfonate.

The brownish liquid was poured into a liter of cold water, extracted with chloroform, washed with 1500 cc. of 10% sulfuric acid, then with water, a saturated sodium bicarbonate solution, and finally with water again. The solution was dried over anhydrous calcium sulfate and solvent was removed under reduced pressure. Distillation under vacuum gave 24.7 g. (68.1%) of a clear liquid, *trans*-2-*p*-tolylmercapto-1-chlorocyclopentane, b.p. 112–113°/0.1 mm., $n^{25}D$, 1.5711 (lit.,[12] b.p. 122–123°/0.1 mm., $n^{25}D$, 1.5711).

The liquid was slowly added to a cold solution of excess perbenzoic acid[13] in chloroform and allowed to stand at 0° for 24 hr. The solution was washed several times with 100-ml. portions of 10% aqueous sodium hydroxide and dried over anhydrous calcium sulfate. Solvent was removed under reduced pressure to give an oil which was chromatographed on a column of acid-washed alumina using pentane as solvent and eluting with pentane–ether mixtures. An almost quantitative yield of *trans*-2-*p*-tolylsulfonyl-1-chlorocyclopentane was obtained, m.p. 47–49° (lit.,[12] m.p. 46.4–48.4°), and its infrared spectrum was compatible with the assigned structure.

A Study of the Reaction between Sodium *p*-Toluenethiolate and *p*-Tolymercaptoethene.—In a 500-ml. round-bottom flask was placed 7.92 g. (0.0528 mole) of *p*-tolylmercaptoethene in 150 ml. of ethanol. To this was slowly added, with stirring, a solution of 1.21 g. (0.0528 g.-atom) of sodium and 6.55 g. (52.8 mmoles) of *p*-toluenethiol in 100 ml. of ethanol. The solution was then refluxed under nitrogen for 11 hr., allowed to cool, and 300 ml. of water added, and the solution was extracted with chloroform. The chloroform solution was washed with 100 ml. of cold 10% aqueous sodium hydroxide and dried over anhydrous calcium sulfate.

From the water layer and basic extracts, 6.25 g. (95.2%) of *p*-toluenethiol was recovered.

The chloroform layer, upon evaporation of solvent and distillation under reduced pressure, gave 7.23 g. (91.3%) of recovered *p*-tolylmercaptoethene.

Preparation of *cis*-2-Phenylsulfonyl-1-methylcyclopentane.—In a 1-l. three-neck flask was placed 155.2 g. (1.9 moles) of 1-methylcyclopentene,[14] 209 g. (1.9 moles) of benzenethiol, and few crystals of 2,2′-azobis(2-methylpropionitrile). The solution was stirred while refluxing for 24 hr. Distillation under reduced pressure gave 57.3 g. (36.9%) of recovered 1-methylcyclopentene, 113.7 g. (54.4%) of recovered benzenethiol, and 135.1 g. (80.9% yield) of a clear liquid b.p. 125–130°/7 mm. believed to be 2-*p*-tolylmercapto-1-methylcyclopentane.

The clear liquid was dissolved in 704 g. of glacial acetic acid, cooled in an ice bath, and 357 ml. of 30% hydrogen peroxide was slowly added. The solution was refluxed for 2 hr. and then poured over crushed ice. The white solid that separated was collected by filtration and recrystallized several times from methanol to give 68.6 g. (43.6%) of *cis*-2-phenylsulfonyl-1-methylcyclopentane, m.p. 57–58°.

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.29; H, 7.14; Found: C, 64.02; H, 7.40.

Preparation of *trans*-2-Phenylsulfonyl-1-methylcyclopentane.—In a 200-ml. round-bottom flask was placed a solution of 3.27 g. (17.0 mmole) a *cis*-2-phenylsulfonyl-1-methylcyclopentane and 0.391 g. (0.0170 g.-atom) of sodium in 100 ml. of *n*-propyl alcohol. The solution was refluxed for 44 hr., poured over crushed ice, acidified with concentrated hydrochloric acid and the solid that separated was collected by filtration. It was crystallized from methanol to give a quantitative yield of a white solid, m.p. 36.5–37.5°. The solid had an infrared spectrum identical to that of *cis*-2-phenylsulfonyl-1-methylcyclopentane, but when the two solids were mixed they formed an oil.

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.29; H, 7.14. Found: C, 64.02; H, 7.40.

Procedure for the Determination of Relative Rates of Isomerization.—*cis*-2-Phenylsulfonyl-1-methylcyclohexane[15] (10.5 g., 45.0 mmoles) was added to a solution prepared from 1.01 g. (0.045 g.-atom) of sodium in 500 ml. of ethanol, and the resulting mixture was immediately heated to reflux. Aliquot portions of 10 ml. were extracted hourly (the length of time between samplings was increased when the reaction was seen to be relatively slow), neutralized with glacial acetic acid and evaporated to a volume of 3 ml. The samples were analyzed with an F and M Scientific Corp. gas chromatograph, Model 500, employing a silicone oil no. 550 column on a support of Chromosorb. The sample size injected was 5 μl. using an attenuation of 4, bridge power of 200 ma., column temperature of 225°, and block temperature of 325°.

We determined, employing known mixtures of *cis*- and *trans*-2-phenylsulfonyl-1-methylcyclohexane, that this method of analysis was accurate to ±2%.

With a solution prepared by adding 10.0 g. (45.0 mmoles) of *cis*-2-phenylsulfonyl-1-methylcyclopentane to 1.01 g. (0.045 g.-atom) of sodium in 500 ml. of ethanol a similar method of analysis was employed, differing only in that a silicone grease on Chromosorb column with bridge power of 165 ma. and a column temperature of 185° was used.

Attempted Isomerization of *cis*-2-Phenylsulfonyl-1-methylcyclopentane with *p*-Toluenethiolate.—To a refluxing solution of 5.54. (45.0 mmoles) of *p*-toluenethiol and 0.10 g. (0.0043 g.-atom) of sodium in 300 ml. of ethanol, 10.0 g. (45.0 mmoles) of *cis*-2-phenylsulfonyl-1-methylcyclopentane in 200 ml. of ethanol was added. Aliquot portions were removed periodically and analyzed *via* the method described above. At the end of 24 hr. no isomerization had occurred.

Addition of *p*-Toluenethiol to 1-*p*-Tolylsulfonylcyclopentene in Dioxane.—In a 200-ml. round-bottom flask equipped with a reflux condenser, mechanical stirrer, and a bypass addition funnel was placed 4.14 g. (19.0 mmoles) of 1-*p*-tolylsulfonylcyclopentene and 0.10 g. (1.9 mmoles) of sodium methoxide in 40 ml. of pure

(12) H. L. Goering, D. I. Relyen, and K. L. Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957).

(13) *Cf.* G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

(14) A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

(15) F. G. Bordwell and W. A. Hewitt, *J. Am. Chem. Soc.*, **79**, 3493 (1957).

dioxane. As the solution was stirred, 2.36 g. (19.0 mmoles) of *p*-toluenethiol and 0.87 g. (19.0 mmoles) of ethanol in 60 ml. of pure dioxane was slowly added. The solution was refluxed for 14 hr. and then worked up in the previously described manner to give 5.59 g. (86.0%) of *trans*-2-*p*-tolylmercapto-1-*p*-tolylsulfonylcyclopentane and 0.28 g. (6.8%) of recovered olefin.

Modified Addition of *p*-Toluenethiol to 1-*p*-Tolylsulfonylcyclopentene. (a) **One Hour.**—The same reaction as previously described was repeated except that it was only allowed to reflux for 1 hr. At the end of this time no reaction had occurred.

(b) **Four Hours.**—In this case the reaction mixture was refluxed for 4 hr. Reaction had occurred to an extent almost equal to that after 14 hr. but only starting material and *trans* adduct were found.

(c) **Fifty Hours at Room Temperature.**—The reaction was stirred for 50 hr. at room temperature. At the end of this period it was shown that no reaction had occurred.

Acknowledgment.—The authors would like to thank Mr. Gunars Vitolins[16] for his exploratory work on this problem. We are pleased to acknowledge the financial support of the American Cyanamid Co. and the Air Force Office of Scientific Research, Project no. AF-49 (638)-531.

(16) G. Vitolins, M.S. thesis, Purdue University, 1959.

Tetracyclic Dienes. II. Acid-catalyzed Rearrangement of 1,4,4a,5,8,8a-Hexahydro-*exo*-*endo*-1,4,5,8-dimethanonaphthalene (I)[1]

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Received September 24, 1962

The addition of formic acid to I produces, through a series of bridged ion intermediates, the bird-cage hydrocarbon IV, both a saturated and unsaturated monoformate fraction, and a saturated diformate fraction. The saturated monoformate portion contains the formate esters of the half-cage alcohol II—OH and the bridged alcohol V—OH. Neither of the formates III—OCOH or VI—OCOH were produced, although these isomers might be predicted to result from the postulated bridged ion intermediates. Two unsaturated alcohols, VII—OH and XIV—OH, were obtained from the unsaturated formate fraction. The saturated diformate fraction possesses the *exo*-*exo* carbon skeleton (XXII) as a result of the addition of formic acid to VII or XIV—OCOH.

The synthesis of 1,4,4a,5,8,8a-hexahydro-*exo*-*endo*-1,4,5,8-dimethanonaphthalene (I)[2] afforded an unusual diene system which reacted readily with ionic reagents to produce rearranged products. Titration of I with bromine showed that only 1.1 moles of bromine was absorbed, yet 80% of the product was saturated dibromide.[3] The addition of formic acid to I with boron fluoride catalysis was a rapid, exothermic reaction which proceeded smoothly in the absence of a solvent to yield both saturated and unsaturated monoformate esters and a saturated diformate ester.

The addition of formic acid was chosen to illustrate the complex rearrangement pattern of I because protonation of the double bond could lead to the bridged carbonium ions shown in Figure 1. These carbonium ion intermediates have been postulated to explain the products formed from the solvolysis of compounds containing this ring system.[4] In addition, saponification of the formate esters should yield the alcohols reported in connection with these solvolysis experiments.

Discussion

When a threefold excess of formic acid was added to I, the monoformate ester fraction, 35–50% of the total yield of product, consisted of 55–75% saturated monoformate and 45–20% unsaturated monoformate. The remainder of the reaction product consisted of a diformate ester (40–55%) and a saturated hydrocarbon (2%). When a formic acid to olefin molar ratio of 4:3 was employed, the monoformate portion 70–80% was formed at the expense of diformate (15%). The unsaturated monoformates were separated from the saturated monoformates by using silver nitrate to complex the unsaturated portion.[5]

Protonation of Bond *a*.—Because of the dissymmetry of the molecule, attack of the proton at either bond would not lead to equivalent carbonium ion species, and two different sets of products would be formed. Attack of the proton to the *exo* side of bond *a* will produce a bridged ion. Shift of electrons toward the positive site generated causes further delocalization of the charge to produce the bridged carbonium ion A. Simple Wagner–Meerwein shifts can produce bridged ion B which shows the interaction possible between the *pi* electrons of the double bond *b* with the positive charge generated by the added proton. Bond *b* entering the carbonium ion scheme then opens the way for formation of the unusual bridged ring systems encountered in the reaction mixture.

Ion B can then produce a series of nonclassical ions. Further rearrangement can occur to produce ions C, D, or E, or attack by the formate anion can produce either the half-cage ester, II—OCOH, or the skewed-cage ester, III—OCOH. Loss of a proton from ion C affords the bird-cage hydrocarbon (IV) which was isolated in small yields (2%) from the reaction mixture.

Rearrangement of ion B to ion D and attack by formate ion produces V—OCOH. Basic hydrolysis of the formate ester afforded an alcohol with properties identical to those of alcohol V of known structure.[4,6]

It is clear that ion D and III—OH are related because of the similar skewed arrangement of the bridges; how-

(1) (a) This research was supported by a grant (NSF G10472) from the National Science Foundation, whose assistance is gratefully acknowledged. (b) This paper taken in part from the Ph.D. thesis of P.R.K., University of Iowa, June, 1962.

(2) First paper in this series: J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **81**, 4273 (1959).

(3) Further work on these bromides was discontinued in view of the potential health hazard.

(4) (a) L. deVries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960). (b) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.*, 405, 590 (1960). (c) S. Winstein, *Experientia Suppl.*, **II**, 137 (1955).

(5) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(6) We wish to thank Professor S. Winstein for supplying us with samples of II—OH and V—OH.