[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

The Dimer of 9,10-Phenanthraquinodimethane. An Attempted Synthesis of the Monomer through Carbonium Ion Intermediates

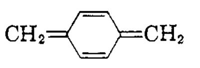
BY PETE D. GARDNER AND HOSSEIN SARRAFIZADEH R.

RECEIVED SEPTEMBER 10, 1959

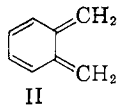
The solvolysis of the 9-halomethyl-10-methylphenanthrenes in ether was effected by silver ion. From the bromo compound there was obtained a mixture of 9,10-dimethylphenanthrene and 9-ethoxymethyl-10-methylphenanthrene. The iodo compound and the chloro compound both gave di-10-methyl-9-phenanthrylmethyl ether as the only isolable product. 10-Methyl-9-phenanthrylmethyltrimethylammonium hydroxide decomposed thermally to give the Diels–Alder dimer of 9,10-phenanthraquinodimethane. The theoretical implications of this as well as the probable mechanism of the solvolysis reactions are discussed.

Although the quinodimethane system has occupied the interests of organic chemists for many years, the synthesis of only one simple member of this class, *p*-xylylene (*p*-quinodimethane, I), has been reported.[1,2] Several reactions which yield I or the *o*-isomer II as transient intermediates are recorded.[3-6]

Much of the interest in this field has undoubtedly come as a result of theoretical work which suggests that the resonance energy (38 kcal.) of I is comparable with that of benzene.[7] Calculations by Coulson and co-workers[7] indicate that the free valence of terminal carbon atoms is very high and that there is little difference in this value between the singlet (ground) and triplet states. Thus, in reactivity I approximates the diradical.

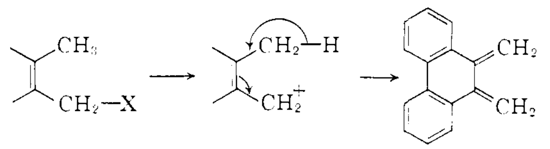


I



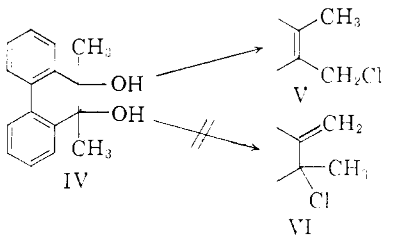
II

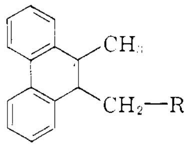
In searching for a method of synthesis of *o*-quinodimethanes, we have examined the behavior of carbonium ion intermediates which should in principle be capable of yielding them by loss of a proton. Thus, the generation of such an ion in an "inert" solvent at low concentration could result in the desired transformation, *viz.*



III

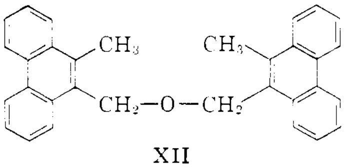
The phenanthrene system III was chosen as the initial objective to minimize the energy difference between the quinodimethane and the normal aromatic parent. The desired starting material, 9-chloromethyl-10-methylphenanthrene (V), was found to be available as the incorrectly formulated product (VI) of the reaction between 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (IV) and phosphorus pentachloride–phosphorus oxychloride.[8] The use of thionyl chloride in ether proved to be more satisfactory. The analogous bromo compound VII was prepared using phosphorus tribromide. The reaction of either V or VII with sodium iodide readily gave the iodo compound VIII. The reactions of these compounds are those characteristics of benzyl-type halides; solvolysis in methanolic potassium hydroxide solution gave the methyl ether IX and reaction with silver nitrate (ether suspension) afforded the nitrate ester X of the parent alcohol.





	R		R
V,	Cl,	XI,	OEt
VII,	Br	XIII,	OH
VIII,	I	XIV,	OAc
IX,	OCH_3	XV,	H
X,	ONO_2	XVI;	$N(CH_3)_3{}^+Br^-$

Ether was initially chosen as a solvent sufficiently inert to give the solvated carbonoium ion time to eject a proton.[9] Several oxonium ions of this type have been prepared and, although reactive, they appear to be stable.[10]



XII

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[1] M. Szwarc, *Disc. Faraday Soc.*, **2**, 46 (1947).

[2] L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

[3] M. Cava and A. Deana, Abstracts of Papers of American Chemical Society Meeting, Chicago, Ill., September, 1958, p. 7-P.

[4] H. W. Bersch, *Angew. Chem.*, **67**, 237 (1957).

[5] F. S. Fawcett, U. S. Patent 2,757,146; *C. A.*, **50**, 14268 (1956).

[6] F. G. Mann and F. H. C. Stewart, *Chemistry & Industry*, 1153 (1953).

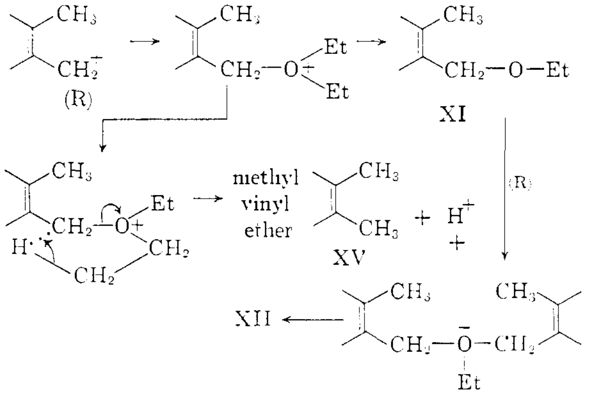
[7] Namiot, Dyatkina and Syrkin, *Compt. rend. U.S.S.R.*, **48**, 233 (1945); C. A. Coulson, D. P. Craig, A. Maccoll and A. Pullman, *Disc. Faraday Soc.*, **2**, 36 (1947).

[8] T. Zincke and W. Tropp, *Ann.*, **362**, 242 (1908). At the time, of course, these authors had no reason to suspect a rearrangement product.

[9] S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957). An interesting example of this concept is the formation of tropylium ion in the mass spectrometer. The conditions here are nearly ideal, of course, as the ion is not solvated and has no immediate environment; intermolecular processes of all types are negated.

[10] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

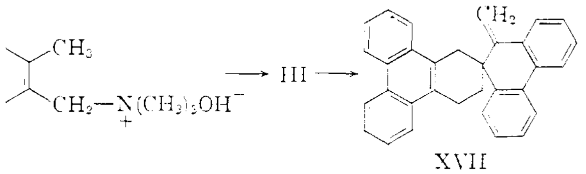
The reactions of all three halo compounds (V, VII and VIII) with anhydrous silver perchlorate in ether were studied. From the chloro or iodo compound there was obtained, di-10-methyl-9-phenathrylmethyl ether (XII). It is probable that traces of the ethyl ether XI remained in the mother liquor which was not thoroughly examined. An independent synthesis of XII was effected by the reaction of 10-methyl-9-phenanthrylcarbinol (XIII), derived from VII *via* the acetoxy compound XIV and the bromo compound VII. The reaction of the bromo compound under essentially identical conditions gave mainly 9,10-dimethylphenanthrene (XV) accompanied by XI in smaller amount. The formation of XV, amounting to the displacement of bromide ion by hydride ion,[11] is best interpreted as originating in the oxonium ion derived from the original carbonium ion and an ether molecule. The entire sequence is pictured below. It is obvious that XV might just as well have formed from the oxonium ion derived from XI by the same mechanism. An authentic sample of XV was prepared for comparison by lithium aluminum hydride reduction of the bromo compound VII.



An especially curious feature of these reactions is that the chloro and iodo compounds invariably gave XII, which could not be obtained from the bromo compound, while the last consistently gave only the dimethylphenanthrene. This effect of halogen is not yet understood. The substitution of benzene for ether in this reaction gave only polymeric material.

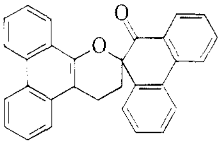
The simpler molecules, benzyl bromide and chloride, have never been studied in ether as a solvent although their behavior in nitromethane containing silver perchlorate has been examined[12] and no evidence for hydride abstraction is recorded. This reaction was studied briefly and found to give a colorless, mobile liquid which is believed to be the perchlorate salt of $C_6H_5CH_2O(CH_2CH_3)_2^+$. Upon gentle warming *in vacuo*, ether was evolved and only polymeric material remained; no evidence for the formation of toluene could be obtained although a small amount of benzaldehyde was isolated as a derivative.

The carbonium ion approach having failed, we next examined the behavior of the quaternary salt, (10-methyl-9-phenanthrylmethyltrimethylammonium bromide (XVI) E_2 elimination conditions).[13] Treatment of XVI with wet silver oxide gave a colorless solution of the quaternary hydroxide. Evaporation of this solution below 80° gave colorless solid which was essentially nitrogen-free. This residue proved to be a mixture of polymeric material and the dimer of 9,10-phenanthraquinodimethane (III) and is formulated as XVII.

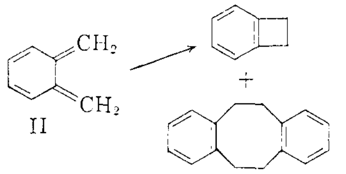


XVII

This substance decolorized bromine solution and, upon hydrogenation, absorbed 0.94 mole equivalent of hydrogen. The exocyclic terminal double bond absorbed in the infrared at 11.1 μ, absorption which disappeared upon hydrogenation to the dihydro compound. The ultraviolet absorption spectrum was quite similar to that of the analogous quinone methide dimer (XVIII)[14] while those of the corresponding dihydro compounds were almost identical. The spectrum of the dihydro compound had absorption in the 320–360 mμ region with extinction coefficients characteristic of a single phenanthrene nucleus. This dimerization, formally of the Diels–Alder type, differs from the course taken by *o*-quinodimethane itself, *viz.*,[3]



XVIII



Compound II, like its *p*-isomer, undoubtedly has a very high free valence at the terminal carbon atoms. The activation energy for bond formation (dimerization or polymerization) must therefore be very low. Dimerization of the phenanthrene compound, on the other hand, with a lower free valence at the terminal carbon atoms would appear to require the localizing assistance offered in complexation; this merely constitutes a reaction path having a lower activation energy.

Experimental[15]

9,10-Dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (IV).—The following procedure was found to be more satisfactory than that reported.[8]

To a cold (0°) solution of methylmagnesium iodide, prepared from 204 g. of methyl iodide and 34.5 g. of magnesium in 700 ml. of anhydrous ether, was added 100 g. of

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[11] M. Gomberg, THIS JOURNAL, **35**, 200 (1913), describes the similar behavior of triphenylmethyl chloride in ethereal zinc chloride solution.

[12] H. Burton and P. F. G. Praill, *Chemistry & Industry*, 939 (1951).

[13] This approach was successful in the preparation of *p*-quinodimethane as a transient species.[5]

[14] P. D. Gardner and H. Sarrafizadeh R., *J. Org. Chem.*, **25**, 641 (1960).

[15] Melting points are corrected. Ultraviolet spectra were obtained using 95% ethanol as solvent. Infrared spectra were determined either in chloroform solution or potassium bromide wafers. Ultraviolet spectra of all compounds are consistent with formulations presented but values are not given except where they bear strongly on the assignment of structure. Phenanthrene derivatives possessing the 9,10-double bond exhibit specific absorption in the 320–360 mμ region which may be relied upon for both qualitative and quantitative application.

purified, finely powdered 9,10-phenanthraquinone[16] in several portions. The mixture was heated under reflux while stirring for 4 hr., cooled again to 0° and treated cautiously with dilute sulfuric acid. Two large-volume extractions with ether sufficed to obtain all organic material from the aqueous phase. The combined extracts were washed with four portions of saturated aqueous sodium bisulfite and then with water followed by drying over anhydrous sodium sulfate. Evaporation of solvent and recrystallization from benzene or ethyl acetate–petroleum ether gave 82.6 g. (70%) of diol IV, m.p. 163–164° (lit.[8] 164°). Acidification of the bisulfite washes regenerated unreacted phenanthraquinone from its complex in a high state of purity.

9-Chloromethyl-10-methylphenanthrene (V).—The following was superior to the reported procedure using phosphorus pentachloride.[8]

To a suspension of 50.0 g. of IV in 300 ml. of anhydrous ether was added 94.2 g. of thionyl chloride, whereupon the mixture became homogeneous. It was stirred at 30° for 10 hr. and then concentrated at an aspirator (magnetic stirring). The remaining mixture of liquid and solid was dissolved in ethyl acetate. This solution was boiled on a steam cone and its volume maintained by slow addition of petroleum ether. When nearly all of the ethyl acetate had been replaced in this way, the solution was cooled and the solid separated. Recrystallization from benzene–petroleum ether gave 23.1 g. (46%) of colorless V, m.p. 155–156° (lit.[8] 155°). The mother liquor contained mainly a dichloro compound. Evaporation of solvent followed by distillation (hydrogen chloride evolution!) gave a fraction boiling 170–200° (0.3 mm.). Crystallization of this material as described gave an additional 10.8 g. of V having the same m.p. (total yield 68%). This substance gave correct analytical data. Its ultraviolet absorption spectrum had maxima in the 320–360 mμ region characteristic of phenanthrene derivatives.

9-Bromomethyl-10-methylphenanthrene (VII).—To a suspension of 4.00 g. of IV in 25 ml. of anhydrous ether was added 13.5 g. of phosphorus tribromide. The mixture was stirred at 30° for 15 hr. Excess reagent was hydrolyzed by the cautious addition of water and the product isolated in part by filtration and the remainder by ether extraction of the filtrate. The combined product amounted to 3.1 g. of solid having a melting range. It was dissolved in a solution of 30 ml. of benzene and 170 ml. of petroleum ether and passed through a column of alumina (120 g.). Evaporation of the eluate to dryness and recrystallization from ethyl acetate–petroleum ether afforded 1.1 g. (28%) of colorless VII, m.p. 166–167°. Ultraviolet spectra showed 320–360 mμ absorption characteristic of phenanthrenes.

Anal. Calcd. for $C_{16}H_{13}Br$: C, 67.38; H, 4.59. Found: C, 67.41; H, 4.72.

Further elution of the alumina column with more polar solvents gave several other substances which were not investigated further.

9-Methoxymethyl-10-methylphenanthrene (IX).—One-half gram of the bromo compound VII was heated under reflux in 50 ml. of 2% methanolic potassium hydroxide. The crude product was isolated by the addition of water and extraction with ether. Recrystallization from ethyl acetate–petroleum ether afforded 0.36 g. (87%) of pure IX, m.p. 113–114°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.18; H, 6.70.

9-Iodomethyl-10-methylphenanthrene (VIII).—To an acetone (100 ml.) solution of 2.0 g. of VII was added 3.3 g. of sodium iodide. After 3 hr. of heating under reflux, the suspension was diluted with water. The resulting solid was isolated by suction filtration and recrystallized from ethyl acetate–petroleum ether to give 2.1 g. (89%) of VIII as pale yellow solid, m.p. 157–158° dec.

Anal. Calcd. for $C_{16}H_{13}I$: C, 57.85; H, 3.94; I, 38.2. Found: C, 57.73; H, 3.70; I, 38.3.

This substance was obtained from V in about the same yield when this procedure was used.

10-Methyl-9-phenanthrylmethyl Nitrate (X).—An ethereal solution (50 ml.) of 1.50 g. of the chloro compound V was treated with 2.0 g. of finely powdered silver nitrate. The mixture was stirred at 30° for 18 hr., filtered and washed with several portions of water. Processing of this solution in the usual manner gave 1.10 g. (68%) of X as colorless solid, m.p. 131.5–132.0°. Strong infrared absorption at 7.9 μ is consistent with the nitrate formulation.

Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.25. Found: C, 71.87; H, 5.30; N, 5.25.

9-Ethoxymethyl-10-methylphenanthrene (XI).—One gram of bromo compound VII was heated under reflux in a solution prepared by dissolving 0.5 g. of sodium in 25 ml. of absolute ethanol. After 3 hr., the suspension was concentrated to a small volume at an aspirator and diluted with water. Crystallization of the resulting solid from aqueous ethanol yielded 0.60 g. (69%) of colorless solid, m.p. 91–92°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.40; H, 7.13.

The picrate, m.p. 112–114° after crystallization from ethanol, was obtained as orange needles.

Anal. Calcd. for $C_{24}H_{21}N_3O_8$: C, 60.12; H, 4.42; N, 8.76. Found: C, 60.05; H, 4.47; H, 9.23.

10-Methyl-9-phenanthrylcarbinol (XIII).—A solution made of 2.50 g. of VII and 3.0 g. of sodium acetate in 90 ml. of acetic acid was heated under reflux for 4 hr. and then poured into 200 ml. of water. Cooling to 0° and filtration of the resulting solid gave 2.20 g. (95%) of the acetate XIV, m.p. 115–116°. This substance was not characterized as such but was instead hydrolyzed to the alcohol by heating 2.00 g. under reflux in 30 ml. of methanolic potassium hydroxide. After 10 hr., the solution was cooled and poured into 100 ml. of cold water. The resulting solid was collected by suction filtration and recrystallized from benzene–petroleum ether to give 1.30 g. (78%) of XIII, m.p. 170–171°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.34; H, 6.34. Found: C, 86.53; H, 6.23.

9,10-Dimethylphenanthrene (XV) (**by Reduction of** VII).—To a solution of 2.00 g. of VII in 40 ml. of dry tetrahydrofuran was added 0.25 g. of lithium aluminum hydride. This suspension was heated under reflux for 10 hr., cooled and treated cautiously with water followed by dilute hydrochloric acid. Isolation by ether extraction, as described previously for other reaction products, afforded the crude material as 1.10 g. (77%) of colorless solid, m.p. 150–152°. Repeated crystallization from ethanol gave pure XV as colorless needles, m.p. 147–148° (lit.[17] 147.5–148.5°.)

10-Methyl-9-phenanthrylmethyltrimethylammonium Bromide (XVI).—Through a solution of 1.04 g. of VII in 50 ml. of benzene was bubbled dry gaseous trimethylamine (prepared by dropping 25% aqueous solution onto a massive excess of solid sodium hydroxide). Formation of the quaternary salt was complete in a few minutes. The mixture was diluted with ether and the solid collected by suction filtration. Two crystallizations from ethanol gave 1.00 g. (79%) of colorless solid, m.p. 223–225° dec.

Anal. Calcd. for $C_{19}H_{22}NBr$: C, 66.28; H, 6.44; N, 4.07. Found: C, 66.07; H, 6.49; N, 3.75.

Reaction of **9-Chloromethyl-10-methylphenanthrene** (V) **with Ethereal Silver Perchlorate.**—To a solution of 8.00 g. of V in 400 ml. of anhydrous ether was added 12.0 g. of anhydrous silver perchlorate.[18] The deposition of silver chloride began immediately. The mixture was stirred at 30° for 1 hr. (an 11-hr. reaction time gave identical results). Following filtration, the solution was washed with distilled water, aqueous sodium chloride solution and again with water. The colorless ethereal solution was dried (sodium sulfate) and concentrated to dryness. The residue was recrystallized from benzene to give 3.15 g. (44%) of di-10-methyl-9-phenanthrylmethyl ether (XII), m.p. 201–202°.

Reaction of the iodo compound VIII under these conditions gave XII in virtually the same yield.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.10; H, 6.14; mol. wt., 427. Found: C, 89.57; H, 6.23; mol. wt., 394 (cryoscopic in benzil).

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[16] H. W. Underwood, Jr., and E. L. Kochmann, THIS JOURNAL, **46**, 2069 (1924).

[17] E. J. Greenhow and D. McNeil, *J. Chem. Soc.*, 3204 (1956). Earlier published values range from 139 to 146°.

[18] G. Frederick Smith Chemical Co., Columbus, Ohio.

An independent synthesis of this substance (XII) was effected as follows. To a solution of 5 ml. of methanol, 45 ml. of xylene and 1.00 g. of carbinol XIII was added 0.11 g. of sodium. After the metal had reacted, the solution was concentrated at atmospheric pressure to a volume of 25 ml. By this time, the sodium salt of XIII had precipitated. The chloro compound (V, 1.09 g.) was added and the mixture was heated under reflux for 7 hr. Solid material was removed by filtration of the hot solution. Concentration of the filtrate to dryness and crystallization of the residue from benzene (cooling only to 25°) gave 0.71 g. (37%) of XII, m.p. 199–201°. This substance did not depress the melting point of that described above. Their infrared spectra were identical.

Reaction of 9-Bromomethyl-10-methylphenanthrene (VII) with Ethereal Silver Perchlorate.—This reaction was conducted in the manner described above for the chloro compound. From 2.00 g. of VII, 4.0 g. of silver perchlorate and 100 ml. of anhydrous ether, there was obtained a solid melting over the range 94–122°. Chromatography on alumina (120 g.) using benzene and petroleum ether for elution afforded 0.70 g. (48%) of 9,10-dimethylphenanthrene (XV). The unusual nature of this reaction prompted a more rigorous proof of identity than the usual mixture melting point. This substance has an ultraviolet spectrum identical with that of XV obtained as described above. The n.m.r. spectrum indicated that all non-aromatic hydrogen atoms are of the same type. Its molecular weight, obtained from the mass spectrum, was 206 (calculated 206).

Further washing of the alumina column with acetone gave 0.30 g. (17%) of material having m.p. 91–92°. This was identified as the ethyl ether XI by mixture melting point and by comparison of infrared and ultraviolet spectra with those of a sample prepared as described above. The reaction between VII and silver perchlorate in benzene under conditions similar to those used in the ether experiment gave a colorless solid (m.p. 190–210°) which appeared to be polymeric. Careful chromatography on alumina did not shorten this melting range.

Dimer of 9,10-Phenanthraquinodimethane (XVII).—One gram of the quaternary ammonium bromide XVI was dissolved in 20 ml. of a suspension of freshly prepared silver oxide in distilled water. The mixture was stirred at 30° for 4 hr. and then filtered. The colorless filtrate was concentrated to dryness at an aspirator (oil-bath, magnetic stirring). The bath temperature did not exceed 80° during this process. The insolubility of the colorless solid residue in water suggested that elimination of trimethylamine had taken place during the concentration process. The solid was boiled with several portions of ethanol and the combined extracts were then concentrated at atmospheric pressure until crystallization began. Well formed crystals of XVII obtained in this way amounted to 0.11 g. (19%), m.p. 252–253°. Recrystallization was best effected by dissolving the material in benzene, in which it is readily soluble, and evaporating on a hot-plate while replacing evaporative loss with ethanol. When crystallization started, the temperature was lowered to 0° and the product collected by suction filtration, m.p. 252–253°.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.84; H, 6.22.

This substance absorbs rather strongly in the infrared at 11.1 μ. Its ultraviolet spectrum (95% ethanol) exhibited high intensity maxima at 245, 256 and 272 mμ with extinction coefficients ($\times 10^4$) 2.75, 2.90 and 2.75, respectively. It almost instantly decolorized a dilute solution of bromine in chloroform.

A 0.290-g. sample of XVII absorbed 15.7 ml. (94% for one double bond) of hydrogen when shaken with palladium–charcoal suspended in ethanol under one atmosphere of hydrogen. The dihydro compound was obtained in an amorphous state, m.p. 140–160°, despite repeated attempts at crystallization. After several reprecipitations (heating and cooling) from ethanol it was analyzed.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38; mol. wt., 410. Found: C, 93.46; H, 6.15; mol. wt., 422 (cryoscopic in benzil).

The infrared spectrum had no absorption in the 11.1 μ region. The ultraviolet spectrum (95% ethanol) exhibited high intensity absorption at 225, 256, 271, 287 and 299 mμ with ε-values ($\times 10^4$) 4.12, 6.56, 3.04, 1.57 and 1.47, respectively. Principal low intensity absorption[14] at 319, 327, 335, 343 and 351 mμ had ε-values ($\times 10^2$) of 3.59, 3.10, 5.16, 2.83 and 5.66, respectively. The corresponding low intensity absorption of 9,10-dimethylphenanthrene (XV) is found at 321, 337 and 353 mμ with ε-values ($\times 10^2$) of 3.57, 4.92 and 4.48, respectively. The similarity in low intensity extinction coefficients indicates XVII to have only one intact phenanthrene nucleus.

Acknowledgment.—The authors are indebted to The Robert A. Welch Foundation for the financial support of this study. We wish also to express our appreciation for the kindness shown by Dr. M. J. O'Neal and his associates at the Houston Research Laboratory of the Shell Oil Co. for n.m.r. data and mass spectra and for their interpretations.

AUSTIN 12, TEX.

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

The Effect of Conformation on Reactivity. II. Rates of Acetolysis of Isomeric Cholestanyl *p*-Toluenesulfonates

BY SHINYA NISHIDA

RECEIVED JANUARY 20, 1960

The rigid molecular structure of the isomeric cholestanols provides a valuable tool for study of the effect of conformation on reactivity. With this objective in mind, the isomeric *p*-toluenesulfonates of cholestan-2α, 2β-, 3α-, 3β- and 6α-ol were synthesized and their rates of acetolysis measured. The observed sequence of rates is $3\beta \approx 6\alpha < 2\alpha < 3\alpha \ll 2\beta$. The above rate sequence is explicable in terms of the 1,3-diaxial interactions previously utilized to account for the variation in rates in the *trans*-decalyl tosylates with related fixed conformations.

It is a problem of considerable importance to attain a quantitative understanding of the effect of conformation in cyclohexane derivatives on their reactivities.[1] Unfortunately, in simple cyclohexane derivatives the problem is complicated by the ready interconversion of axial and equatorial bonds in these molecules.[2-4]

One attempt to circumvent this difficulty is based on the use of *t*-butylcyclohexyl derivatives.[5] An alternative approach to this problem is to utilize a system with a fixed conformation, such as the *trans*-decalyl tosylates.[1] The value of this

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(1) I. Moritani, S. Nishida and M. Murakami, THIS JOURNAL, **81**, 3420 (1959).

(2) K. Kojima and T. Yoshino, *ibid.*, **75**, 166 (1953).

(3) M. Larnaudie, *Compt. rend.*, **236**, 909 (1953).

(4) For a detailed discussion of this field see W. Hückel, *Ann.*, **624**, 142 (1959).

(5) S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).