days. The solution was poured into ice-water, and the precipitate of crude tosylate was collected. Recrystallization from ether-petroleum ether (b.p.  $60-80^{\circ}$ ) gave 3,5-dimethyl-1,4-dihydrobenzyl tosylate (59.2 g.), m.p. 53.5-54°.

Anal. Calcd. for  $C_{16}H_{20}O_{3}S\colon$  C, 65.78; H, 6.90. Found: C, 65.92; H, 7.06.

1,4-Dihydrobenzyl Tosylate.—1,4-Dihydrobenzyl tosylate was prepared as previously described<sup>12</sup> except that the crude tosylate was purified by crystallization from ether-petroleum ether (b.p.  $40-60^{\circ}$ ) at  $-50^{\circ}$ .<sup>33</sup>

(33) 1,4-Dihydrobenzyl tosylate was not obtained in crystalline form in the earlier work.  $^{12}$ 

Anal. Calcd. for  $C_{14}H_{16}O_{3}S$ : C, 63.60; H, 6.10. Found: C, 63.56; H, 6.07.

Rate Measurements.—The tosylates were solvolyzed as 0.03 M solutions in acetic acid 0.06 M in sodium acetate. The consumption of sodium acetate was followed by titration with perchloric acid in acetic acid as previously described<sup>34</sup> using the ampoule technique.<sup>34</sup> The sodium acetate solution was prepared by refluxing sodium carbonate (6.36 g.) in glacial acetic acid (1900 ml.) and acetic anhydride (100 ml.) for 2 hours. Temperatures were measured with a thermometer calibrated by the National Bureau of Standards.

(34) S. Winstein, C. Hanson and E. Grunwald, J. Am. Chem. Soc., 70, 812 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON, EUGENE, ORE.]

## The Mechanism of the Prins Reaction. II. The Solvolysis of trans-2-Hydroxymethylcyclohexyl Brosylate and trans-2-Acetoxymethylcyclohexyl Brosylate<sup>1</sup>

### By Lloyd J. Dolby, Claire N. Lieske, David R. Rosencrantz and Maurice J. Schwarz Received August 24, 1962

The preparation and solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate and *trans*-2-acetoxymethylcyclohexyl brosylate is reported. The solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate in aqueous dioxane yields mainly 3-hydroxymethylcyclohexene and a mixture of the *cis*- and *trans*-2-hydroxymethylcyclohexanols containing 40% of the *trans* isomer. The large amount of net retention of configuration is ascribed to the intervention of cyclic ions A or B. Acetolysis of *trans*-2-acetoxymethylcyclohexyl brosylate in the presence of added acetate gives 3-acetoxymethylcyclohexene and the diacetate of *cis*-2-hydroxymethylcyclohexanol, while in the absence of added acetate the olefin is accompanied by a mixture of the acetates of the *cis*- and *trans*-2-hydroxymethylcyclohexanol, while in the absence of added acetate the olefin is accompanied by a mixture of the acetates of the *cis*- and *trans*-2-hydroxymethylcyclohexanol, while on C is formed. In the presence of high concentrations of acetate ion, the cyclic ion C suffers displacement at the primary carbon to give the *cis*-diacetate, while in the absence of acetic acid reacts at C-1 to give the *trans*-diacetates. Evidence for the cyclic intermediate C was obtained by isolating the ethyl orthoacetate of *cis*-2-hydroxymethylcyclohexanol from the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate in anhydrous ethanol. It is concluded that there are two possible stereoselective paths for the acid-catalyzed reaction of formaldehyde with olefins to produce 1,3-diol derivatives. In acetic acid solutions, the reaction may proceed by a mixtures another path is available through ions similar to A or B.

The mechanism of the Prins reaction has been the subject of several investigations.<sup>2-6</sup> One example of the Prins reaction, the sulfuric acid-catalyzed reaction of cyclohexene and formaldehyde in acetic acid solution, has been studied quite extensively.<sup>2,3,6,7</sup> The mixture of products from the reaction is quite complex, but the main products are derivatives of *trans*-2-hydroxymethyl-cyclohexanol and none of the *cis* isomer is found.

The stereospecificity of the Prins reaction is not consistent with a simple carbonium ion mechanism. We should like to consider three types of mechanisms. The first accounts for the stereospecificity by suggesting a solvated trimethylene oxide<sup>5</sup> intermediate or an intramolecularly solvated carbonium ion in which the principal solvation comes from the oxygen of a hydroxyl group in a four-membered ring.<sup>2</sup> This mechanism, proposed by Blomquist and Wolinsky,<sup>2</sup> is



<sup>(1)</sup> Supported in part by the Petroleum Research Fund of the American Chemical Society, 915-A4, and a Faculty Research Grant from the Graduate School of the University of Oregon.

- (2) A. T. Blomquist and J. Wolinsky, J. Am. Chem. Soc., 79, 6025 (1957).
- (3) E. Smissman and R. A. Mode, *ibid.*, **79**, 3447 (1957).
- (4) E. E. Smissman and D. T. Witiak, J. Org. Chem., 25, 471 (1960)
- (5) H. W. Zimmerman and J. English, Jr., J. Am. Chem. Soc., 75, 2367 (1953).
- (6) L. J. Dolby, J. Org. Chem., 27, 2971 (1962).

In a previous report from these laboratories<sup>6</sup> we suggested an alternate mechanism which more readily rationalizes the formation of the side products. The intermediate which controls the stereochemistry of the reaction is the three-membered cyclic ion B, similar to the intermediates formulated for other examples of electrophilic addition to double bonds.



We should like to add a third mechanism for consideration. In acetic acid solution the attacking species might arise from hydroxymethyl acetate by protonation and loss of water. This species would be capable of



 <sup>(7)</sup> J. Matti, Bull. soc. chim. France, [4] 51, 974 (1932); S. Olsen and
 H. Padberg, Z. Naturforsch., 1, 448 (1946); S. Olsen, *ibid.*, 1, 671 (1946);
 S. Olsen, Angew. Chem., 59, 32 (1947); S. Olsen, Z. Naturforsch., 3b, 314 (1948).

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yielding a six-membered cyclic ion C, which would yield only *trans*-2-hydroxymethylcyclohexanol derivatives upon reaction with a nucleophile at the secondary carbon atom.

 $CH_{3}CO_{2}H + CH_{2}O \xrightarrow{\phantom{a}} CH_{3}CO_{2}CH_{2}OH$  $CH_{3}CO_{2}CH_{2}OH + H^{+} \xrightarrow{\phantom{a}} CH_{3}CO_{2}CH_{2}^{+} + H_{2}O$ 

Cyclic cations of this type have been demonstrated in several reactions.<sup>8</sup> In the present investigation we have obtained evidence for internal assistance by neighboring acetate in the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate both in acetic acid solution and in ethanol.

We hoped to obtain evidence for or against the several possible intermediates from studies of the stereochemistry of the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate and *trans*-2-acetoxymethylcyclohexyl brosylate. If either the four-membered cyclic oxonium ion A or the three-membered cyclic ion B intervene in the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate, there should be a considerable amount of retention of configuration in the products.



Furthermore, since the cyclic four-membered oxonium ion is capable of maintaining optical activity while the three-membered cyclic ion is not, it should be possible to distinguish between these.

A test of the third mechanism involving neighboring acetate is the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate which should also yield material of retained configuration if the six-membered cyclic ion C is important.



The required arenesulfonates were prepared from *trans*-2-hydroxymethylcyclohexanol obtained by the lithium aluminum hydride reduction of methyl *trans*-2-hydroxycyclohexanecarboxylate prepared in turn from crystalline *trans*-2-hydroxycyclohexanecarboxylic acid. Acetylation of *trans*-2-hydroxymethylcyclohexanol with a limited amount of acetic anhydride in pyridine solution afforded the primary acetate of *trans*-2-hydroxymethylcyclohexanol

(8) (a) S. Winstein and R. E. Buckles, J. Am. Chem. Soc., 64, 2780 (1942);
(b) S. Winstein and R. E. Buckles, *ibid.*, 64, 2787 (1942);
(c) S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, 64, 2796 (1942);
(d) S. Winstein and R. E. Buckles, *ibid.*, 64, 2796 (1942);
(d) S. Winstein and R. E. Buckles, *ibid.*, 65, 613 (1943);
(e) S. Winstein and D. Seymour, *ibid.*, 68, 119 (1946);
(f) S. Winstein, C. Hanson and E. Grunwald, *ibid.*, 70, 812 (1948);
(h) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, 70, 816 (1948);
(h) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, 70, 821 (1948).

droxymethylcyclohexanol contaminated with some of the diacetate. Pure *trans*-2-acetoxymethylcyclohexyl brosylate was obtained from the reaction of the impure monoacetate with *p*-bromobenzenesulfonyl chloride. Very mild methanolysis of *trans*-2-acetoxymethyl cyclohexyl brosylate gave *trans*-2-hydroxymethylcyclohexyl brosylate which differed in its melting point and infrared spectrum from the primary brosylate of *trans*-2hydroxymethylcyclohexanol obtained directly from the *trans*-diol and *p*-bromobenzenesulfonyl chloride in pyridine solution. Acetylation of the *trans*-2-hydroxymethylcyclohexyl brosylate regenerated *trans*-2-acetoxymethylcyclohexyl brosylate identical with the starting material. These results confirm the structures of the materials used in the solvolysis studies.

The solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate in aqueous dioxane with a phosphate buffer at pH 7 gave 3-hydroxymethylcyclohexene in 60% yield and a mixture of the *cis*- and *trans*-2-hydroxymethylcyclohexanols in 30% yield, of which the *trans* isomer was present to the extent of 40%. The remaining material (10%) was not identified. The product analysis was carried out by a combination of vapor phase chromatography and infrared spectroscopy.

The relatively large amount of net retention of configuration observed in the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate is not the result of a normal solvolysis.

Acetolysis of *trans*-4-*t*-butylcyclohexyl tosylate proceeds with 98% inversion<sup>9</sup> and the substitution products from the methanolysis of *trans*-2-methylcyclohexyl tosylate show 86% inversion of configuration, 8% retention of configuration and 6% of rearrangement product 1-methyl-1-methoxycyclohexane.<sup>10</sup> We conclude that the material of retained configuration arises from either the four-membered cyclic oxonium ion A or the three-membered cyclic ion B.

In an effort to obtain some information about the possible intervention of the six-membered bridged acetate species C, the solvolysis of *trans*-2-acetoxymethyl-

#### TABLE I

PRODUCTS OF SOLVOLYSIS OF *trans*-2-ACETOXYMETHYLCYCLO-HEXYL BROSYLATE

	3- Acetoxy- methyl- cyclo- hexene,	Diacetate of <i>trans</i> - 2-hy- droxy- methyl- cyclo- hexanol,	Diacetate of cis- 2-hy- droxy- methyl- cyclo- hexanol,	Other products,
$Solvent^a$	%	%	%	%
HOAc–1.2 M KOAc	<b>2</b> 0		80	
HOAc	40	11	4	$45^{b}$
HOAc−10% H <sub>2</sub> O	12	6	57	$25^{\circ}$
HOAc-0.1 M p-toluenesul-				
fonic acid	30	14	1	$55^{\circ}$
HOAc-1.0 M p-toluenesul-				
fonic acid	30	14	1	$55^{\circ}$
Ethanol-0.34 M KOAc	38			c

<sup>a</sup> All solvolyses were carried out at reflux. <sup>b</sup> In the absence of added potassium acetate three other unidentified products are formed. The new products all had longer retention times than the diacetates of the 2-hydroxymethylcyclohexanols. These same compounds were formed from the reaction of 3-acetoxymethylcyclohexene and acetic acid in the presence of *p*-toluenesulfonic acid and hence the product distribution is subject to large error. <sup>c</sup> Ethyl orthoacetate of *cis*-2-hydroxymethylcyclohexanol, 19; *cis*-2-ethoxycyclohexylcarbinyl acetate, 34; unident. prod. 9. This material has the same retention time as the products from the hydrolysis of the ethyl orthoacetate of *cis*-2-hydroxymethylcyclohexanol.

<sup>(9)</sup> S. Winstein and H. J. Holness, ibid., 77, 5562 (1955).

<sup>(10)</sup> W. Hückel, R. Bross, O. Fechtig, H. Feltkamp, S. Geiger, M. Hanack, M. Heinzel, A. Hubele, J. Kurz, M. Maier, D. Maucher, G. Näher, R. Neidlein and R. B. Rashigkar, *Ann.*, **624**, 208 (1959).

cyclohexyl brosylate was examined under a variety of conditions. These results are summarized in Table I.

The solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate in acetic acid with added potassium acetate may be a simple displacement with inversion at the secondary carbon. However, we would like to suggest that the cyclic ion C is formed and this ion suffers displacement on the primary carbon C-5 to yield the *cis*-diacetate.

A feature of the reaction that lends some support to this hypothesis is the high yield of substitution product (80%). This is in contrast to the usual yield of substitution product which is on the order of 20-40%. For example, the acetolysis of *trans*-4-*t*-butylcyclohexyl tosylate affords only 28% of substitution product.<sup>9</sup>

tosylate affords only 28% of substitution product.<sup>9</sup> The acetolysis of *trans*-2-acetoxymethylcyclohexyl brosylate shows a striking change when potassium acetate is not added to the reaction mixture. The yield of substitution product is greatly diminished and the stereochemical composition of the product is changed drastically. The mixture of diacetates obtained under these conditions contains 70% of the trans isomer. Predominant retention of configuration in the absence of added acetate ion is good evidence for internal assistance by neighboring acetate. The reaction mixture is considerably more complex under these conditions. There are three new compounds present among the products in addition to the olefinic product and the mixture of the acetates of the cis- and trans-2-hydroxymethylcyclohexanols. In control experiments, it was found that the diacetate of cis-2-hydroxymethylcyclohexanol is not appreciably isomerized to the trans isomer under the reaction conditions, but the reaction of 3acetoxymethylcyclohexene with acetic acid and 0.1 Mp-toluenesulfonic acid leads to the diacetate of cis-2hydroxymethylcyclohexanol in small yield accompanied by much larger amounts of the three compounds noted in the acetolyses carried out in the absence of added potassium acetate. The control experiments assure that the trans-diacetate is a primary reaction product under these conditions and is not formed by isomerization of the cis isomer or the addition of acetic acid to 3acetoxymethylcyclohexene.

Direct evidence was obtained for internal assistance by neighboring acetate when the solvolysis was carried out in anhydrous ethanol and potassium acetate. The solvolysis under these conditions gave 19% of the ethyl orthoacetate of cis-2-hydroxymethylcyclohexanol along with 38% of 3-acetoxymethylcyclohexene and 34% of *cis*-2-ethoxycyclohexylcarbinyl acetate, the product of normal solvolytic displacement. The orthoester was identified by comparison of its retention time on vapor phase chromatography and its infrared spectrum with those of an authentic sample. The cis-2ethoxycyclohexylcarbinyl acetate was identified similarly by comparison with an authentic sample. Pure cis-2-ethoxycyclohexylcarbinol was isolated after saponifying the higher boiling products from a large scale solvolysis of trans-2-acetoxycyclohexyl brosylate in ethanol and potassium acetate. The cis-2-ethoxycyclohexylcarbinol isolated from the solvolysis reaction was identical with an authentic sample in its retention time on vapor phase chromatography and infrared spectrum. The p-nitrobenzenesulfonate of the solvolysis product was identical with an authentic sample of the p-nitrobenzenesulfonate of cis-2-ethoxycyclohexylcarbinol in melting point, mixed melting points and infrared spectrum. Authentic cis-2-ethoxycyclohexylcarbinol was prepared by ethylating methyl cis-2hydroxycyclohexanecarboxylate with triethyloxonium fluoborate to furnish methyl cis-2-ethoxycyclohexanecarboxylate which was reduced with lithium aluminum

hydride to the desired alcohol. Acid-catalyzed acetylation yielded the acetate of *cis*-2-ethoxycyclohexylcarbinol.

It is of interest to compare the reactions of *trans*-2acetoxycyclohexyl tosylate<sup>8</sup> and *trans*-2-acetoxymethylcyclohexyl brosylate. While the over-all behavior of the two compounds is similar, there are certain differences. The solvolysis of *trans*-2-acetoxycyclohexyl tosylate in dry acetic acid with added potassium acetate shows complete retention of configuration<sup>8c</sup> while the acetolysis of *trans*-2-acetoxymethylcyclohexyl brosylate exhibits complete inversion under these conditions. However, this difference may be the result of the greater reactivity of the primary carbon in the latter compound.

A fundamental difference in behavior is noted when pure dry acetic acid is used as the solvent. Under these conditions, trans-2-acetoxycyclohexyl tosylate solvolyzes with essentially complete inversion<sup>sc</sup> whereas trans-2acetoxymethylcyclohexyl brosylate gives predominantly retention of configuration. In the former case it has been suggested that the cis-orthodiacetate is an intermediate and subsequently isomerizes to the normal cisdiacetate, but in the present case it seems that the formation of the orthodiacetate is not so greatly favored over attack at C-I to give the trans-diacetate. It is also possible that in the absence of added acetate ion, the lifetime of the bridged ion C is long enough to allow isomerization to a new bridged ion D with a trans ring juncture. The orthodiacetate derived from D would give the trans-diacetate. By analogy with the carbon compounds it is expected that there would be more driving force for a cis to trans isomerization of two fused six-membered rings than for a system containing a fivemembered ring fused cis to a cyclohexane ring.

The effect of added p-toluenesulfonic acid is to increase the proportion of net retention of configuration in the solvolysis. Since the concentration of acetate ion in anhydrous acetic acid is on the order of  $10^{-6} M$ ,<sup>11</sup> it seems unlikely that the effect of added *p*-toluenesulfonic acid is manifested through a lowered acetate ion concentration. It may be that p-toluenesulfonic acid catalyzes the regeneration of the bridged cation C from the *cis*-orthodiacetate which would otherwise rearrange to the cis-diacetate. On this basis, it would be anticipated that the addition of water to the reaction mixture would serve to trap the bridged ion C to give the cisorthomonoacetate which should isomerize to the cishydroxyacetate.<sup>8c</sup> This was indeed the case since the addition of 10% of water to the solvolysis medium gave predominantly cis-2-acetoxymethylcyclohexyl acetate as the product. A possible mechanism is shown.

In an effort to gain some further insight into the nature of the solvolysis processes, we examined the reaction of the ethyl orthoacetate of *cis*-2-hydroxymethyl-cyclohexanol with 0.1 M p-toluenesulfonic acid in acetic acid containing acetic anhydride. Under these conditions the solvolysis of *trans*-2-acetoxymethylcyclohexyl brosylate gives practically pure *trans*-2-acetoxymethylcyclohexyl acetate, but the orthoester gives predominantly the *cis* isomer (*cis/trans* = 3).

There is also some difference in behavior between trans-2-acetoxycyclohexyl tosylate and trans-2-acetoxymethylcyclohexyl brosylate upon solvolysis in dry ethanol. Cyclohexene ethyl orthoacetate and some cis-1,2-cyclohexanediol, probably from hydrolysis of the orthoester, were the only products isolated from the ethanolysis of trans - 2 - acetoxycyclohexyl tosylate. There were no products reported which would arise from a normal solvolytic displacement. Ethanolysis of trans-2-acetoxymethylcyclohexyl brosylate under the same conditions affords only 19% of the orthoester and

(11) I. M. Kolthoff and A. Willman, J. Am. Chem. Soc., 56, 1007 (1934).



34% of the normal displacement product cis-2-ethoxy-cyclohexycarbinyl acetate, along with 38% of the ole-finic product.

From our results on the solvolysis of trans-2-acetoxymethylcyclohexyl brosylate, a mechanism for the Prins reaction involving neighboring acetate may operate. The solvolyses which were carried out under conditions most nearly like those of the Prins reaction showed that the cyclic ion C gives rise to nearly pure trans-diacetate. The small amount of cis material in the product may arise from the addition of acetic acid to 3-acetoxymethylcyclohexene. Under the conditions of the Prins reaction the corresponding alcohol, 3-hydroxymethylcyclohexene, is converted to a mixture of cis-3-oxabicyclo[4.3.0]-6-nonene and the acetates of *anti*-9-hydroxy-3-oxabicyclo [3.3.1] nonane and trans-6-hydroxy-cis-3oxabicyclo [4.3.0] nonane<sup>12</sup> and this source of the cis-diacetate is probably negligible. However, we find that the aqueous sulfuric acid-catalyzed reaction of formaldehyde with cyclohexene<sup>13</sup> furnishes the cyclic formal of trans-2-hydroxymethylcyclohexanol as shown by its hydrolysis to pure trans-2-hydroxymethylcyclohexanol. This means that another stereoselective path is available other than one involving neighboring acetate. It is possible that in the absence of acetic acid a cyclic sulfate ester might be involved in the reaction, but our results from the solvolysis of trans-2-hydroxymethylcyclohexyl brosylate suggest a path via the bridged ions A or B. Of these two intermediates we prefer the threering intermediate from arguments previously presented.6

### Experimental<sup>14</sup>

Methyl *cis*-2-Hydroxycyclohexanecarboxylate.—A mixture of 212 g. of methyl salicylate, 7.8 ml. of acetic acid and 5.2 g. of a 5% rhodium-on-alumina catalyst was hydrogenated at room temperature at an initial pressure of 3 atmospheres. After 5 days, 99% of the theoretical amount of hydrogen had been absorbed. Distillation of the crude product yielded 214.5 g. (97%) of methyl *cis*-2-hydroxycyclohexenecarboxylate, b.p. 103-105° (7 mm.),  $n^{25}$ D 1.4700 (lit.<sup>15</sup> b.p. 100.5-102° (12 mm.),  $n^{21}$ D 1.467).

*cis*-2-Hydroxymethylcyclohexanol was prepared by the reduction of methyl *cis*-2-hydroxycyclohexanecarboxylate as previously described. The product, which crystallized readily, melted at  $47-47.5^{\circ}$  (lit.<sup>16</sup> m.p.  $49-50^{\circ}$ ).

cis-2-Acetoxymethylcyclohexyl acetate was prepared by acetylating pure cis-2-hydroxymethylcyclohexanol with acetic anhydride and a drop of perchloric acid. The material showed b.p.  $118-120^{\circ}$  (2.5 mm.),  $n^{25}$ D 1.4493 (lit.<sup>17</sup> b.p. 85° (0.4 mm.),  $n^{25}$ D 1.4487).

trans-2-Hydroxycyclohexanecarboxylic acid was prepared from methyl cis-2-hydroxycyclohexanecarboxylate by the procedure of Smissman and Mode.<sup>3</sup>

Methyl trans-2-hydroxycyclohexanecarboxylate was prepared in 80% yield by sulfuric acid-catalyzed esterification with methanol. The methyl trans-2-hydroxycyclohexanecarboxylate had b.p. 100-103° (6 mm.),  $n^{25}$ D 1.4555 (lit.<sup>3</sup> b.p. 99.8-101.8° (2 mm.),  $n^{25}$ D 1.4632).

trans-2-Hydroxymethylcyclohexanol was obtained in 96% yield from the lithium aluminum hydride reduction of methyl trans-2hydroxycyclohexanecarboxylate. The trans-2-hydroxymethylcyclohexanol prepared in this manner boiled at 122–124° (2 mm.) and had  $n^{2t}$ D 1.4829 (lit.<sup>3</sup> b.p. 103.5–104° (0.9 mm.),  $n^{25}$ D 1.4829).

trans-2-Acetoxymethylcyclohexyl acetate was prepared by acetylating pure trans-2-hydroxymethylcyclohexanol with acetic anhydride and a drop of concentrated perchloric acid. The material boiled at  $124-126^{\circ}$  (6 mm.),  $n^{25}$ D 1.4497 (lit.<sup>18</sup> b.p. 90-91° (0.25 mm.),  $n^{05}$ D 1.4546.

trans-2-Acetoxymethylcyclohexanol.—To a solution of 14.0 g. of trans-2-hydroxymethylcyclohexanol and 50 ml. of dry pyridine was added dropwise 12.1 g. of acetic anhydride with stirring. Stirring was continued at room temperature for an additional 3 hours and the reaction mixture was diluted with water and extracted with ether. Distillation yielded 15.8 g. (ca. 85%) of impure trans-2-acetoxymethylcyclohexanol. Vapor phase chromatography on a Carbowax 20M column at 200° showed two peaks. The minor peak was found to be the diacetate from its retention time and infrared spectrum. The material was not purified further but used directly in the next step.

further but used directly in the next step. trans-2-Acetoxymethylcyclohexyl Brosylate.—A stirred solution of 55.2 g. of trans-2-acetoxymethylcyclohexanol was cooled in an ice-bath and treated with 85.4 g. of p-bromobenzenesulfonyl chloride. The reaction mixture was allowed to warm up to room temperature and stirring was continued for 20 hours. The reaction mixture was worked up in the usual manner to afford 33 g. (26%) of trans-2-acetoxymethylcyclohexyl brosylate, m.p. 89-90° after one crystallization from ethyl acetate-petroleum ether. The analytical sample melted at 91.5-93° after crystallization from isopropyl ether-petroleum ether.

Anal. Calcd. for  $C_{15}H_{19}O_{5}SBr$ : C, 46.04; H, 4.89; S, 8.20. Found: C, 46.13; H, 4.80; S, 8.27.

trans-2-Hydroxymethylcyclohexyl Brosylate.—A solution of 2.71 g. of trans-2-acetoxymethylcyclohexyl brosylate, 50 ml. of methanol and 4 drops of concentrated perchloric acid was stirred for 48 hours at room temperature. The reaction mixture was diluted with water and extracted with ether. Evaporation of the ether afforded 2.12 g. (89%) of trans-2-hydroxymethylcyclohexyl brosylate, m.p. 56.5-60°. The analytical sample melted at 67-68° after crystallization from isopropyl ether-petroleum ether.

Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>SBr: C, 44.70; H, 4.91; S, 9.18. Found: C, 44.85; H, 4.90; S, 9.26.

A small sample of the *trans*-2-hydroxymethylcyclohexyl brosylate was acetylated with acetic anhydride and pyridine to furnish *trans*-2-acetoxymethylcyclohexyl brosylate identical with authentic material.

The Primary Brosylate of trans-2-Hydroxymethylcyclohexanol. —trans-2-Hydroxymethylcyclohexanol was converted to the primary brosylate, m.p. 73–77°, as described by Henbest and Millward<sup>15</sup> (lit.<sup>15</sup> m.p. 82–84°). The infrared spectrum of the primary brosylate is different from that of trans-2-hydroxymethylcyclohexyl brosylate.

3-Hydroxymethylcyclohexene and 3-acetoxymethylcyclohexene were prepared as previously described.<sup>19</sup> The Ethyl Orthoacetate of *cis*-2-Hydroxymethylcyclohexanol.

The Ethyl Orthoacetate of cis-2-Hydroxymethylcyclohexanol. —The orthoester was prepared essentially as described by Winstein and Buckles<sup>8d</sup> for the preparation of ethyl cis-cyclohexeneorthoacetate. A solution of 4.47 g. of cis-2-hydroxymethylcyclohexanol, 6.10 g. of ethyl orthoacetate and ca. 5 mg. of p-toluenesulfonic acid was placed in a distilling flask fitted with a capillary and attached to a 9-inch Vigreux column. Ethanol was distilled from the reaction mixture at atmospheric pressure after which the pressure was reduced to 14 mm. and the residue was distilled. The ethyl orthoacetate of cis-2-hydroxymethylcyclohexanol boiled at 105–106° (14 mm.) and showed  $n^{25}$ D 1.4534.

(19) A. T. Blomquist, J. Verdol, C. L. Adami, J.Wolinsky and D. D. Phillips, J. Am. Chem. Soc., 79, 4978 (1957).

<sup>(12)</sup> Unpublished observation of D. R. Rosencrantz.

<sup>(13)</sup> L. A. Mikeska and E. Arundale, U. S. Patent, 2356,683.

<sup>(14)</sup> All melting points and boiling points are uncorrected; distillations were carried out using a 65-cm. modified Podbielniak tantalum spiral column. Microanalyses are by Micro-Tech Laboratories, Skokie, III., Berkeley Analytical Laboratories, Berkeley, Calif., and Pascher and Pascher Microanalytical Laboratory, Bonn, Germany. Infrared spectra were determined with a Beckman IR-7 infrared spectrophotometer.

<sup>(15)</sup> H. B. Henbest and B. B. Millward, J. Chem. Soc., 3575 (1960).

<sup>(16)</sup> S. Siegel, J. Am. Chem. Soc., 75, 1317 (1953).

<sup>(17)</sup> Reference 2, p. 6028.

<sup>(18)</sup> Reference 2, p. 6029.

Anal. Caled. for  $C_{11}H_{20}O_3$ : C, 65.97; H, 10.07. Found: C, 65.50; H, 10.00.

Samples of the orthoester hydrolyzed completely during storage in ordinary sample vials for a period of 9 months. The infrared spectrum of the hydrolysis products showed peaks at 1250, 1740, 1725 and 3400 cm.<sup>-1</sup> suggesting that monoacetates of *cis*-2hydroxymethylcyclohexanol are likely products. **Methyl** *cis*-2-Ethoxycyclohexanecarboxylate.—Triethyloxonium fluoborate was prepared as described by Meerwein and coworkers<sup>20</sup> and dissolved in enough methylene chloride to make a 12-15 M solution. A mixture of 14-68 g of methyl *cis*-2-hy-

Methyl cis-2-Ethoxycyclohexanecarboxylate.—Triethyloxonium fluoborate was prepared as described by Meerwein and coworkers<sup>20</sup> and dissolved in enough methylene chloride to make a 1.3-1.5~M solution. A mixture of 14.68 g. of methyl cis-2-hydroxycyclohexanecarboxylate and 85 ml. of ca. 1.3 M triethyloxonium fluoborate in methylene chloride was stored 3 days at room temperature. The reaction mixture was washed with water then sodium carbonate solution and flash distilled. Fractionation of the residue provided 10.61 g. (63%) of methyl cis-2-ethoxycyclohexanecarboxylate, b.p. 95–98° (13 mm.), n<sup>25</sup>D 1.4432.

Anal. Caled. for  $C_{10}H_{18}O_3$ : C, 64.49; H, 9.74. Found: C, 64.39; H, 10.07.

cis-2-Ethoxycyclohexylcarbinol.—A solution of 5.092 g. of methyl cis-2-ethoxycyclohexanecarboxylate in anhydrous ether was added to a slurry of 3.0 g. of lithium aluminum hydride in dry ether. The resulting mixture was heated under reflux overnight and worked up by the procedure of Amundsen and Nelson.<sup>21</sup> Distillation of the crude product yielded 3.47 g. (79%) of cis-2ethoxycyclohexylcarbinol, b.p. 93–95° (13 mm.),  $n^{25}$ D 1.4573.

Anal. Calcd. for C<sub>9</sub>H<sub>15</sub>O<sub>2</sub>: C, 68.31; H, 11.47. Found: C, 68.20; H, 11.11.

The p-nitrobenzenesulfonate of cis-2-ethoxycyclohexylcarbinol was prepared in the usual manner and melted at  $31-32^{\circ}$  after several crystallizations from  $60-90^{\circ}$  petroleum ether.

Anal. Caled. for  $C_{15}H_{21}O_6NS;\ C,\ 52.46;\ H,\ 6.16;\ N,\ 4.08.$  Found: C, 52.86; H, 5.96; N, 4.00.

cis-2-Ethoxycyclohexylcarbinyl Acetate.—A 1.383-g. sample of cis-2-ethoxycyclohexylcarbinol was acetylated with acetic anhydride and a drop of perchloric acid. Distillation of the crude product afforded 1.502 g. (87%) of cis-2-ethoxycyclohexylcarbinyl acetate, b.p. 103–105° (13 mm.),  $n^{28}$ D 1.4422.

Anal. Calcd. for  $C_{11}H_{20}O_3$ : C, 65.97; H, 10.07. Found: C, 65.95; H, 9.99.

Solvolysis of trans-2-Hydroxymethylcyclohexyl Brosylate .--- A solution of 0.875 g. of trans-2-hydroxymethylcyclohexyl brosylate, 35 ml. of purified dioxane and 70 ml. of 0.2 M phosphate buffer of pH 7 was heated under reflux for 96 hours. The solution was continuously extracted with ether for 24 hours and the ether was flash distilled under a fractionating column. The residue was subjected to gas phase chromatography using an Aerograph gas phase chromatograph equipped with a 5-foot Carbowax 20M on firebrick column at 200°. The vapor phase chromatograms showed three peaks. It is assumed that the area under the effluent peaks is directly proportional to the mole fraction of the component. The first component eluted, corresponding to 60% of the products, was identified as 3-hydroxymethylcyclohexene by comparing its retention time and infrared spectrum with those of an authentic sample. The second peak (10%) was unidentified. The third peak (30%) was found by infrared spectroscopy to be trans-2-hydroxymethylcyclohexanol and cis-2-hydroxymethyl-cyclohexanol in the ratio of 2:3. Samples of the components were obtained by collecting the effluents from multiple injections. It was shown that cis- and trans-2-hydroxymethylcyclohexanol were not separated by vapor phase chromatography under these conditions or any others that we examined. The analysis by infrared spectroscopy was done by comparing at all wave lengths the spectrum of the mixture of diols with spectra of mixtures of known composition. The accuracy of the analysis carried out by this procedure is probably no better than 5%.<sup>22</sup> Duplicate runs gave the same results.

Solvolysis of *trans*-2-Acetoxymethylcyclohexyl Brosylate. A. Acetolysis in Anhydrous Acetic Acid with Added Acetate Ion.— A solution of 12 ml. of anhydrous acetic acid (distilled from triacetyl borate), 1.56 g. of dry potassium acetate and 0.7 ml. of acetic anhydride was heated under reflux for 19 hours. A 1.70-g. sample of *trans*-2-acetoxymethylcyclohexyl brosylate was added and the mixture was heated under reflux for 22 hours. The cooled reaction mixture was diluted with water and neutralized with sodium carbonate. The reaction products were isolated by extracting with ether and flash distilling the extracts. The crude product was subjected to vapor phase chromatography using a 5-foot column packed with Carbowax 20M at a tempera-

(21) L. H. Amundsen and L. S. Nelson, J. Am. Chem. Soc., 73, 242 (1951).

ture of 180°. The vapor phase chromatogram showed two peaks. The first eluted component was identified as 3-acetoxymethylcyclohexene by comparing its retention time and infrared spectrum with those of an authentic sample. The second component was identified as pure *cis*-2-acetoxymethylcyclohexyl acetate from its infrared spectrum which was identical with that of an authentic sample. The presence of 5% of the *trans* isomer was discernible in the infrared spectrum of a mixture. Again it was assumed that the area under a component peak is directly proportional to the mole fraction of the component. A similar run was carried out and the mixture of acetates was saponified to provide the corresponding alcohols which were examined as described for the products from the solvolysis of *trans*-2-hydroxymethylcyclohexyl brosylate. The product diol was found to be pure *cis*-2-hydroxymethylcyclohexanol from its infrared spectrum.

B. Acetolysis of trans-2-Acetoxymethylcyclohexyl Brosylate in Anhydrous Acetic Acid.—A solution of 1.0 ml. of acetic anhydride and 14 ml. of anhydrous acetic acid was refluxed 8 hours. A 1.0-g. sample of trans-2-acetoxymethylcyclohexyl brosylate was added and the solution was heated under reflux for 30 hours after which it was worked up as described previously. The vapor phase chromatogram of the products showed five peaks. Two of the peaks were identified as 3-acetoxymethylcyclohexene (ca. 40%) and the diacetates of the 2-hydroxymethylcyclohexanols from their retention times and infrared spectra. The mixture of diacetates amounted to about 15% of the total products. The three new peaks which were not observed in the products. The the solvolysis was carried out in the presence of acetate ion all had retention times longer than the diacetates of the 2-hydroxymethylcyclohexanols. The mixture of the diacetates of cis- and trans-2-hydroxymethylcyclohexanol was found to consist of 70% of the trans isomer and 30% of the cis isomer by infrared spectroscopy.

Č. Acetolysis of *trans*-2-Acetoxymethylcyclohexyl Brosylate in Wet Acetic Acid.—A 1.0-g. sample of *trans*-2-Acetoxymethylcyclohexyl brosylate was solvolyzed and analyzed as described in part B except that acetic acid containing 10% by weight of water was used as the solvent. The vapor phase chromatogram of the product showed 63% of the diacetates of the 2-hydroxymethylcyclohexanols, 12% of 3-acetoxymethylcyclohexene and 25% of the higher boiling compounds noted previously. The diacetate mixture was found to contain 90% of the *cis* isomer.

D. Acetolysis of trans-2-Acetoxymethylcyclohexyl Brosylate in Anhydrous Acetic Acid and p-Toluenesulfonic Acid.—Solutions of 0.10 M and 1.0 M p-toluenesulfonic acid in anhydrous acetic acid were prepared by refluxing the required amount of ptoluenesulfonic acid monohydrate, anhydrous acetic acid and excess acetic anhydride for 24 hours; 1-g. samples of trans-2acetoxymethylcyclohexyl brosylate were solvolyzed and the products analyzed as described in part B. The reaction products were similar to those obtained in parts B and C. The mixtures of the diacetates of cis- and trans-2-hydroxymethylcyclohexanol were richer in the trans isomer than obtained previously. Infrared analysis showed the mixture to contain greater than 90% of the trans isomer.

E. Ethanolysis in Anhydrous Ethanol in the Presence of Acetate Ion.—A mixture of 0.974 g. of *trans*-2-acetoxymethyl-cyclohexyl brosylate and 0.342 g. of potassium acetate was placed in a small reaction flask fitted with a magnetic stirrer. The material was dried for 3 days over phosphorus pentoxide in an evacuated desiccator. A total of 10 ml. of anhydrous ethanol was distilled into the flask from sodium ethoxide and diethyl phthalate. The flask was fitted with a condenser and drying tube and heated under reflux with stirring for 36 hours. The cooled reaction mixture was treated with 0.5 g. of potassium carbonate, then diluted with anhydrous ether and filtered. The ether and ethanol were distilled through a fractionating column under reduced pressure. The residue, containing some inorganic salts, was triturated with 1 ml. of ether and filtered. The filtrate was subjected to vapor phase chromatography using a freshly prepared 5-foot column packed with Carbowax 20M on firebrick heated at 140° with the injection port at 110°.23 The vapor phase chromatogram showed three main peaks and one small peak at a much longer retention time. The first component (38%) eluted was identified as 3-acetoxymethylcyclohexene from its infrared spectrum and retention time. The second component (19%) was identified as the ethyl orthoacetate of *cis*-2-hydroxymethylcyclohexanol by comparison of its infrared spectrum and retention time with those of an authentic sample. The last peak (9%) had a retention time which corresponded to the retention time of the products of hydrolysis of the orthoester. It was ob-served that the orthoester had hydrolyzed completely after the ether solution had been exposed to the atmosphere for 5 hours.

Large Scale Ethanolysis of trans-2-Acetoxymethylcyclohexyl Brosylate.—A mixture of 22.6 g. of trans-2-acetoxymethylcyclohexyl brosylate and 6.10 g. of potassium acetate was placed in a

<sup>(20)</sup> H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, J. prakt. Chem., 154, 111 (1939).

<sup>(22)</sup> At the suggestion of the referee, control experiments were carried out to establish that the products are stable under the reaction conditions. In separate experiments *cis*-2-hydroxymethylcyclohexanol and 3-hydroxymethylcyclohexane were recovered unchanged after a 36-hour reflux in aqueous dioxane which was  $1.5 \times 10^{-4} M$  in *p*-toluenesulfonic acid.

<sup>(23)</sup> The orthoester was found to decompose when the injection port temperature was raised above 140°. After extensive use, columns seem to acquire something which catalyzes the decomposition of the orthoester.

300-ml. round-bottomed flask equipped with a magnetic stirring bar. The material was dried for 3 days over phosphorus pentoxide in an evacuated desiccator. A total of 150 ml of anhydrous ethanol was distilled into the flask from sodium ethoxide and diethyl phthalate. The flask was fitted with a condenser and a drying tube and heated under reflux for 42 hours after which most of the ethanol was distilled at atmospheric pressure. The cooled reaction mixture was treated with 6.0 g. of potassium carbonate then diluted with water and extracted with chloroform. The chloroform extracts were dried over magnesium sulfate and flash distilled. Fractional distillation of the residue yielded 1.561 g. (18%) of pure 3-acetoxymethylcyclohexene, b.p.  $80-85^{\circ}$  (13 mm.); identified by vapor phase chromatography and infrared spectroscopy; 0.289 g. of intermediate, b.p.  $85-103^{\circ}$  (13 mm.); and 6.877 g. (ca. 65%) of a mixture of cis-2-ethoxycyclohexylcarbinyl acetate and monoacetates of cis-2-hydroxymethylcyclohexanol.

The 6.877 g. of higher boiling material obtained above was saponified with 3.4 g. of potassium hydroxide in 20 ml. of methanol and 10 ml. of water. Most of the methanol was distilled and the residue was diluted with 10 ml. of water and extracted four times with chloroform. The chloroform was flash distilled and the residue was fractionated to yield 0.807 g. (9% based on *trans-2*-acetoxymethylcyclohexyl brosylate) of *cis-2*-ethoxycyclohexylcarbinol, b.p. 103-105°,  $n^{25}$ D 1.4588; 0.355 g. of intermediate, b.p. 106-135°; and 1.145 g. (14% based on *trans-2*-acetoxymethylcyclohexyl brosylate) of pure *cis-2*-hydroxymethylcyclohexanol, b.p. 135-137° (13 mm.), m.p. 47-48° (lit.<sup>17</sup> m.p. 49-50°).

The infrared spectrum and retention time on vapor phase chromatography of the *cis*-2-ethoxycyclohexylcarbinol obtained above were identical with those of authentic material. A sample of the *cis*-2-ethoxycyclohexylcarbinol was converted to the *p*nitrobenzenesulfonate which melted at  $31-32^{\circ}$  undepressed upon mixing with authentic *cis*-2-ethoxycyclohexylcarbinyl *p*-nitrobenzenesulfonate and their infrared spectra in chloroform solution were superimposable.

The Reaction of 3-Acetoxymethylcyclohexene with Acetic Acid in the Presence of p-Toluenesulfonic Acid.—A solution of 0.500 g. of 3-acetoxymethylcyclohexene in 15 ml. of 0.1 M p-toluenesulfonic acid in anhydrous acetic acid was heated under reflux for 30 hours. The reaction mixture was worked up and examined as described for the solvolysis of trans-2-acetoxymethylcyclohexyl brosylate in acetic acid. The vapor phase chromatogram of the products showed five peaks which corresponded exactly to the products from the solvolysis of trans-2-acetoxymethylcyclohexyl brosylate in acetic acid without added potassium acetate. The product diacetate of 2-hydroxymethylcyclohexanol (ca. 4%) was found to be pure cis-2-acetoxymethylcyclohexyl acetate by comparison of its infrared spectrum with that of an authentic sample. The Reaction of cis-2-Acetoxymethylcyclohexyl Acetate in Acetic Acid in the Presence of p-Toluenesulfonic Acid.—A solution of 0.500 g. of *cis*-2-acetoxymethylcyclohexyl acetate in 15 ml. of 0.1 molar *p*-toluenesulfonic acid in anhydrous acetic acid was heated under reflux for 30 hours. Analysis of the products as described previously showed about 8% of 3-acetoxymethylcyclohexene and 90% of *cis*-2-acetoxymethylcyclohexyl acetate of greater than 95% purity. In addition there was a trace of the three compounds noted previously with retention times longer than that of the diacetates of the 2-hydroxymethylcyclohexanols.

The Reaction of the Ethyl Orthoacetate of cis-2-Hydroxymethylcyclohexanol with Acetic Acid in the Presence of p-Toluenesulfonic Acid.—A solution of 0.8453 g. of the orthoester and 12 ml. of 0.1 M p-toluenesulfonic acid in anhydrous acetic acid was heated under reflux for 3 hours and worked up as described for the solvolysis of trans-2-acetoxymethylcyclohexyl brosylate in acetic acid. The reaction products were analyzed by a combination of vapor phase chromatography and infrared spectroscopy as previously described. The products were 10% of 3-acetoxymethylcyclohexene, 65% of cis-2-acetoxymethylcyclohexyl acetate and 25% of trans-2-acetoxymethylcyclohexyl acetate.

The Reaction of Cyclohexene and Formaldehyde in Aqueous Sulfuric Acid.<sup>24</sup>—The following procedure was adapted from the directions of Mikeska and Arundale.<sup>13</sup> In a 1-1. 3-necked flask fitted with a stirrer, condenser and a dropping funnel was placed 150 g. of 50% (by volume) sulfuric acid and 90 g. of paraformal-dehyde. A total of 249 g. of cyclohexene was added dropwise with vigorous stirring. After the addition was complete the heterogeneous mixture was neutralized with sodium carbonate and steam distilled. Fractionation of the organic layer yielded 150 g. of cyclohexene and 60 g. (ca. 14% based on total cyclohexene) of impure cyclic formal of *trans*-2-hydroxymethylcyclohexanol, b.p. 193–198° (atm.), n<sup>25</sup>D 1.4680–1.4648. The material showed three major peaks on vapor phase chromatography using a 5-foot Carbowax 20M column at 150°. The first eluted component was shown to be cyclohexanol from its retention time and infrared spectrum.

A sample of the impure material obtained above was dissolved in methanol containing 10% by volume of concentrated sulfuric acid and allowed to stand at room temperature. Alliquots were removed from the reaction mixture, neutralized with sodium carbonate and extracted with ether. The ether extracts were evaporated and the residue subjected to vapor phase chromatography. After 4 days it was found that the products consisted of about 80% of pure *trans*-2-hydroxymethylcyclohexanol by comparing the retention time and infrared spectrum of an effluent peak with those of an authentic sample, and 20% of lower boiling materials. The composition of the reaction mixture did not change after 4 days.

(24) The authors are indebted to Mr. Herbert M. Swick for carrying out this experiment.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

# Unsaturated Macrocyclic Compounds. XXVIII.<sup>1</sup> 1,2,7,8,13,14-Hexamethyltridehydro-[18]-annulene and 1,2,7,8,13,14-Hexamethyl-[18]annulene

#### By Franz Sondheimer and David A. Ben-Efraim

RECEIVED AUGUST 20, 1962

3-Butyn-2-ol (I) is converted to 3-bromo-1-butyne (II), which on reaction with magnesium in tetrahydrofuran yields 3,4-dimethyl-1,5-hexadiyne (III). Isomerization of the diyne III with potassium *t*-butoxide in *t*-butyl alcohol leads to 3,4-dimethyl-1,3-hexadien-5-yne (IV), as evidenced by the ultraviolet spectrum. Oxidation of the diyne III with cupric acetate in pyridine and subsequent isomerization with potassium *t*-butoxide in *t*-butyl alcohol and benzene gives rise to a mixture of polymethyl-dehydrogenation of the dehydrogenatule VI apparently leads, in very low yield, to 1,2,7,8,13,14-hexamethyl-[18]annulene (VIII), although this substance was not obtained in pure form.

It has been shown that 1,5-hexadiyne by oxidative coupling and subsequent base isomerization may be converted to a series of fully conjugated cyclic polyenepolyynes (dehydroannulenes),<sup>2</sup> which on partial hydrogenation yield the corresponding conjugated cyclic polyenes (annulenes).<sup>3</sup> It was of interest to utilize this type of synthesis for the preparation of substituted

(1) For Part XXVII, see L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky and A. A. Bothner-By, J. Am. Chem. Soc., in press.

(3) F. Sondheimer, R. Wolovsky and Y. Amiel, ibid., 84, 274 (1962).

dehydroannulenes and annulenes, in order that the effect of the substituents on the physical and chemical properties might be studied. In the present paper we report the synthesis of 1,2,7,8,13,14-hexamethyltridehydro-[18]annulene (VI) and of 1,2,7,8,13,14-hexamethyl-[18]annulene (VIII), the former substance, but not the latter, being isolated in pure form. These compounds differ from the previously described tridehydro-[18]annulene<sup>2</sup> and [18]annulene<sup>3</sup> in possessing six methyl substituents, most probably directed "outside" the ring as shown.

<sup>(2)</sup> F. Sondheimer and R. Wolovsky, ibid., 84, 260 (1962).