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NEIGHBOURING GROUP PARTICIPATION—I

AcO-6 PARTICIPATION IN THE SOLVOLYSIS OF 2-HYDROXYMETHYLCYCLOHEXANOL DERIVATIVES*

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Abstract—The partial inversion observed in the acetolysis of *cis*-2-tosyloxymethylcyclohexyl acetate (VIa), the formation of 2-ethoxy-2-methyl-*cis*-1,3-dioxadecalin (XVIa) isolated in 71% yield subsequent to ethanolysis, and the isolation of 2-methyl-*cis*-4,5-tetramethylene-1,3-dioxenium tetrafluoroborate (X-BF_4) from the corresponding *cis*-2-brosyloxymethyl derivative (VIb) constitute substantial evidence to show that the above processes proceed through the cyclic acetoxonium ion X. None of these reactions could be observed with the *trans* isomer (VII). In the solvolysis of *cis*-2-acetoxymethylcyclohexyl tosylate (VIIIa) olefin formation is the main reaction exceeding 90%. The acetolysis of *trans*-2-acetoxymethylcyclohexyl tosylate (IXa) is accompanied by some partial inversion, its ethanolysis by the formation of 22·5% ortho-ester (XVIa), and the corresponding brosylate (IXb) gives also X-BF_4. However, the considerable olefin formation in acetolysis in the presence of potassium acetate (29·7% and 34·7%, respectively), indicate that the cyclic acetoxonium ion X is only partly involved as intermediate in the above reactions of IX. The mechanisms of the solvolytic reactions is discussed.

IN THE course of their classical investigations leading to the recognition and examination of neighbouring group participation, Winstein *et al.* found that the solvolysis of *trans*-2-acetoxycyclohexyl bromide (IIa) and *trans*-2-acetoxycyclohexyl *p*-toluenesulphonate (IIb) in anhydrous acetic acid and in the presence of acetate ions gave rise to *trans*-1,2-diacetoxycyclohexane (IV).[1,2] This result amounts to an overall retention of configuration which was explained[1-3] by the participation of the acetoxy group *via* the cyclic *cis*-cyclohexane-acetoxonium ion III (Fig. 1). The isolation of cyclohexane ethyl orthoacetate (V) from the solvolysis product of IIb in dry ethanol,[4] the kinetic evidence obtained from the acetolysis of I and IIc,[5-6] and very recently, preparation of the tetrafluoroborate of the 2-methyl-*cis*-tetramethylene-1,3-dioxolenium ion (III-BF_4)[7] provided definite conformation of Winstein's previous ideas.[1-4,8] The structural and stereochemical consequences of AcO-5 participation have been reproduced by Winstein's school in a number of

* Preliminary communications see Refs. 22 and 37.

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[1] S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.* **64**, 2780 (1942).
[2] S. Winstein, H. V. Hess and R. E. Buckles, *J. Am. Chem. Soc.* **64**, 2796 (1942).
[3] S. Winstein and R. Heck, *J. Am. Chem. Soc.* **74**, 5584 (1952).
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[5] S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *J. Am. Chem. Soc.* **70**, 816 (1948).
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[7] C. B. Anderson, E. C. Friedrich and S. Winstein, *Tetrahedron Letters* 2037 (1963).
[8] R. M. Roberts, J. Corse, R. Boschan, D. Seymour and S. Winstein, *J. Am. Chem. Soc.* **80**, 1247 (1958).

systems.[9-13] Neighbouring acetoxy group participation served as an important tool to explain reaction mechanisms in several fields of organic chemistry, reviewed by several authors.[14-19]

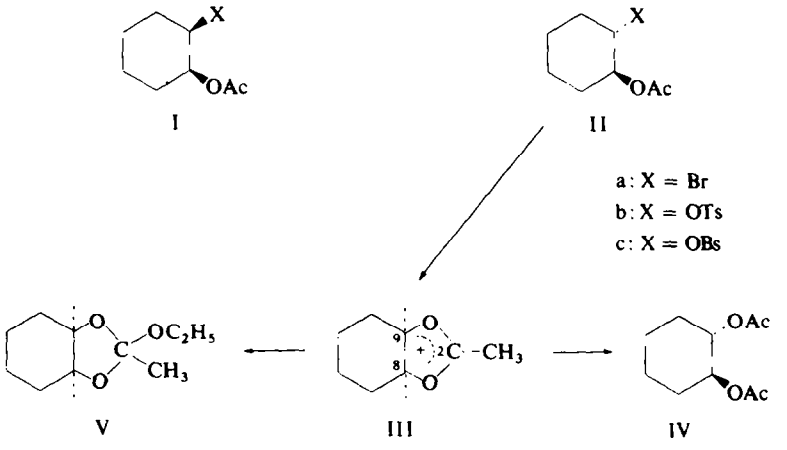

FIG. 1

In comparison to the great number of AcO-5 participation, only very few cases of AcO-6 participation are known: besides the AcO-6 participation observed with *cis*- and *trans*-2-hydroxymethylcyclohexanol mixed arylsulphonate-acetate derivatives,[20-22] there is only one example,[23] in the field of steroids, which has been carefully studied and proved in several papers.[24-30] In this case the 6-membered acetoxonium ion is linked to the steroid nucleus in 3α,5α-position. Furthermore, a

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[14] R. U. Lemieux, *Advan. Carbohyd. Chem.* **9**, 1 (1954).
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[17] S. Hünig, *Angew. Chem.* **76**, 400 (1964).
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[20] L. J. Dolby, C. N. Lieske, D. R. Rosencrantz and M. J. Schwarz, *J. Am. Chem. Soc.* **85**, 47 (1963).
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[22] Ö. K. J. Kovács, Gy. Schneider and L. K. Láng, *Proc. Chem. Soc.* 374 (1963).
[23] The other known 6-membered acetoxonium ion, isolated in salt form, was prepared from its preformed cyclic ortho-ester; H. Meerwein, K. Bodenbenner, P. Borner, F. Kunert and K. Wunderlich, *Liebigs Ann.* **632**, 38 (1960).
[24] Pl. A. Plattner and W. Lang, *Helv. Chim. Acta* **27**, 1872 (1944).
[25] Pl. A. Plattner, A. Fürst, F. Koller and W. Lang, *Helv. Chim. Acta* **31**, 1455 (1948).
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[27] J. W. Blunt, M. P. Harsthorn and D. N. Kirk, *Chem. and Ind.* 1955 (1963); *J. Chem. Soc.* 1073 (1964).
[28] M. J. Coppen, M. P. Hartshorn, D. N. Kirk, *J. Chem. Soc.* (C) 576 (1966).
[29] A. D. Cross, E. Denot, R. Acevedo, R. Urquiza and A. Bowers, *J. Org. Chem.* **29**, 2195 (1964).
[30] B. W. Sands and A. T. Rowland, *Steroids* **4**, 175 (1964).

6-membered acetoxonium ion intermediate is presumed to explain the subsequent isomerization of 3,4,6-tri-O-acetyl-α-D-glucopyranose-1,2-O-acetoxonium-hexachloroantimonate.[31]

In our laboratory a considerable 0^{-}–4 neighbouring group participation was observed in the alkaline hydrolysis of *cis*-2-tosyloxymethylcyclohexanol[32] and *cis*-2-tosyloxymethylcyclopentanol,[33] and a slight one in the case of *trans*-2-tosyloxymethylcyclonexanol.[32] On basis of these results it appeared reasonable to extend

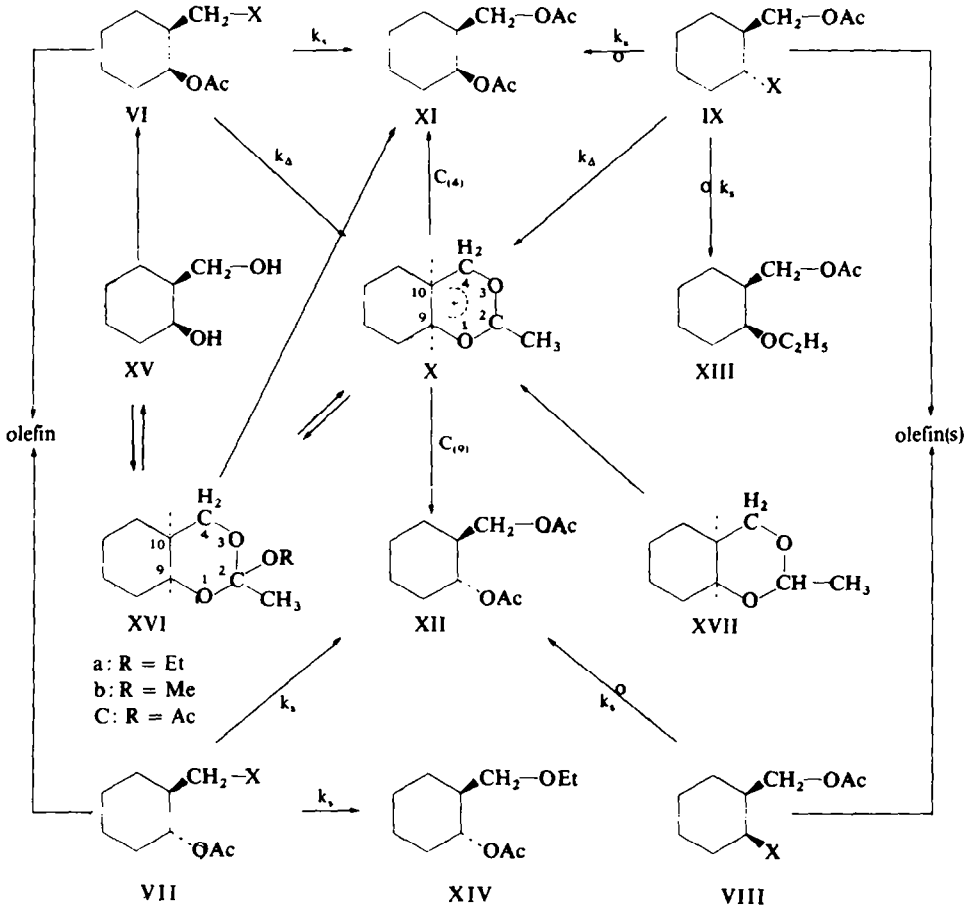

FIG. 2

[31] H. Paulsen, W. P. Trautwein, F. G. Espinosa and K. Heyns, *Tetrahedron Letters* 4137 (1966).

[32] Ö. K. J. Kovács, Z. Tuba, I. Weisz and Gy. Schneider, *Chem. and Ind.* 1222 (1961); *Magyar Kém. Folyóirat* **69**, 37 (1963).

[33] Ö. K. J. Kovács, J. Szilágyi and Gy. Schneider, *Magyar Kém. Folyóirat* **71**, 93 (1965).

the examinations to the corresponding mixed tosylate-acetates (VIa–IXa)* to get a more quantitative picture about the role of the gamma-neighbouring group in these systems. Moreover, we wished to compare the solvolytic behaviour of these tosylate-acetate isomers (VIa–IXa) with the corresponding reactions of *cis*- and *trans*-2-acetoxycycloalkyl arylsulphonates (I and II) studied by Winstein *et al.*;[1-8] namely, the two systems differ from each other (*a*) in the relative distance of the neighbouring groups from the reaction centre, (*b*) therefore in the $-I$ effect exerted by the neighbouring acetoxy group, (*c*) in the primary or secondary character of the two functional groups, and finally (*d*) in the energetic relations of the cyclic intermediates (dioxahydrindan and dioxadecalin structure).

RESULTS

Acetolysis of VIa–IXa. Acetolysis of the *cis*- and *trans*-tosylate-acetates and the acetate-toxylates, resp. (VIa–IXa) was carried out in 0·8 molar concentration in a mixture of anhydrous acetic acid and 0·8 equivalent acetic anhydride in the presence of 1·2 equivalent potassium acetate, or in the absence of the latter, at reflux temperature.[2] The olefin content of the crude reaction product was determined according to Kaufmann's double-bond titration,[34] the quantitative relations of the diacetates by infrared analysis (base-line method),[35] identification of the substances present was achieved by comparison with respective test-materials by means of gas chromatography (cf. Table 1).

Acetolysis of *cis*- and *trans*-tosylate-acetates (VIa and VIIa) (Fig. 2), both in the absence and presence of potassium acetate, yielded, in addition to some 2-methylenecyclohexyl acetate (XX; 3·96 and 8·15%, respectively), 2-acetoxymethylcyclohexyl acetate (XI and XII) as the main product. IR analysis revealed that while VIIa gave the *trans*-diacetate (XII) with complete retention, the acetolysis of VIa of *cis* configuration afforded a mixture of the *cis*- and *trans*-diacetates (XI and XII).

Of the compounds containing a secondary arylsulphonyloxy group, the *cis*-acetate-tosylate (VIIIa) gave on acetolysis olefinic products in higher than 90% yield, namely a mixture of 1-acetoxymethylcyclohexene (XVIII) and 3-acetoxymethylcyclohexene (XIX) in the ratio of about 2:1. Gas chromatographic analysis revealed the presence of some diacetate which was shown by IR analysis to have *trans* configuration (XII) (complete inversion). The acetolysis of *trans*-acetate-tosylate (IXa) yielded with some deviations (cf. Table 1), but characteristically diacetate as the main product and 3-acetoxymethylcyclohexene (XIX), both in the absence and presence of potassium acetate. The main product consisted of a *mixture* of *cis*- and *trans*-diacetate (XI and XII).

* *Abbreviations in text*: 1. *cis*- and *trans*-2-tosyloxymethylcyclohexanol acetate = *cis*- and *trans*-tosylate-acetate, resp. (VIa and VIIa); 2. *cis*- and *trans*-acetoxymethylcyclohexyl tosylate = *cis*- and *trans*-acetate-tosylate, resp. (VIIIa and IXa); the abbreviations are similar in the brosyloxy series (VIb-IXb); 3. 2-methyl-*cis*-4,5-tetramethylene-1,3-dioxenium ion = cyclic acetoxonium ion or cyclic intermediate (X); 4. *cis*- and *trans*-acetoxymethylcyclohexyl acetate = *cis*- and *trans*-diacetate, resp. (XI and XII); 5. 2-ethoxy-2-methyl-*cis*-1,3-dioxadecalin = orthoester (XVIa).

[34] H. P. Kaufmann, *Studien auf dem Fettgebeit* p. 23. Verlag Chemie, Berlin (1935).
[35] J. J. Heigl, M. F. Bell and J. V. White, *Analyt. Chem.* **19**, 293 (1947).

TABLE 1. ACETOLYSIS OF VIa—IXa

Compound	Per cent of component[a]				Total olefin[b]	XI:XII ratio[c]
	XI or/and XII	XVIII	XIX	XX		
VIa	94·5	—	—	5·5	3·96	80:20
	90·5	—	—	9·5	8·15	75:25
VIIa	98	—	—	2	0·76	0:100
	92·5	—	—	7·5	5·44	0:100
VIIIa	7	59	34	—	92·2	0:100
	4·5	60·5	35	—	97·1	0:100
IXa	89	—	11	—	9·75	90:10
	72	—	27·5	—	29·7	70:30

[a] Determined by gas chromatography.
[b] Determined by double bond titration.
[c] Determined by IR analysis.
Top lines: in the presence of potassium acetate.
Bottom lines: in the absence of potassium acetate.

Ethanolysis of VIa–IXa. The ethanolysis[4] in the presence of potassium acetate (0·45 molar concentration, 1·2 equivalent potassium acetate) gave a similar picture to that obtained in the acetolysis (cf. Table 2). Gas chromatography of the crude product from VIa revealed the presence of two compounds; the one present in smaller amount proved to be *cis*-diacetate (XI) by identification and IR analysis. The other compound, 2-ethoxy-2-methyl-*cis*-1,3-dioxadecalin (XVIa) was isolated in 71% yield[36] and its structure confirmed by synthesis starting with *cis*-hydroxymethylcyclohexanol (XV). The analogous reaction of the *trans*-tosylate-acetate (VIIa) yielded, in addition to some 2-methylenecyclohexyl acetate (XIV), *trans*-diacetate (XII) as the main product, resulting from simple substitution.

Of the compounds containing secondary tosyloxy group (VIIIa and IXa), in the case of the *cis* derivative VIIIa elimination was the predominant reaction again (cf. Table 2), the small amount of diacetate isolated had *trans* configuration (XII) and originated from inversion. Ethanolysis of the *trans*-acetate-tosylate (IXa) gave rise to four compounds: in addition to a considerable amount of 3-acetoxymethylcyclohexene (XIX) and some *cis*-diacetate (XI), a product was isolated in 47·3% yield,

[36] One of the most important conditions for a successful reaction was the complete absence of moisture.[4] Namely, formation of the orthoester (XVIa) is accompanied by the formation of one equivalent of acetic acid, which in the presence of traces of water may give rise to the acid-catalysed hydrolysis of the orthoester. The acetic acid released in the reaction may be titrated with sodium methoxide standard solution in the presence of bromothymol blue indicator; in this way the quantity of the orthoester formed may be determined (cf. Table 2). Obviously, the method cannot be used if there are other processes leading to acetic acid formation, such as the ethanolysis of IXa.

TABLE 2. ETHANOLYSIS OF VIa—IXa

Compound	Per cent of component[a]							Total olefin[b]	XI:XII ratio[c]
	XI or/and XII	XVIa	XIV	XIII	XVIII	XIX	XX		
VIa	27·5 (21)	72·5 (71) 76)[d]	— —	— —	— —	— —	— —	—	100:0
VIIa	90 (83)	— —	· 5 ( )	— —	— —	— —	5 ( )	3·18	0:100
			└———(8)———				——┘		
VIIIa	11 (6)	— —	— —	— —	52·5 ( )	36·5 ( )	— —	92·3	0:100
					└—(83)—┘				
IXa	9·5 (11·5)	24·5 ( )	— —	34·5 ( )	— —	31·5 29	— —	34·7	100:0
		└———(46·5)———		——┘					

[a] Determined by gas chromatography.
[b] Determined by double bond titration.
[c] Determined by infrared analysis.
[d] Calculated quantity (in per cent) on the basis of acetic acid titration.
Figures in parentheses refer to the isolated quantity (in per cent).

which, according to gas chromatographic examination and hydrolysis followed by fractionated distillation, consisted of a 1:1 mixture of *cis*-2-ethoxycyclohexylcarbinyl acetate (XIII) and 2-ethoxy-2-methyl-*cis*-1,3-dioxadecalin (XVIa).

Isolation of the 2-*methyl*-CIS-4,5-*tetramethylene*-1,3-*dioxenium tetrafluoroborate salt* (X-BF_4). In the course of our experiments—in analogy to the work of Anderson *et al.*[7]—X-BF_4 has been prepared[37] in three ways.[38, 39] The orthoester XVIa afforded with BF_3-etherate the crystalline X-BF_4 salt almost in quantitative yield. The process is reversible; by means of alkali alkoxide the orthoester XVI may be recovered. The reaction[40] of the cyclic acetal XVII with triphenylmethyl fluoroborate[39, 41] again gave X-BF_4 in good yields.

Finally, all four mixed brosylate-acetates (VIb–IXb) were reacted with an equivalent of silver tetrafluoroborate[42] in 0·4M concentration at 25°. In the case of VIb and IXb a fast reaction took place, which was complete in 2 hr, and after working up 2-methyl-*cis*-4,5-tetramethylene-1,3-dioxenium tetrafluoroborate (X-BF_4) could be isolated. Under identical conditions neither VIIb nor VIIIb reacted: when after

[37] Gy. Schneider and Ö. K. J. Kovács, *Chem. Comm.* 202 (1965).
[38] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning and E. Pfeil, *J. Prakt. Chem.* **147**, 257 (1937).
[39] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. Prakt. Chem.* **154**, 83 (1940).
[40] H. Meerwein, V. Hederich, H. Morschel and K. Wunderlich, *Liebigs Ann.* **635**, 1 (1960).
[41] H. Meerwein, P. Borner, O. Fuchs, H. J. Sasse, H. Schrode and J. Spille, *Chem. Ber.* **89**, 2060 (1956).
[42] H. Meerwein, V. Hederick and K. Wunderlich, *Arch. Pharm.* **291**, 541 (1958).

standing 48 hr the reaction mixture was worked up, both starting materials were recovered. In case of VIIIb about 20% olefin was also isolated.

DISCUSSION

On basis of the above results, the solvolysis of the mixed tosylate-acetates VIa and VIIa can unambiguously be explained. The acetolysis of *cis*-tosylate-acetate (VIa) results in a mixture of two diacetates (XI and XII), of which *cis*-diacetate (XI) might be formed, partially or completely, through the participation of the solvent (k_s), but the partial inversion at the secondary carbon atom ($C_{(1)}$), i.e. the formation of *trans*-diacetate (XII) may be considered anomalous. In order to explain the partial inversion we have supposed, on the analogy of III[1,2] that the carbonyl oxygen of the acetoxy group at the secondary carbon atom takes part, *via* an S_Ni reaction, in the ionization of the *p*-toluenesulphonyloxy group attached to the primary carbon atom, and in the first step a cyclic acetoxonium ion (X) intermediate is formed. In contrast with III, the intermediate of the k_Δ process is not symmetric, and ring opening in dry acetic acid, due to the ambident character of the cation,[17] expected to occur at $C_{(4)}$ and $C_{(9)}$, affords two different diacetates (XI and XII).[43] In principle, the $C_{(9)}—O_{(1)}—C_{(2)}—O_{(3)}—C_{(4)}$ system in the cyclic intermediate (X) may suffer cleavage in five ways: only the splitting of the $C_{(9)}—O_{(1)}$ bond is accompanied by inversion and results in *trans*-diacetate (XII). Participation of the acetoxy group present in the *cis*-tosylate-acetate (VIa) has also been confirmed by our preliminary kinetic measurements:[22] the rate of acetolysis of VIa was about 100 times as high as that of the respective *trans* isomer (XIIa), and about 460 times greater than that of cyclohexylcarbinyl tosylate containing no neighbouring group.[44]

Ready formation of the cyclic intermediate X in case of VIa can be attributed to its conformation (Fig. 3). In the conformational equilbrium of *cis*-tosylate-acetate

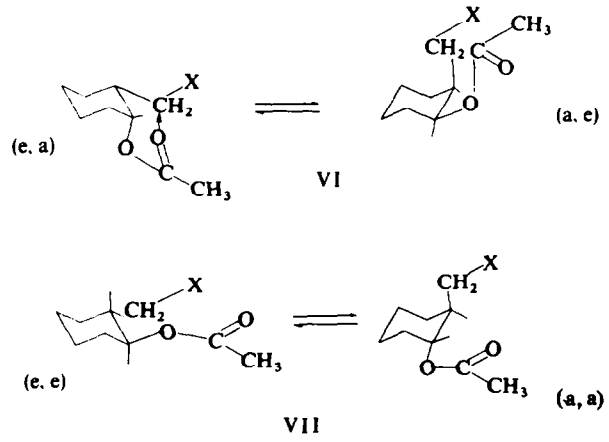

Fig. 3

[43] The *cis*-diacetate XI may also be produced, considering that 0·8 equivalent of acetic anhydride is present, through the orthoester-acetic acid mixed anhydride (XVIc), which is tautomerized to XI by acid catalysis; see Refs. 7, 8.

[44] Details of these investigations will be reported in succeeding papers of this series.

(VIa), the population of the *e,a* conformer (—CH_2OTs *equatorial*, —OAc *axial*) is considerably higher than that of the *a,e* one, owing to the space requirement of the —CH_2OTs group. Participation of the acetoxy group, too, is more probable in the *e,a* conformation, since interference by the $C_{(4)}$ and $C_{(6)}$ *meta* hydrogens in the *a,e* conformation turns the tosyloxy group toward the acetoxy group, and thus reduces the possibility of a rear-side attack at the primary carbon atom.

The high yield (71%) of orthoester (XVIa) isolated from the ethanolysis of VIa proves not only that the k_Δ process is in operation proceeding through the ion X, but also that it is predominating over k_s.[45] In this process, thermodynamic factors are involved in addition to kinetic control: the cyclic intermediate ion (X) probably has a chair-halfchair conformation owing to considerable resonance in the hetero-ring;[46] thus stabilization is preferred in the direction of *cis*-1,3-dioxadecalin arrangement with chair-chair conformation.[47,48] Finally, the 2-methyl-*cis*-4,5-tetramethylene-1,3-dioxenium tetrafluoroborate salt (X-BF_4) prepared from VIb, the identity of which was confirmed by synthesis *via* two other ways, provides an unambiguous proof for the existence of the 6-membered acetoxonium ion (X) in the solvolysis of VI.

On the other hand, the facts that (*a*) pure *trans*-diacetate (XII) was obtained in the acetolysis of VIIa, (*b*) the *trans*-isomer corresponding to the *cis*-orthoester (XVIa) could neither be isolated from, nor detected even by gas chromatographic examination in the ethanolysis product, and (*c*) VIIb was recovered unchanged from the reaction with silver tetrafluoroborate, prove that in the case of VII the substitution occurs with no acetoxy participation. AcO-6 participation would be a possibility also in this case, owing to the *e,e* conformation of VII, and to the stability originating from the *trans* junction of the expected intermediate (*trans*-1,3-dioxadecalin structure). Failure of such a participation may be explained by the conformational relation of the two reacting groups; namely, in the probably predominating *e,e* conformation, the tosyloxy group always has to assume such a position about the $C_{(2)}$–$C_{(7)}$ axis that it will hinder rear-side attack at the carbonyl oxygen.

To gain further insight into the stereochemistry of the reaction,[49] a similar investigation of the four isomers corresponding to VI and VII containing a 4-t-butyl group is in progress.[50]

Solvolysis of the *cis*- and *trans*-acetate-tosylates (VIIIa and IXa) gives a slightly more complicated picture. Both the acetolysis (either in the absence or presence of potassium acetate) of VIIIa yielded a mixture of two unsaturated compounds (XVIII and XIX) over 90% yield as the main product. In all three cases the *trans*-diacetate (XII) was formed in less than 8% yield, and no *cis* isomer (XI) could be detected; from this the conclusion has been drawn that XII is produced by simple

[45] Recently, the methanolysis of VIa has also been achieved; quantitative formation of 2-methoxy-2-methyl-*cis*-1,3-dioxadecalin (XVIb) proved by the quantity of 2N MeONa consumed by the acetic acid produced in the reaction and by gas chromatographic analysis. XVIb isolated in 94% yield in very pure state (b.p. 112–115°, n_D^{20} 1·4575; synthesized from XV with methyl orthoacetate). See Ref. 22.

[46] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison: *Conformational Analysis* p. 426. Interscience, New York (1965).

[47] M. Hanack: *Conformation Theory* p. 308. Academic Press, New York (1965).

[48] Ref. 47, p. 65 and 172.

[49] J. F. King and A. D. Allbutt, *Chem. Comm.* 14 (1966).

[50] Ö. K. J. Kovács to be published.

substitution. The ratio of the two olefins was practically the same in each reaction product (1-acetoxymethylcyclohexene: 3-acetoxymethylcyclohexene = 2:1), in accordance with the Saytzeff rule. Accordingly, the results of the solvolysis of VIIIa, under the conditions applied by us, show no similarity to the solvolysis of 2-alkylcyclohexyl tosylates[51-53] or menthyl and neomenthyl tosylates.[54] Hence, neither an E_1 type elimination mechanism involving hydrogen participation[54] of the β-neighbouring tertiary hydrogen, nor an E_2 type elimination involving nucleophilic participation by the solvent seems probable. Considering that both olefins (XVIII and XIX) are formed, the mechanism is most probably an E_1 type process involving a solvated classical carbonium ion (XXI), since this ion can be converted into both olefins (Fig. 4).

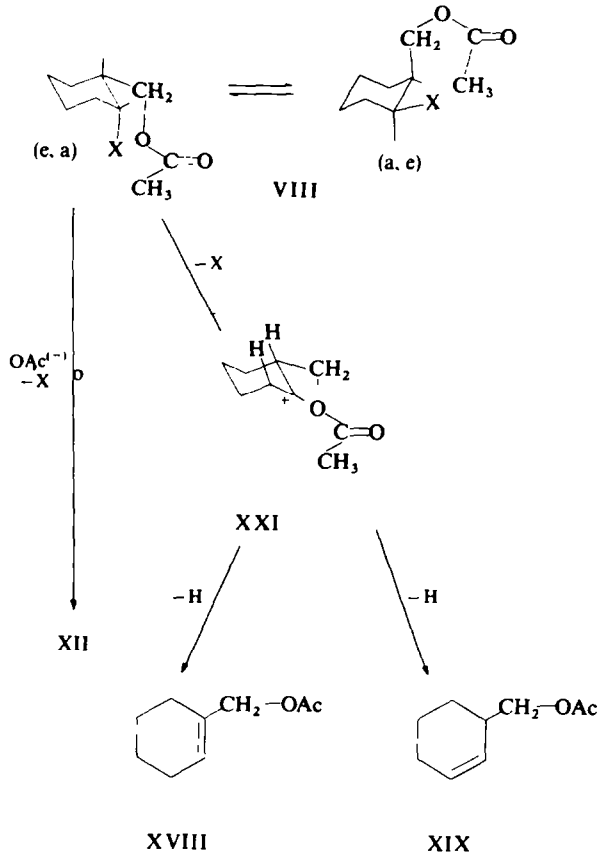

FIG. 4

[51] W. Hückel, D. Mancher, O. Fechtig, J. Kurz, M. Heinzel and A. Hubele, *Liebigs Ann.* **645**, 115 (1961).
[52] W. Hückel and S. K. Gupté, *Liebigs Ann.* **685**, 105 (1965).
[53] H. L. Goering and R. L. Reeves, *J. Am. Chem. Soc.* **78**, 4931 (1956).
[54] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *J. Am. Chem. Soc.* **74**, 1127 (1952).

The acetolysis of *trans*-acetate-tosylate (IXa) afforded mainly diacetate, resulting from substitution. The suppression of the elimination process was particularly striking in the acetolysis made in the presence of potassium acetate (overall olefin content 9·75%). This fact supports the participation of the acetoxy group, since a decrease in olefin formation indicates that the processes involving a classical carbonium cation are less pronounced.[54,55] The measure of participation is well illustrated by a comparison of the amount of olefins formed in the solvolysis of IXa with the considerable amount of olefin reported in similar reactions of 2-alkylcyclohexyl arylsulphonates.[51-54] Considering that 22·5% orthoester (XVIa) was isolated in the ethanolysis of IXa and that 31·6% X-BF_4 could be obtained from the reaction of *trans*-acetate-brosylate (IXb) with silver tetrafluoroborate, the assumption that the acetoxy group attached to the primary carbon atom takes part in the ionization of the secondary arylsulphonyloxy group seems perfectly evident. This is further confirmed by the partial retention observed in the acetolysis (cf. Table 1), that is to say, by the formation of *trans*-diacetate (XII).

On the other hand, the relatively large amounts of olefin formed in the acetolysis in the absence of potassium acetate and in ethanolysis (29·7% and 34·7%, respectively) indicate that the conversion proceeds only in part through the carbonium ion X (Fig. 5). Presumably, in the first step of the reaction a classical carbonium ion (XXII)

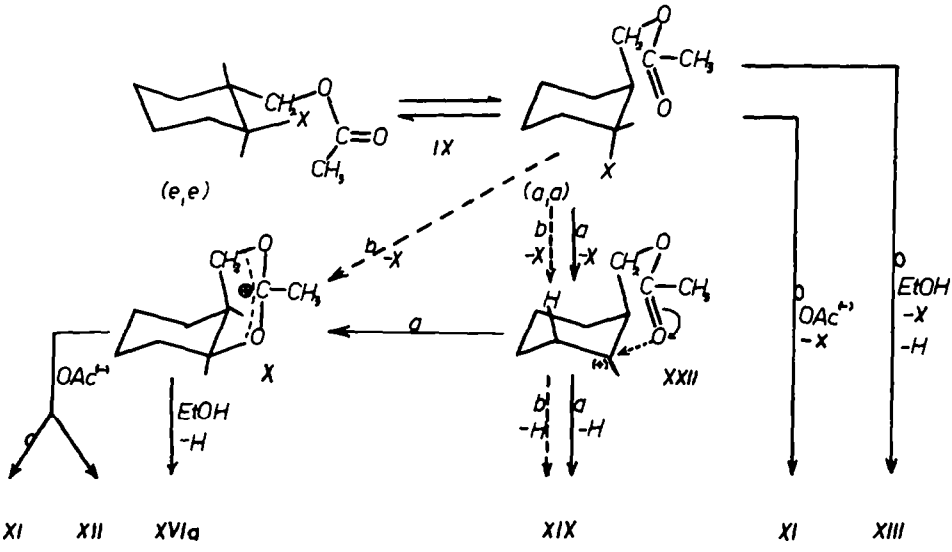

FIG. 5

is formed which may react in different ways; on one hand, by deprotonation it may yield olefin (XIX), on the other, subsequent participation of the acetoxy group may afford the cyclic acetoxonium ion (X). The latter gives, in the manner described for VIa, a mixture of XI and XII, and XVIa, respectively (pathway *a*). However, there is also possibilities for a direct acetoxy participation in the ionization of the arylsulphonyloxy group accompanied by a non-anchimeric process leading to the formation of the classical carbonium ion (XXII) (pathway *b*).

[55] S. Winstein and N. J. Holness, *J. Am. Chem. Soc.* 77, 5562 (1955).

As it is known, the k_{cis}/k_{trans} ratio in the solvolysis (e.g. ethanolysis) of 2-alkylcyclohexanol arylsulphonates is by an order of magnitude larger (e.g. ~90 for 2-methylcyclohexyl toluenesulphonate[56]), than for the corresponding 3- or 4-alkyl derivatives (e.g. 3·69 for 3-methylcyclohexyl toluenesulphonate;[57] 3·9 for 4-t-butylcyclohexyl toluenesulphonate[55]). This particular behaviour of 2-alkycyclohexyl toluenesulphonates has been interpreted in different ways.[58] In the ethanolysis of VIIIa and IXa (at 90°), we observed a k_{cis}/k_{trans} ratio of 3·3, while in the acetolysis (at 80°) this ratio was 5·1.[22] In our opinion the decrease of this ratio is to be attributed to the increase of the solvolysis rate of the *trans*-acetate-tosylate (IXa), i.e. to acetoxy group participation. In order to gain further insight into the formation of the 6-membered acetoxonium ion X we are studying the reaction of XI and XII with anhydrous hydrogen fluoride.[59]

Dolby *et al.*[20] reported the acetolysis of IXb under various conditions (without additive, in the presence of Ac_2O, KOAc, H_2O and TsOH) as well as the ethanolysis of the compound in connection with a study of the mechanism of the Prins reaction. Isolation of the orthoester (XVIa) in 19% yield and the observation of partial retention, i.e. formation of the *trans*-diacetate (XII) represent essentially the same result as obtained by us. After our experiments had been finished we learned about the newest results of Dolby and Schwarz.[21] An outstanding proof offered by this thorough and inventive work is that "the acetolysis of *trans*-2-acetoxymethylcyclohexyl brosylate-carbonyl-O^{18} (IXb) yields *cis*-diacetate (XI) containing nearly all of the O^{18}; saponification of the labelled diacetate yields *cis*-2-hydroxymethylcyclohexanol (XV) containing about 80% of the label indicating that the 6-membered acetoxonium ion (X) is an important intermediate". These authors express an opinion in full agreement with ours concerning the course of the reaction;[21] they conclude that "the acetolysis of *trans*-2-acetoxymethylcyclohexyl brosylate (IXb) proceeds in part by a normal solvolytic pathway".

There is only one discrepancy between the experimental results of Dolby *et al.* and our own, concerning the acetolysis[20,21] of IXb in the *presence* of potassium acetate. These authors did not find any of the *trans* compound (XII) formed with retention either in the diacetate, or in the diol obtained from it by hydrolysis, or in the acetonide derivative of the latter, though careful gas chromatographic and IR analyses were made. In contrast to this, we succeeded in detecting the presence of about 10·0% *trans*-diacetate (XII) in the same experiment, though in a spectroscopic way only. In our opinion, this discrepancy of the results is to be attributed to the difference in the concentrations and in the amount of potassium acetate employed. Dolby *et al.* worked at considerably lower concentrations (0·3M[20] and 0·172M[21]) and used more KOAc (3·65[20] and 2·35[21] equivalent) than we (0·8M concentration and 1·2 equivalent of KOAc). In the presence of higher acetate ion concentrations one may expect that the normal solvolytic displacement becomes prominent, because the experiments with labelled IXb[21] indicate that "the *cis*-diol obtained from acetolysis in the presence of acetate ion contained less O^{18} than the *cis*-diol resulting

[56] W. Hückel, R. Bross, O. Fechtig, H. Feltkamp, S. Geiger, M. Hanack, M. Heinzel, A. Hubele, J. Kurz, M. Mainer, D. Maucher, G. Näher, R. Neidlein and R. B. Rashingkar. *Liebigs Ann.* **624**, 142 (1959).

[57] W. Hückel, K. Thiele. *Chem. Ber.* **94**, 2027 (1961).

[58] see Ref. 47 p. 259.

[59] C. Petersen. *Tetrahedron Letters* 511 (1967).

from acetolysis in pure acetic acid". The deviation in the olefin ratio between the acetolysis experiments with *cis*-2-acetoxymethylcyclohexyl brosylate (VIIIb) (4:1)[21] and with VIIIa (2:1) may also be ascribed to the difference in the concentrations employed.

It is worth mentioning that on account of the difference in basicity of acetic acid and ethanol, Dolby and Schwarz[21] attach greater importance to the internally assisted pathway in acetic acid (about 80% participation,[21] on basis of the acetolysis of labelled IXb) than in ethanol (on basis of the isolation of the orthoester XVIa in 19% yield[20]). This conclusion is further evidence of our view that acetoxy participation, i.e. the k_Δ process is almost exclusively predominant in the acetolysis of *cis*-2-tosyloxymethylcyclohexyl acetate (VIa) under the conditions employed by us.

EXPERIMENTAL

All m.ps were determined on a Kofler block and are uncorrected.

cis-2-*Hydroxymethylcyclohexane* (XV) *and diacetate* (XI)

2-Hydroxymethylcyclohexanone (b.p. 114–118° at 16 mm, n_D^{20} 1·4792) was prepared in 21·1% yield according to Mannich and Brose[60] with the slight modification that as the reaction proceeded it was checked with bromothymol blue indicator. The ketoalcohol (58 g, 0·4 mole) was hydrogenated in MeOH (200 ml) in the presence of Raney-Ni catalyst (20 g) at 72 atm.[61] The crude product (49·5 g) was fractionated[32] and the main fraction (41·5 g, 76·7%, b.p. 143–146° at 7 mm, n_D^{25} 1·4871) converted to the acetonide derivative. A mixture of the crude diol (XV, 130 g, 1·0 mole), abs acetone (150 ml), abs benzene (500 ml) and a catalytic amount of *p*-toluenesulfonic acid was heated for 12 hr in a Soxhlet apparatus filled with anhyd $CaCl_2$. The mixture was neutralized with CaO and fractionated to yield the pure *cis*-2-hydroxymethylcyclohexane acetonide (152 g, 89·3%, b.p. 105° at 15 mm, n_D^{20} 1·4643, lit.[21] n_D^{20} 1·4566). (Found: C, 70·47; H, 10·43. Calc. for $C_{10}H_{18}O_2$: C, 70·56; H, 10·65%.) A mixture of the acetonide (85 g; 0·5 mole) and 1N HCl (20 ml) was heated to remove acetone, the mixture was neutralized with 1N NaOH in the presence of methyl orange indicator, extracted with ether, worked up in the usual way, and fractionated, to yield XV, which soon crystallized on standing (55·2 g, 85%, b.p. 144–146° at 7 mm, m.p. 50–51°[32], lit.[20] m.p. 47–47·5°). Compound cis-XI was prepared from XV in the usual way with Ac_2O–pyridine (b.p. 132° at 10 mm, n_D^{25} 1·4515; lit.[20] b.p. 118–120° at 2·5 mm, n_D^{25} 1·4493).

trans-2-*Hydroxymethylcyclohexanol and diacetate* (XII)

The reaction was carried out according to Matti,[62] starting with cyclohexene (480 g, 5·8 mole); the crude product was fractionated, the 4th fraction (392 g, b.p. 103–107° at 6 mm, n_D^{24} 1·4550) was deacetylated[32] according to Zemplén,[63] and the diol thus obtained (288 g) was converted to the acetonide. The procedure was similar to that described for XV, and 130 g (1·0 mole) of diol gave 148 g (86·9%) of acetonide, (b.p. 106–107° at 15 mm, n_D^{20} 1·4672; lit.[21] n_D^{25} 1·4588) (Found: C, 70·35; H, 10·52. Calc. for $C_{10}H_{18}O_2$: C, 70·56; H, 10·65%.) The hydrolysis of the acetonide (85 g, 0·5 mole), as described for XV, yielded 58 g (89·2%) of pure *trans*-2-hydroxymethylcyclohexanol (b.p. 103–105° at 1 mm, n_D^{20} 1·4858; lit.[20] b.p. 122–124° at 2 mm, n_D^{25} 1·4829). Compound XII was prepared in the usual way from *trans*-diol with Ac_2O–pyridine (b.p. 133–134° at 10 mm; n_D^{25} 1·4510; lit.[20] b.p. 124–126° at 6 mm; n_D^{25} 1·4497).

Preparation of cis- *and* trans-2-*arylsulfonyloxymethylcyclohexyl acetate* (VIa, VIb, VIIa, VIIb)

p-Toluenesulfonyl chloride (19·0 g; 0·1 mole) or *p*-bromobenzenesulfonyl chloride (25·55 g; 0·1 mole) was added dropwise to a soln of *cis*-XV (13·0 g, 0·1 mole) in abs pyridine (20 ml) at 0°. After standing 24 hr, pyridine hydrochloride was filtered off, and the filtrate added to ice-cool 20% H_2SO_4. The mixture was extracted with ether, washed with water and sat $NaHCO_3$aq, and worked up. The product, which usually crystallized spontaneously, was crystallized from ether. The corresponding *trans* derivative was prepared analogously.

[60] C. Mannich and W. Brose. *Ber. Dtsch. Chem. Ges.* **56**, 833 (1923).

[61] M. Mousseron, J. Julien and F. Winternitz. *Bull. Soc. Chim. Fr.* 878 (1948).

[62] J. Matti. *Bull. Soc. Chim. Fr.* 974 (1932).

[63] G. Zemplén. *Ber. Dtsch. Chem. Ges.* **61**, 1646 (1928).

A soln of the so-obtained *cis*- or *trans*-2-*p*-toluensulfonyloxymethylcyclohexanol (28·43 g, 0·1 mole) and *cis*- or *trans*-2-*p*-bromobenzenesulfonyloxymethylcyclohexanol (34·92 g; 0·1 mole), respectively, in abs pyridine (40 ml) was treated with Ac_2O (15·58 g; 0·15 mole). After standing 24 hr, the mixture was poured into ice-cool 20% H_2SO_4. The crystalline arylsulfonyloxy-acetate was filtered off, dissolved in ether, the soln washed with sat $NaHCO_3$ aq until neutral, dried, decolourized and concentrated to half or one-third of its original volume. A crystalline product was obtained, which was filtered off and washed with ether.

cis-2-p-*Toluenesulfonyloxymethylcyclohexyl acetate* (VIa), m.p. 67°, yield 29·5 g, 90·2%. (Found: C, 58·82; H, 6·72. $C_{16}H_{22}O_5S$ requires: C, 58·88; H, 6·79%) The intermediate 2-tosyloxymethylmonool had m.p. 59° (17·1 g, 60·5%). (Found: C, 59·19; H, 6·99. $C_{14}H_{20}O_4S$ requires: C, 59·12; H, 7·05%.)

cis-2-*Bromobenzenesulfonyloxymethylcyclohexyl acetate* (VIb), m.p. 50–51°, yield 35·2 g, 89·9%. (Found: C, 45·98; H, 4·92. $C_{15}H_{19}O_5SBr$ requires: C, 46·04; H, 4·89%.) The intermediate 2-brosyloxymethylmonool (22·1 g, 63·1%) had m.p. 47–48° (lit.[64] m.p. 47–49°).

trans-2-p-*Toluenesulfonyloxymethylcyclohexyl acetate* (VIIa), m.p. 80°, yield 28·6 g, 87·7%. (Found: C, 58·72; H, 6·74. $C_{16}H_{22}O_5S$ requires: C, 58·88; H, 6·79%.) The intermediate 2-tosyloxymethylmonool (18·5 g, 65·0%) had m.p. 75–76° (lit.[65] m.p. 75·5–76·5°).

trans-2-p-*Bromobenzenesulfonyloxymethylcyclohexyl acetate* (VIIb), m.p. 67°, yield 33·5 g, 85·6%. (Found: C, 46·12; H, 4·78. $C_{15}H_{19}O_5SBr$ requires: C, 46·04; H, 4·89%.) The intermediate 2-brosyloxymethylmonool (25·8 g, 73·9%) had m.p. 83–84° (lit.[64] 82–84°).

Preparation of cis- *and* trans-2-*acetoxymethylcyclohexyl arylsulfonates* (VIIIa, VIIIb, IXa, IXb)

cis-XV, and *trans*-2-Hydroxymethylcyclohexanol (13·0 g; 0·1 mole) respectively, was dissolved in abs pyridine (40 ml) and Ac_2O (10·39 g; 0·1 mole) was added dropwise at about −20°. After standing 24 hr, the mixture was diluted with water, the oily phase dissolved in ether, the soln washed with 10% H_2SO_4, water, and finally with sat $NaHCO_3$ aq. The solvent was removed in vacuum and the oily product fractionated. A soln of 17·22 g (0·1 mole) of each of the thus obtained 2-acetoxymethylcyclohexanols in abs pyridine (20 ml) was cooled to 0° and *p*-toluenesulfonyl chloride (19·05 g; 0·1 mole) or *p*-bromobenzenesulfonyl chloride (25·55 g; 0·1 mole), respectively, in abs pyridine (20 ml) was added. The soln was kept for 24 hr, filtered and poured into ice-cool 20% H_2SO_4. The crystalline product was filtered off, dissolved in ether, the soln washed with sat $NaHCO_3$ aq to neutral, dried, decolourized, and concentrated in vacuum. The residue was crystallized from ether–petrol ether.

cis-2-*Acetoxymethylcyclohexyl* p-*toluenesulfonate* (VIIIa), m.p. 70–72°, yield 25·5 g (78·12%). (Found: C, 58·99; H, 6·83. $C_{16}H_{22}O_5S$ requires: C, 58·88; H, 6·79%.) The intermediate *cis*-2-acetoxymethylmonool (14·2 g, 82·4%) had b.p. 128° at 6 mm, (main fraction); n_D^{23} 1·4630. (Found: C, 62·84; H, 9·45. $C_9H_{16}O_3$ requires: C, 62·78, H, 9·36%.)

cis-2-*Acetoxymethylcyclohexyl* p-*bromobenzenesulfonate* (VIIIb), m.p. 90–92° (lit.[21] 98–99°), yield 25·0 g, 63·8%. (Found: C, 46·12; H, 4·82. Calc. for $C_{15}H_{19}O_5SBr$: C, 46·04; H, 4·89%.)

trans-2-*Acetoxymethylcyclohexyl* p-*toluenesulfonate* (IXa), m.p. 83°, yield 28·0 g (85·7%). (Found: C, 58·63; H, 6·89. $C_{16}H_{22}O_5S$ requires: C, 58·88; H, 6·79%.) The intermediate *trans*-2-acetoxymethylmonool (13·0 g, 75·4%) had b.p. 129–130° at 6 mm (main fraction), n_D^{23} 1·4625. (Found: C, 62·71; H, 9·28. $C_9H_{16}O_3$ requires: C, 62·78; H, 9·36%.)

trans-2-*Acetoxymethylcyclohexyl* p-*bromobenzenesulfonate* (IXb), m.p. 91–92° (lit.[20] m.p. 91·5–93°; lit.[21] m.p. 91–92°), yield 21·5 g, 54·9%. (Found: C, 46·15; H, 4·85. Calc. for $C_{15}H_{19}O_5SBr$: C, 46·04; H, 4·89%.)

2-*Ethoxy*-2-*methyl*-cis-1,3-*dioxadecalin* (XVIa)

Compound *cis*-XV (13·0 g; 0·1 mole) was dissolved in ethyl orthoacetate (16·22 g; 0·1 mole) and the soln was heated in the presence of catalytic amount of *p*-toluenesulfonic acid to distil off the EtOH formed. At the end of the reaction the *p*-toluenesulfonic acid was neutralized with CaO, and the soln filtered and distilled to yield 17·5 g (87%) product, b.p. 98–100° at 6 mm, n_D^{25} 1·4536 (lit.[20] b.p. 103–106° at 15 mm, n_D^{25} 1·4534). (Found: C, 65·85; H, 9·98. Calc. for $C_{11}H_{20}O_3$: C, 65·97; H, 10·07%.)

Hydrolysis of the orthoester (XVIa) *in aqueous alcohol and in aqueous acetic acid*

Compound *cis*-XVIa (10·0 g, 0·05 mole) was dissolved in 96% EtOH (50 ml) containing a catalytic

[64] H. B. Henbest and B. B. Millward, *J. Chem. Soc.* 3575 (1960).

[65] S. Siegel, *J. Am. Chem. Soc.* **75**, 1317 (1953).

amount of *p*-toluenesulfonic acid. After standing for 3 hr the soln was neutralized with CaO, filtered and concentrated. The oily product (8·2 g, 94·6%; n_D^{23} 1·4648), which proved by gas chromatographic analysis to consist of a mixture of *cis*-2-acetoxymethylcyclohexanol and *cis*-2-hydroxymethylcyclohexanol (XV) was refluxed 1 hr with dry MeOH (50 ml) containing metallic Na (0·5 g). The solvent was removed in vacuum, the residue dissolved in ether (100 ml), the soln washed with water several times, and worked up to yield 5·7 g (76·1%) product, b.p. 143–146° at 7 mm, n_D^{25} 1.4876.[26] According to the IR spectrum, the product was identical with an authentic sample.

Repetition of the above experiment in 92% AcOH (in the absence of *p*-toluenesulfonic acid) gave 6·1 g (81·5%) homogeneous cis-XV.

trans-2-*Ethoxymethylcyclohexyl acetate* (XIV)

A soln of EtONa [2·75 g (0·12 g-atom) of Na in 50 ml of abs EtOH] was added to a soln of *trans*-2-*p*-toluenesulfonyloxymethylcyclohexanol (28·4 g; 0·1 mole) (cf., preparation of VIIa) in abs EtOH (100 ml), and the mixture was kept for 10 days. Na *p*-toluenesulfonate precipitated was filtered off, and the soln neutralized with 1N HCl in the presence of methyl red indicator. The solvent was removed in vacuum and the residue extracted with ether. The ethereal soln was dried, concentrated in vacuum, and the residue fractionated to yield 11·5 g (72·6%) of 2-ethoxymethylmonool, b.p. 110° at 13 mm, n_D^{25} 1·4590. (Found: C, 68·39; H, 11·55. $C_9H_{18}O_2$ requires: C, 68·31; H, 11·55%.)

A sample (7·91 g, 0·05 mole) of the above material was acetylated in 5 ml Ac_2O in the presence of 1 drop of H_2SO_4. After the usual working up and fractionation 7·8 g (77·0%) of XIV was obtained, b.p. 114–115° at 15 mm, n_D^{25} 1·4448. (Found: C, 65·92; H, 9·88. $C_{11}H_{20}O_3$ requires: C, 65·97; H, 10·07%.)

cis-2-*Ethoxycyclohexylcarbinyl acetate* (XIII)

Methyl *cis*-2-hydroxycyclohexanecarboxylate was dissolved in CH_2Cl_2, and triethyloxonium fluoroborate soln[39] added. The product, methyl *cis*-2-ethoxycyclohexanecarboxylate, b.p. 101–103° at 15 mm, n_D^{25} 1·4438 (lit.[21] b.p. 95–98° at 13 mm, n_D^{25} 1·4432) was reduced with LAH in ether and the resulting *cis*-2-ethoxycyclohexylcarbinol (b.p. 97–98° at 15 mm, n_D^{25} 1·4578; lit.[20] b.p. 93–95° at 13 mm, n_D^{25} 1·4573) was acetylated with Ac_2O in the presence of one drop H_2SO_4, b.p. 106–107° at 15 mm, n_D^{25} 1·4430 (lit.[20] b.p. 103–105° at 13 mm, n_D^{25} 1·4422). (Found: C, 65·85; H, 10·12. Calc. for $C_{11}H_{20}O_3$ C, 65·97; H, 10·07%.)

2-*Methylenecyclohexyl acetate* (XX)

2-Methylenecyclohexanol (b.p. 184° at 760 mm, n_D^{20} 1·4843, obtained from our earlier experiments[32]) was acetylated with Ac_2O–pyridine. The product had b.p. 82–83° at 15 mm, n_D^{25} 1·4546 (lit.[66] b.p. 83–84° at 20 mm, n_D^{25} 1·4552).

1-*Acetoxymethylcyclohexene* (XVIII)

Compound *cis*-VIIIb (39·13 g, 0·1 mole) was dissolved in isopropyl alcohol (200 ml) and the soln previously heated at 120°, was heated under reflux with $CaCO_3$ for 18 hr, (20·0 g; 0·2 mole). The soln was filtered, EtONa soln from (0·8 g of Na) was added, and the mixture heated under reflux for 2 hr. After cooling, the mixture was neutralized with 0·1N HCl in the presence of methyl red indicator, concentrated to $\frac{1}{3}$ its original volume, and diluted with 5 parts water. The soln was saturated with $(NH_4)_2SO_4$ and extracted with ether. Working up of the mixture gave an oily product which was distilled, yield: 4·6 g. (41·0%), b.p. 90–91° at 20 mm, n_D^{23} 1·4862 (lit.[67] b.p. 125° at 23 mm, n_D^{25} 1·4881).

1-Hydroxymethylcyclohexene was converted into the corresponding acetate (XVIII) in 77·5% yield with Ac_2O–pyridine. The product had b.p. 92–94° at 20 mm, n_D^{23} 1·4571 (Found: C, 69·92; H, 9·35. $C_9H_{14}O_2$ requires: C, 70·10; H, 9·15%.)

3-*Acetoxymethylcyclohexene* (XIX)

3-Bromocyclohexene[68] (16·1 g, 0·1 mole) was reacted with Mg turnings 2·9 g; 0·12 g-atom) in ether to give the Grignard reagent. Paraformaldehyde (12 g, 0·4 mole) was added in portions, the mixture was refluxed for 8 hr and added to a mixture of 10% H_2SO_4 (50 ml) and ice (200 g). The product was filtered off, the organic phase separated, and the aqueous layer extracted several times with ether. Working up of

[66] W. J. Bailey and J. C. Goossens, *J. Am. Chem. Soc.* **78**, 2804 (1956).
[67] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.* **75**, 939 (1953).
[68] E. A. Braude and E. S. Waight, *J. Chem. Soc.* 1116 (1952).

the combined organic phase and ethereal extracts and distillation of the product yielded 6·5 g (57·9%) of 3-hydroxymethylcyclohexene, b.p. 89–90° at 20 mm, n_D^{23} 1·4820 (lit.[69] b.p. 95° at 8 mm, n_D^{25} 1·4820). Acetylation of this compound with Ac_2O–pyridine gave XIX, b.p. 93–95° at 20 mm, n_D^{23} 1·4560 (lit.[69] b.p. 95–96° at 15 mm, n_D^{25} 1·4575).

cis-2-*Methyl*-1,3-*dioxadecalin* (XVII)

Compound *cis*-XV (13·0 g; 0·1 mole) was heated under reflux in acetaldehyde diethylacetal (17·71 g, 0·15 mole) in the presence of a catalytic amount of benzoyl chloride for 2 hr. The EtOH formed was removed and the mixture diluted with 1 vol ether, washed with water and sat $NaHCO_3$ aq, dried and concentrated in vacuum. The residue was fractionated to obtain XVII (14·3 g; 91·6%) as the main fraction, colourless oil, b.p. 94° at 18 mm, n_D^{25} 1·4575. (Found: C, 69·55; H, 10·24. $C_9H_{16}O_2$ requires: C, 69·68; H, 10·27%.)

2-*Methyl*-cis-4,5-*tetramethylene*-1,3-*dioxenium tetrafluoroborate* (X-BF_4)

(*a*) *From* 2-*ethoxy*-2-*methyl*-cis-1,3-*dioxadecalin* (XVIa). A soln of XVIa (4 g; 0·02 mole) in abs ether (5 ml) was cooled in acetone-dry ice, and BF_3-etherate (3·7 g; 0·026 mole) was added dropwise. A faint pink oily substance separated, which soon solidified. The ether was decanted with exclusion of moisture, the crystalline material was dissolved in dry acetonitrile and the soln was covered with a thin layer of petrol ether. The dioxenium salt deposited as long needles, in 97·1% yield (4·70 g), m.p. 52° (in sealed capillary tube). (Found: BF_4^-, 35·80. $C_9H_{15}O_2BF_4$ requires: BF_4^-, 35·87%.)

(*b*) *From* 2-*methyl*-cis-1,3-*dioxadecalin* (XVII). Compound XVII (6·24 g, 0·04 mole) was added to a soln of trityl fluoroborate[41] (6·6 g, 0·02 mole) in acetonitrile (10 ml) with ice-cooling. The reaction mixture soon became coloured and the orange-red soln deposited a crystalline material after standing several hr. This product (3·8 g, 78·1%) was filtered off with the exclusion of moisture, and crystallized from acetonitrile–pet. ether. The product was identical with the material (X-BF_4) obtained as described under (*a*).

(*c*) *From* VIb *and* IXb. Compound *cis*-VIb (7·84 g, 0·019 mole) was dissolved in abs. CH_2Cl_2 (10 ml), and a soln of silver tetrafluoroborate[42] (38 ml; 0·5M; 0·019 mole) in CH_2Cl_2 was added. The reaction mixture soon became turbid and squanous silver *p*-bromobenzenesulfonate deposited. The reaction was completed by keeping the mixture in a thermostat at 25° for 24 hr. The crystals were collected with the exclusion of moisture, and the soln concentrated under slightly reduced press at 20°. The oily residue was crystallized as above, to give 2·52 g (54·1%) of X-BF_4, m.p. 52°. (Found: BF_4^-, 35·72. $C_9H_{15}O_2BF_4$ requires BF_4^-, 35·87%.)

When the above reaction was carried out with *trans*-IXb as the starting material, 1·15 g (31·6%) of X-BF_4 was obtained on seeding, m.p. 52°. (Found: BF_4^-, 35·68. $C_9H_{15}O_2BF_4$ requires: BF_4^-, 35·87%.)

From a similar reaction of VIIb (25°, 24 hr) the starting material was recovered unchanged practically in quantitative yield. In the case of VIIIb some Ag brosylate precipitation and some darkening of the soln could be observed. The reaction mixture was filtered, diluted with CH_2Cl_2, washed with sat $NaHCO_3$ aq and dried. This soln contained 21·5% of olefin,[34] calculated on the starting material. After evaporation of the solvent 5·65 g (72·2%) of VIIIb was recovered; m.p. 85–89°, mixed m.p. with an authentic sample: 88–90°

Reaction of 2-*methyl*-cis-4,5-*tetramethylene*-1,3-*dioxenium tetrafluoroborate* (X-BF_4) *with sodium alkoxide*

X-BF_4 (4·84 g, 0·02 mole) was added to a EtONa soln (25 ml, 1N) at 0° with the exclusion of moisture. After standing a few hr the alcohol was distilled, the residue extracted with ether and evaporated. Distillation of the residue yielded 1·4 g (35·1%) of *cis*-XVIa, b.p. 98–100° at 6 mm, n_D^{25} 1·4537.

A similar reaction with MeONa gave *cis*-XVIb in about the same yield, b.p. 112–115° at 20 mm, n_D^{20} 1·4575. (Found: C, 64·38; H, 9·72. $C_{10}H_{18}O_3$ requires: C, 64·50; H, 9·74%.)

Acetolysis of VIa-IXa

A mixture of anhyd AcOH (10 ml), Ac_2O (0·5 ml) and anhyd AcOK (1·2 g; 0·012 mole) was heated under reflux with the exclusion of moisture for 2 hr.[2] The corresponding mixed tosylateacetates (VIa-IXa; 3·26 g, 0·01 mole) were added to the cooled soln which was then again heated under reflux for 8 hr. After cooling, the soln was diluted with water, carefully neutralized with $NaHCO_3$ and thoroughly extracted

[69] A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.* **81**, 667 (1959).

with ether. The ethereal soln was dried, evaporated to dryness in vacuum, and the residual crude product subjected to gas chromatographic and IR[35] analysis, and to Kaufmann titration[34] (cf. Table 1).

The second series of experiments were carried out analogously but without AcOK (cf. Table 1).

Ethanolysis of VIa-IXa

A mixture of the mixed tosylate-acetate (VIa-IXa; 32·64 g; 0·1 mole), anhyd AcOK (12 g; 0·12 mole; dried over P_2O_5) and abs EtOH (200 ml) was heated under reflux for 6–40 hr with the exclusion of moisture (cf. Table 2). The mixture containing a ppt was neutralized with 2N EtONa in the presence of bromothymol blue indicator; abs ether was added, and the crystalline potassium *p*-toluenesulfonate was filtered off. The filtrate was concentrated to $\frac{1}{3}$ its original vol and more abs ether (100 ml) was added to complete the precipitation of potassium tosylate. After filtration, the solvent was removed and a sample of the oily residue was subjected to gas chromatographic, spectroscopic[35] and titrimetric analyses[34] (cf. Table 2). The oily residue was fractionated using a 5 cm long column filled with Helipack. The fractions were identified by their physical constants and by gas chromatographic analysis. The configurations of the diacetates (XVI and XVII) were checked by spectroscopy.[35] For the sake of simplicity, in the following the original weights of crude products, i.e. those measured prior to drawing samples will be given together with the yields based thereon.

Processing of the reaction mixture

(a) *Crude product* VIa: 19·6 g. Fraction 1: Compound XVIa (14·2 g; 71%), b.p. 116–118° at 10 mm, n_D^{25} 1·4534. Fraction 2: *cis*-XI (4·5 g; 21%), b.p. 138–140° at 10 mm, n_D^{25} 1·4495.

(b) *Crude product* VIIa: 20·2 g. Fraction 1: 1·7 g. (8·1%), b.p. up to 110° at 15 mm. According to gas chromatographic analysis this fraction was a mixture of XX and *trans*-XIV. Fraction 2: *trans*-XII, (17·6 g; 83%), b.p. 144–146° at 15 mm, n_D^{25} 1·4540.

(c) *Crude product* VIIIa: 14·9 g. Fraction 1: 12·7 g (83%), b.p. 92–95° at 20 mm, n_D^{25} 1·4557. According to gas chromatographic analysis this fraction consisted of a 2:1 mixture of XVIII and XIX. Fraction 2: *trans*-XII (1·3 g; 6%), b.p. 145–148° at 15 mm, n_D^{25} 1·4548.

(d) *Crude product* IXa: 17·5 g. Fraction 1: Compound XIX (4·45 g; 29%), b.p. 77–79° at 10 mm, n_D^{25} 1·4558. Fraction 2: 9·3 g (46·5%), b.p. 100–120° at 10 mm; gas chromatographic analysis showed it to be approx a 1:1 mixture of *cis*-XIV and XVIa. Fraction 3: *cis*-XI (2·45 g; 11·5%, b.p. 139–140° at 10 mm, n_D^{25} 1·4492.

Fraction 2 (9·3 g, oil) was hydrolysed (1 g of Na in 50 ml abs MeOH, 1 hr under reflux). After cooling, the reaction mixture was neutralized with 1N HCl, concentrated, and the residue extracted with ether. The ethereal extract was worked up in the usual way and fractionated. *Fraction* 1: *cis*-2-ethoxycyclohexylcarbinol (3·4 g; 21·5%), b.p. 98–99° at 15 mm, n_D^{25} 1·4576. Fraction 2: *cis*-XV (2·9 g; 22·5%), b.p. 132–134° at 5 mm, n_D^{25} 1·4862.

Gas chromatographic analyses

These analyses were carried out with a Willy Giede GCHF 18·2 type apparatus, using H_2 as carrier gas and silicon grease supported on thermolyt in a 100 cm long column as the stationary phase. Thermostat temp: 120–180°.

IR analyses

An UR-10 (Jena) apparatus was applied using the base line method.[35] Various mixtures of *cis*-XI and *trans*-XII were measured and a diagram was constructed on basis of the 1132 and 910 cm^{-1} peaks, respectively; this was used for determining the ratio of the *cis*-XI and *trans*-XII, respectively.

Determination of double bonds

It was accomplished according to Kaufmann:[34] A 0·05N bromine soln was prepared in MeOH previously saturated with KBr. An excess of this soln was added to the sample containing the unsaturated compound. After the reaction was over, the excess bromine was titrated iodometrically.

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