The Role of Neighboring Groups in Replacement Reactions. V. The Effect of the Neighboring Acetoxy Group on the Course of the Replacement of the Tosylate Group of trans-2-Acetoxycyclohexyl p-Toluenesulfonate[1]
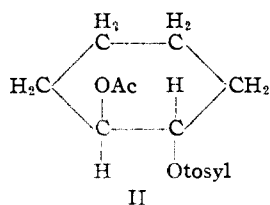
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In a recent communication it was reported that the erythro- and threo-2-acetoxy-3-bromobutanes and trans-1-acetoxy-2-bromocyclohexane are converted by silver acetate in dry acetic acid to diacetates with retention of configuration.[2] This steric result and the loss of optical activity when active 1-acetoxy-2-bromocyclohexane was treated with silver acetate in dry acetic acid led to the idea that the acetoxy group participated in the replacement process to give rise to the intermediate I. The presence of enough water in the acetic

I
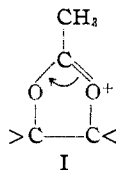
acid used as a medium for the action of silver acetate on the halides mentioned gave rise to an odd number of inversions[3] in contrast to the even number of inversions under anhydrous conditions.

We now report quite analogous results in the homogeneous solvolysis of trans-2-acetoxycyclohexyl p-toluenesulfonate[4] II in acetic acid containing potassium acetate.

II

When trans-2-acetoxycyclohexyl tosylate is refluxed with potassium acetate in dry acetic acid a diacetate is produced which is at least 93% trans so that retention of configuration is by far the predominant steric result.[5] Thus the bulk of the replacement process must be by way of the intermediate I, which reacts with acetate ion.[2]

This is further indicated by the loss of activity[2] which is experienced when the replacement process is carried out with the acetate-tosylate derived from active trans-1,2-cyclohexanediol by first tosylating and then acetylating the glycol. Almost pure levorotatory glycol, m. p. 111°, $[\alpha]D$ 30.2°, (0.221 g. in 25.0 ml. solution, chloroform as solvent) when converted to active acetate–tosylate, then to diacetate and then back to glycol, gave rise to completely inactive, almost pure trans-glycol. This, on recrystallization, yielded pure inactive trans-glycol, m. p. 104°. This is a more satisfactory demonstration of the loss of activity due to a neighboring acetoxy group than was possible before.[2]

In the presence of enough water in the acetic acid, the acetate-tosylate gave rise to the ester of pure cis-glycol, and intermediate amounts of water caused the production of esters of both cis- and trans-glycol.[6] A series of experiments was carried out in which small amounts of acetate-tosylate were treated with potassium acetate in acetic acid of varying water content. The crude diacetate was saponified and the resulting crude glycol was recrystallized. Under the conditions of concentration employed, acetic acid of higher melting point than 15.75° yielded a glycol mixture from which trans-glycol could be obtained by recrystallization. Acetic acid of melting point below 15.50° yielded a mixture from which cis-glycol was obtained.

Table I summarizes the results of the series of experiments. The third column indicates where very low recoveries of pure glycol were obtained by the recrystallization. The arrows indicate the directions of increase in these recoveries. Included in Table I are the results of three other qualitative experiments which yielded glycols very largely cis.

Several larger runs were made in which the acetate–tosylate was treated with potassium acetate in acetic acid of varying water content and

(1) A portion of the material reported in this paper was presented before the Organic Division at the St. Louis meeting of the American Chemical Society, April, 1941.

(2) Winstein and Buckles, THIS JOURNAL, 64, 2780 (1942).

(3) Winstein and Buckles, ibid., 64, 2787 (1942).

(4) Criegee and Stanger, Ber., 69B, 2753 (1936).

(5) cis-Diacetate is not transformed to trans under the conditions of the replacement process.

(6) Criegee and Stanger[4] have recommended the reaction of the trans-acetate–tosylate with potassium acetate in acetic acid for preparing cis-1,2-cyclohexanediol. These authors must have used acetic acid with a considerable water content.

TABLE I

SUMMARY OF QUALITATIVE EXPERIMENTS ON THE EFFECT OF WATER CONTENT OF ACETIC ACID ON THE STERIC RESULT OF CONVERSION OF *trans*-2-ACETOXYCYCLOHEXYL *p*-TOLUENESULFONATE TO MONO- AND DIACETATE

M. p. of AcOH, °C.	Config. of recryst. glycol	Recovery on recryst.
16.7[a]	*trans*	
16.0	*trans*	
15.85	*trans*	
15.75	*trans*	low
15.50	*cis*	low
15.30	*cis*	
15.0	*cis*	
14.6	*cis*	
14.1	*cis*	
13.1	*cis*	
10.4	*cis*	
16.7[a,b]	*cis*	high
14.6[b]	*cis*	high
[c]	*cis*	high

[a] Small excess of acetic anhydride present. [b] No potassium acetate added. [c] Solvent was absolute alcohol.

the ester was isolated by distillation. Here it is possible to estimate the steric results quite accurately.[2] Table II summarizes some of the results.

TABLE II

STERIC RESULTS AND PRODUCTS OF REACTION OF *trans*-2-ACETOXYCYCLOHEXYL TOSYLATE WITH POTASSIUM ACETATE IN ACETIC ACID

M. p. of AcOH, °C.	% H_2O	Mole ratio H_2O/-tosylate	Mole % mono-acetate	M. p. of glycol,[a] °C.	Steric result
..	0	0	0	100	93% Retention
16.0	0.35	0.20	16	85	68% Retention
10.3	4.0	2.3	65	98	100% Inversion

[a] M. p. of *trans*-glycol, 104°; *cis*-glycol, 98°.

In line with the previous discussion,[3] the most likely explanation of the effect of water is that it reacts with intermediate I to give orthomonoacetate III which isomerizes to ordinary monoacetate IV. The validity of this explanation has
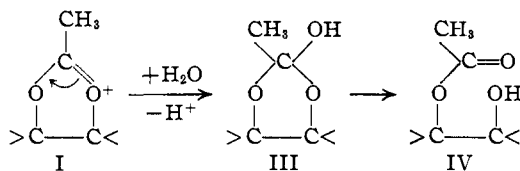

been indicated by the study of the acetate-tosylate II in alcohol. Criegee and Stanger[4] have already reported that the acetate–tosylate gives rise to quite pure *cis*-ester on refluxing with potassium acetate in absolute alcohol. We have confirmed this steric result in alcohol (see Table I and experimental part). Also, we have isolated the ester

product and found it to be pure monoacetate. Potassium acetate can be dispensed with. When the *trans*-acetate–tosylate is heated in absolute alcohol, to which a trace of water is added and in which calcium carbonate is suspended, a product is obtained which can be saponified directly to quite pure *cis*-glycol without being isolated.

The facts that acetate ion may be dispensed with in alcohol and that little or no ethyl ether V is produced are consistent only with the following mechanism for the replacement process.
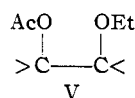

There is formed intermediate I which reacts with ethyl alcohol to give VI.[7] This loses a proton to give an orthoacetate derivative VII which eventually[8] gives the ordinary monoacetate IV. We plan to prepare VII and show whether the conversion to monoacetate does indeed proceed. Also we shall attempt to isolate VII from the reaction mixtures.
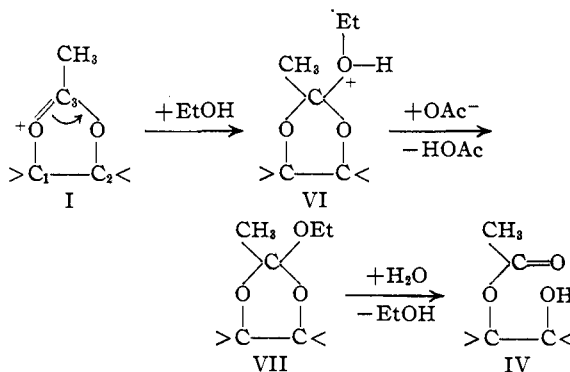
From the previous[3] and the present work, it appears that intermediate I reacts with water and alcohol at carbon atom C-3 and with acetate ion

(7) It must be noticed that part, at least, of VI might be formed from reaction of molecules to which alcohol has already added, as follows
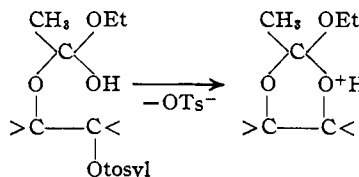
(8) A possible route from VII to IV is as follows
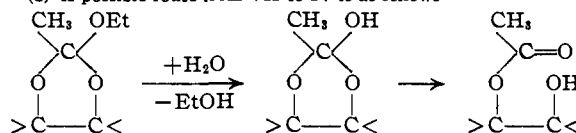
It is possible that the orthoacetate exists up to the time that water is added in isolating monoacetate from the reaction mixture.

TABLE III

SOME REPLACEMENT REACTIONS WITH A STERIC RESULT OF RETENTION OF CONFIGURATION BECAUSE OF PARTICIPATION OF NEIGHBORING GROUPS

| Neighboring group	Compound	Diastereomer used — dl or trans or threo — inactive	active	erythro or meso — inactive	active	Leaving group	Extracting reagent	Entering group	Ref.
—O⁻ of							Solvent	OH⁻	
—COO⁻	RCHBrCOO⁻					Br⁻	Ag⁺	OC₂H₅⁻	10
—Br	CH₃CHBrCH(OH)CH₃	✓	✓	✓	✓	OH₂	Solvent	Br⁻	11, 12
	2-Bromocyclohexanol	✓							
—Cl	CH₃CHClCH(OH)CH₃	✓	✓	✓	✓	OSOCl⁻?		Cl⁻	13
—Br	2-Bromocyclohexyl p-Toluenesulfonate	✓				OTs⁻	Solvent	Br⁻	12
—Br	CH₃CHBrCHBrCH₃	✓	✓	✓		Br⁻	AgOAc	OAc⁻	2
	1,2-Dibromocyclohexane	✓							
—Br	CH₃CHBrCH(OH)CH₃	✓		✓		OPBr₂⁻?		Br⁻	12, 14
	2-Bromocyclohexanol	✓							
—OH	CH₃CH(OH)CHBrCH₃	✓				Br⁻	AgOAc	OAc⁻	3
	2-Bromocyclohexanol	✓							
—OAc	CH₃CH(OAc)CHBrCH₃	✓		✓		Br⁻	AgOAc	OAc⁻	2
	1-Acetoxy-2-bromocyclohexane	✓	✓						
—OAc	2-Acetoxycyclohexyl p-Toluenesulfonate	✓	✓			OTs⁻	Solvent	OAc⁻	Present work

at carbon atoms C-1 and C-2. Also, the reactions with water and alcohol are very much faster than with acetate ion. One more reaction of intermediate I seems indicated. In dry acetic acid in the absence of potassium acetate, the acetate-tosylate II yields, on heating, a diacetate which is about 90% *cis*, so that predominant inversion is the steric result (see Table I and experimental part). Apparently, without any acetate ions to react with intermediate I at carbon atoms C-1 or C-2, a reaction path to *cis*-diacetate is available. This may be as follows
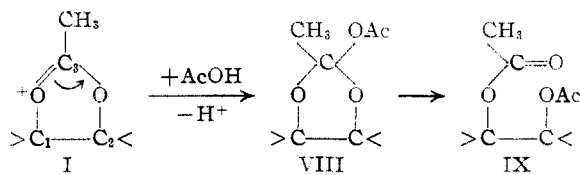
I reacting at carbon atom C-3 with even the poor electron-donor, acetic acid. The subsequent loss of a proton gives the orthodiacetate VIII which, under the conditions prevailing, is isomerized to the normal diacetate IX.[9] The only inversion in the whole process is during the formation of intermediate I. We may attempt to synthesize and study VIII.

(9) If the mechanisms we have outlined are correct, acetate ion reacts with intermediate I at C-1 and C-2 faster than acetic acid at C-3. Therefore, it must react at C-1 and C-2 very much faster than acetic acid at C-1 and C-2. This seems to be evidence that the opening[2] of the ring of I by acetate ion is S_N2 in character. Also, it would appear that in the previous[2] work with silver acetate, the intermediate I reacts with acetate ion and not acetic acid. In the reaction mixtures using silver acetate, acetate ion is as effective as it is in 1 M potassium acetate solution in the homogeneous work.

Summary of Retentions of Configuration.—

There has been reported by us and others a number of S_N1 type replacement reactions which have a steric result of predominant retention of configuration. These have been discussed from the standpoint of the role of a neighboring group in causing this steric result and they are summarized in Table III.

Experimental

cis- and *trans*-1,2-Cyclohexanediol.—These substances were the same as those previously used.[2,3,12]

cis- and *trans*-1,2-Diacetoxycyclohexane.—These materials were prepared as before.[2]

Cyclohexene Oxide.—This material was prepared as before.[12]

dl-trans-2-Hydroxycyclohexyl-*p*-toluenesulfonate.—The monotosylate of *trans*-1,2-cyclohexanediol was produced from cyclohexene oxide and purified by the method of Criegee and Stanger.[4]

As mentioned by Criegee and Stanger,[4] the glycol monotosylate may also be prepared from *trans*-1,2-cyclohexanediol. To 1.00 g. of glycol in 10 ml. of dry pyridine was added 1.64 g. of good grade tosyl chloride and the mixture was allowed to stand overnight. Treatment of the mixture with dilute sulfuric acid and stirring yielded after several minutes a solid product, 1.58 g., 68%, after washing and drying. This product was suitable to acetylate without further purification.

dl-trans-2-Acetoxycyclohexyl-*p*-toluenesulfonate.—The acetylation of the glycol monotosylate was performed with excess acetic anhydride containing a trace of concentrated sulfuric acid (1 drop in 10 ml.). After the mixture had

(10) Cowdrey, Hughes and Ingold, *J. Chem. Soc.*, 1208 (1937).
(11) Winstein and Lucas, THIS JOURNAL, **61**, 1576, 2845 (1939).
(12) Winstein, *ibid.*, **64**, 2792 (1942).
(13) Lucas and Gould, *ibid.*, **63**, 2541 (1941).
(14) Winstein, *ibid.*, **64**, 2791 (1942).

stood overnight, it was poured into water. There was obtained a nearly quantitative yield of product which soon crystallized; m. p. 73–76°; recryst. from ligroin, m. p. 78°. The acetates from the monotoluenesulfonates prepared from oxide and glycol proved identical in melting point and mixed melting point.[4]

Active *trans*-1,2-Cyclohexanediol.—This substance was obtained by the resolution of *trans*-1,2-cyclohexanediol as carried out by Wilson and Read.[15] *l*-Menthoxyacetic acid was prepared by the method of Frankland and O'Sullivan[16] but the acid was distilled as Read and Grubb did.[17] The rotation of the distilled acid agreed with the report of Read and Grubb.

The *l*-menthoxyacetate from the *trans*-1,2-cyclohexanediol and *l*-menthoxyacetyl chloride in pyridine was obtained in ether solution by treatment of the reaction mixture with hydrochloric acid, extraction with ether, washing of the ether extracts with potassium carbonate solution, and drying of the ether extracts over potassium carbonate. Evaporation of the ether solvent yielded a residue of which nearly all turned solid on cooling. Washing of the residue with petroleum ether yielded a dry white solid. Several crystallizations of this solid from benzene consistently gave a small yield of the high-melting diastereomer of mono-*l*-menthoxyacetate of *trans*-1,2-cyclohexanediol, m. p. 126–127°.

The active glycol was conveniently obtained from the menthoxyacetate by saponification and then vacuum sublimation of the glycol from salts. A mixture of 1.00 g. of menthoxyacetate, 17 ml. of alcohol, and 1 ml. of 35% aqueous sodium hydroxide was refluxed for two hours. Then the solution was poured into an evaporating dish and saturated with carbon dioxide by the careful addition of dry-ice. Evaporation of the solvent left a solid, from which the glycol was sublimed at about 3 mm. A total of 3.46 g. menthoxyacetate yielded 1.11 g., 86%, of glycol, m. p. 109–110.5°, 109–111° (different preparations). This glycol was evidently not quite as pure as that of Wilson and Read,[15] m. p. 113–114°, but as pure as that of Derx,[18] m. p. 110.5°. The glycol on mixing with *dl-trans*-glycol showed a m. p. of 95–98°. A chloroform solution of 0.221 g. of the glycol in 25 ml. had αD (2 dcm.) 0.53°, $[\alpha]$D 30.2°.

Qualitative Experiments on the Conversion of *dl-trans*-2-Acetoxycyclohexyl-*p*-toluenesulfonate to Glycol.—To 10 ml. of acetic acid of known melting point was added 1 g. of potassium acetate. Sometimes a slight excess of acetic anhydride was added and the mixture heated two hours to destroy the water. Three grams of acetate–tosylate was added and the solution was heated four hours under reflux. The reaction mixture was allowed to cool and then it was poured into water. The mixture was neutralized with potassium carbonate and extracted with ether. The ether extracts were dried over potassium carbonate, the ether was distilled off and then the residue was directly saponified to glycol according to the saponification procedure previously[2] used for analyzing ester mixtures.

When the conversion was carried out in the absence of potassium acetate, the procedure was similar except that

(15) Wilson and Read, *J. Chem. Soc.*, 1269 (1935).
(16) Frankland and O'Sullivan, *ibid.*, 2329 (1911).
(17) Read and Grubb, *J. Soc. Chem. Ind.*, **51**, 329T (1932).
(18) Derx, *Rec. trav. chim.*, **41**, 312 (1922).

50 ml. of acetic acid was used and the reaction time was five hours at 100°.

To obtain the glycols, the saponification mixtures were at first saturated with carbon dioxide and allowed to evaporate, whereupon the glycol was extracted out of the solid with chloroform. The yields by this procedure were about 60%. Later, the glycols were extracted from the saponification mixture as in the saponification-analysis method used on the esters previously.[2] The yields by this method were in excess of 80%.

The glycols thus prepared tended to be impure and they melted at temperatures considerably lower than when the ester product could be isolated by distillation. However, by recrystallization from carbon tetrachloride, the predominant glycol could be obtained pure or still contaminated with the other glycol if the mixture was originally one with comparable amounts of the two glycols.

When sodium acetate replaced potassium acetate in dry or quite wet acetic acid, the results were quite unchanged.

When absolute alcohol was used as the solvent, 4.5 g. of acetate–tosylate, 6 g. of potassium acetate and 50 ml. of Commercial Solvents Gold Shield absolute alcohol were refluxed for thirty-six hours. At the end of the heating period, the mixture was filtered, the solid was washed with ether, the alcohol and ether were boiled off of the combined filtrate and ether washings and the residue was treated according to the saponification procedure. A 71% yield of glycol was obtained, which on recrystallization from carbon tetrachloride gave better than an 80% recovery of pure *cis*-glycol, m. p. 98.5°.

Conversion Reactions with Isolation of the Ester Products.—To a mixture of 100 ml. of glacial acetic acid (m. p. 16.0°), 5 ml. of acetic anhydride and 9.8 g. of potassium acetate, which had been refluxed one hour, was added 30 g. of acetate–tosylate and the solution was refluxed five hours. It was allowed to cool, poured into water, neutralized, extracted with ether and then the ether extracts were dried. Evaporation of the ether and distillation of the residue through a Weston[19] type column yielded 13.0 g., 68%, of diacetate, b. p. (12.5 mm.) 120.4–121.4°, n^{25}D 1.4476. The saponification method yielded a glycol melting at 100°, which corresponds to 93% *trans*. The refractive index of the sample was somewhat high. On redistillation, the main fraction had b. p. (12 mm.) 119.5–119.8°, n^{25}D 1.4470, the refractive index still high.

The same experiment was carried out using acetic acid of different water contents. Acetic acid, m. p. 10.3°, yielded 14.1 g., 85%, of product, b. p. (12 mm.) 114–116°, n^{25}D 1.4574 and saponification equivalent,[20] 128. This product yielded *cis*-glycol, m. p. 98°, on saponification. Acetic acid, m. p. 16.0°, yielded 15.4 g., 83%, of product b. p. (12 mm.) 114–118°, n^{25}D 1.4490 and saponification equivalent 105. This material yielded a glycol, m. p. 85°, predominantly *trans*.

In the absence of potassium acetate, 480 ml. of acetic acid (m. p. 16.4°) and 8 ml. of acetic anhydride were refluxed one hour, 30 g. of acetate–tosylate was added, and the mixture was held at about 100° for five hours. After the reaction mixture was cool, 0.1 mole of potassium acetate was added. Most of the acetic acid was distilled off

(19) Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).
(20) Redemann and Lucas, *ibid.*, **9**, 521 (1937).

at reduced pressure and the residue was poured into water. The mixture was neutralized with potassium carbonate and the diacetate was taken up in ether. The ether extract was dried over potassium carbonate, the ether was distilled off and the diacetate was isolated at reduced pressure; 12.9 g., 67%, of material, b. p. (12 mm.) 117.5–117.8°, n^{25}D 1.4480, saponification equivalent 99 (theoretical 100). By the saponification procedure, this product appeared to be 89% cis. A small part of the steric result may be due to reaction of some unreacted acetate–tosylate with potassium acetate during the distillation of acetic acid.

For the reaction in absolute alcohol, the procedure was as for the qualitative experiment except that 30 g. of acetate–tosylate was used. When the ether washings and alcohol solution were concentrated, the residue was poured into water and the ester was extracted out with ether. The ether extract was dried over potassium carbonate and the ester isolated by distillation at reduced pressure; 9.2 g., 60%, of material, b. p. (12 mm.) 113–113.2°, n^{25}D 1.4650, saponification equivalent 156.5, 99 mole per cent. monoacetate, was obtained. By the saponification procedure a glycol, mostly cis, m. p. 93°, was obtained. This result, together with the melting point of 96° obtained for the product in the absence of potassium acetate (see later) and the melting point of 96–98° reported by Criegee and Stanger[4] indicates that essentially pure cis-product is obtained in alcohol.

Conversion of Acetate–Tosylate of Active trans-1,2-Cyclohexanediol to the Diacetate of dl-trans-1,2-Cyclohexanediol.—1.02 g. of active glycol was tosylated as in the case of the dl-glycol, yielding 1.67 g., 70%, of crude monotosylate. As in the case of the dl-compound, the crude monotosylate was acetylated directly. The addition of water to the reaction mixture gave an oil which did not crystallize. The oil was finally extracted with 100 ml. of warm ligroin and the solution was dried over potassium carbonate. When the ligroin solution was cooled an oil came down which turned solid in a dry-ice bath and more loose solid developed on longer cooling. The solid could be filtered rapidly but it melted on the filter paper as it warmed up toward room temperature. Thus it appeared that the acetate–tosylate of the active glycol was quite low melting compared to the analogous dl-compound. The solid which was filtered off rapidly at low temperature was taken up in carbon tetrachloride, the carbon tetrachloride solution was washed with carbonate solution to remove any traces of acetic acid present and then dried over potassium carbonate. The volume of the solution was 34.5 ml., and the αD (2 dcm.) 1.22°. The carbon tetrachloride was pumped off at low pressure with the aid of a bath at 40–50° and the residue was refluxed four hours with a solution of potassium acetate in dry acetic acid. The reaction mixture was poured into water and treated in the usual way. The extracted diacetate was saponified in the usual way after the ether was driven off. The saponification mixture was saturated with carbon dioxide and allowed to evaporate. Vacuum sublimation yielded 0.24 g. of glycol. A much larger yield of glycol was obtained when dl-trans-glycol was carried through this whole procedure. One reason for the low yield was that considerable active acetate–tosylate was left in the ligroin solvent. When the ligroin solution remaining after filtration from the active acetate–tosylate was washed with carbonate solution, dried over potassium

carbonate, and pumped down to a volume of 29 ml., it had αD (2 dcm.) 0.44°. Another reason for the lower yield is the loss attending the extra handling which was necessary for the liquid acetate–tosylate.

The glycol in 25 ml. of chloroform showed αD (2 dcm.) ±0.00°. It melted over a range up to 96°. Mixing with dl-trans, m. p. 104°, raised the melting point. Recrystallization from carbon tetrachloride yielded 0.18 g. of glycol, m. p. 103.5–104°, no change on mixing with pure dl-trans glycol. The glycol in 25 ml. of chloroform showed αD (2 dcm.) ±0.00°.

Conversion of Acetate–Tosylate to cis-Ester in Alcohol without Potassium Acetate.—A mixture of 1.50 g. of acetate–tosylate, 0.50 g. of calcium carbonate, 17 ml. of absolute alcohol and two drops of water was heated under reflux for thirty-nine hours, and then filtered. Saponification of the ester and sublimation of the glycol yielded 0.33 g., 59%, of product, m. p. 90–96°. Recrystallization from carbon tetrachloride gave a nearly quantitative recovery of cis-glycol, m. p. 98° and the same on mixing with authentic cis-glycol.

Tests on the Stability of Esters under Reaction Conditions.—Two-gram portions of cis- or trans-1,2-diacetoxycyclohexane were subjected to the reaction conditions prevailing in the conversion reactions. Then the reaction mixtures were worked up as for the small qualitative experiments previously described.

cis-1,2-Diacetoxycyclohexane, after refluxing four hours with 1 g. of potassium acetate in 10 ml. of dry acetic acid yielded nearly pure cis-glycol, m. p. 96.5°. The trans-diacetate on refluxing four hours with 1 g. of potassium acetate and 0.54 g. of water in 10 ml. of acetic acid yielded nearly pure trans-glycol, m. p. 102.5°. The trans-diacetate after being held five hours at 100° with 1.72 g. of p-toluenesulfonic acid in 50 ml. of dry acetic acid yielded nearly pure trans-glycol, m. p. 102°.

Summary

trans-2-Acetoxycyclohexyl p-toluenesulfonate is converted to diacetate with predominant retention of configuration when it is heated with potassium acetate in dry acetic acid. Also, active trans-2-acetoxycyclohexyl p-toluenesulfonate gives rise to inactive diacetate. These results are explained by the participation of the neighboring acetoxy group in the replacement process to give rise to the intermediate
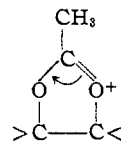
which reacts with acetate ion with a second inversion.

When trans-2-acetoxycyclohexyl p-toluenesulfonate is heated in sufficiently wet acetic acid with or without potassium acetate, in absolute alcohol with or without potassium acetate, or in dry acetic acid without potassium acetate, there are

isolated products (mono- or diacetates or mixtures) which are entirely or very largely of the cis-configuration. It is considered most probable

that orthoacetate intermediates are involved in these transformations.

Reversible Photochemical Processes in Rigid Media: The Dissociation of Organic Molecules into Radicals and Ions

By Gilbert N. Lewis and David Lipkin

In previous papers[1] we have studied the phosphorescent state of dye molecules. This phosphorescent state returns to the initial state with light emission and is to be regarded as isomeric with the normal molecule. On the other hand, the present paper deals with the photo-dissociation of organic molecules into radicals, ions and electrons.

In a study of the absorption spectra of odd molecules we desired to investigate diphenylnitrogen, the free radical of tetraphenylhydrazine, but at any temperature at which the dissociation is appreciable the radical disappears as fast as it is formed, through processes of rearrangement or disproportionation. We therefore attempted to produce diphenylnitrogen by illuminating a solution of tetraphenylhydrazine in our EPA solvent (see experimental section) at low temperature.

The solution in a quartz tube was immersed in liquid air contained in a quartz Dewar. After a minute or two of exposure to the light from a high-pressure mercury arc the solution acquired a green color which we attributed to the formation of the diphenylnitrogen radical, although we shall see presently that other substances are also produced. The color persists for many days at the temperature of liquid air but rapidly disappears when the temperature is raised sufficiently to make the solvent fluid.[2] This rise of temperature for EPA is about 10°. That the disappearance of color is not primarily the effect of temperature but of the change in rigidity of the solvent is shown by the fact that most of the phe-

nomena that we are going to describe are duplicated when the tetraphenylhydrazine is dissolved in glycerol or triethanolamine and illuminated at 190°K. and in a few cases similar phenomena have been obtained in glucose at room temperature.[3]

When the green solution is studied spectroscopically we find that, instead of one band, several prominent bands appear and we shall see that these belong to different substances, since their relative intensities vary greatly according to the way in which the solutions are prepared and treated. The absorption curves are shown in Fig. 1, in which the ordinates of each curve are proportional to the extinction coefficient, but with an arbitrary proportionality factor for each curve, since we have not yet determined the absolute concentration of any one of the substances.
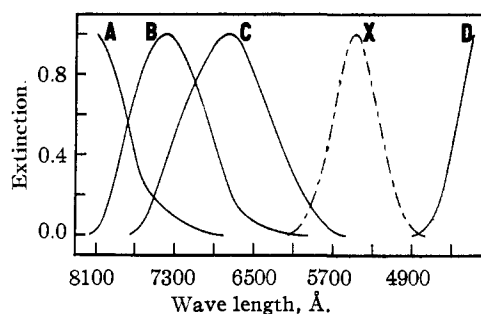

Fig. 1.—Absorption bands of tetraphenylhydrazine illuminated and measured in EPA at about 90°K. The ordinates for each curve are in arbitrary units.

In attempting to identify substances produced by illumination we are handicapped by

(1) (a) Lewis, Lipkin and Magel, This Journal, 63, 3005 (1941); (b) Lewis, Magel and Lipkin, ibid., 64, 1774 (1942).

(2) The production of color by illumination in the cold and its disappearance on warming may be repeated many times with the same sample, although eventually a permanent yellow color appears. Quantitative experiments show that when the initial illumination is carried to the point where all of the tetraphenylhydrazine is gone, more than 90% of it is regenerated on warming. From the fact that diphenylnitrogen is one of the chief products of the photo-dissociation and that this returns to tetraphenylhydrazine, even at very low temperatures, we have recently drawn certain conclusions regarding the heat of dissociation of the latter compound [Lewis and Lipkin, This Journal, 63, 3232 (1941)].

(3) The only antecedents that we have been able to find in the literature to the phenomena that are to be here described are in the inorganic field the coloration of glasses after long exposure to light and in the organic field the observations of Wieland [Ann., 381, 216 (1911)], who exposed crystalline substances such as the tetraarylhydrazines to electron bombardment at the temperature of liquid air. He obtained strong coloration which he attributed to free radicals. The color disappeared within a few minutes after the bombardment ceased.