Fraction 66 and subsequent fractions gave 100 mg. of an amorphous sirup which did not afford crystalline products.

Preparation of Hepta-O-acetyl-N-acetyl-α-lactosylamine.—Twenty five milligrams of IX was dissolved in 1.2 ml. of a 1:1 pyridine–acetic anhydride mixture, the solution was boiled for a few minutes, and allowed to stand for 24 hr. at room temperature. On removing the excess of reagents in a vacuum dessicator, the residue was dissolved in water. The solution on standing at +5° deposited 20 mg. of a solid material, m.p. 181–183°; $[\alpha]^{27}\text{D}$ +66.6° (*c*, 0.06; $CHCl_3$.)

D. Isolation of Hepta-O-acetyl-N-acetyl-α-lactosylamine from the Residual Sirup.—The mother liquors from which the N,N′-diacetyllactosylidenediamine was obtained, as described under B, were evaporated and the residue was exhaustively dried weighing 300 mg.; then it was dissolved in 7 ml. of a 1:1 mixture of pyridine–acetic anhydride. After 24 hr. at room temperature and warming for 30 min. in a boiling water bath, the solution was poured into ice–water. Practically all of the product was soluble. The aqueous solution was extracted with seven 20-ml. portions of chloroform, the combined chloroform extracts were washed with 2 *N* sulfuric acid, saturated sodium hydrogen carbonate solution, and water; then they were evaporated to dryness. On removing the chloroform by distillation, an amorphous solid was obtained, which did not crystallize from different solvents; consequently it was chromatographed on a column of talcum powder (5 parts) Celite 503 (1 part), 170 mm. by 30 mm. The substance was applied to the column in a solution of 3 ml. of benzene and 4 ml. of chloroform. The elution was performed with mixtures of benzene–absolute ethanol in the following way.

Fraction	Benzene:abs. ethanol	Volume, ml.
I	100:0,1	120
II	100:0,5	150
III	100:1	300
IV	100:1,5	150

The ratio benzene–absolute ethanol was gradually raised to 100:5, and the column was washed finally with acetone.

Fraction IV gave 120 mg. of material melting at 175°. After two recrystallizations from water, rhombic crystals of hepta-O-acetyl-N-acetyl-α-lactosylamine were obtained, m.p. 181–183°. A mixture of this compound and the hepta-O-acetyl-N-acetyl-lactosylamine obtained by direct acetylation of IX described under C, showed no melting point depression; $[\alpha]^{27}$°D +68,1° (*c*, 0.21; chloroform).

Anal. (for a sample dried at 120° and 2 mm.) Calcd. for $C_{28}H_{39}O_{18}N$: C, 49.61; H, 5.80; N, 2.07. Found: C, 49.62; H, 5.71; N, 2.07.

Abnormal Reaction of Benzoin with Thionyl Chloride

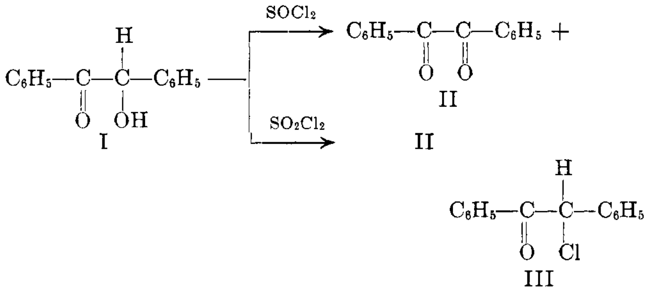
YASUAKI OKUMURA[1a]

Chemical Laboratory, Harvard University, Cambridge, Massachusetts

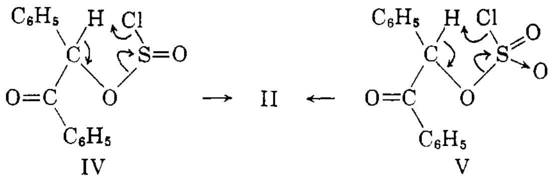
Received March 16, 1962

The formation of benzil (II) from benzoin (I) in the reaction with thionyl chloride at room temperature was proved to proceed *via cis*-stilbene-α,α′-diol sulfite (VI) by the fact that 2,2′,4,4′,6,6′-hexamethylstilbene-α,α′-diol sulfite (XIII) afforded mesitil (XI) and sulfur monoxide in pyrolysis, and that mesitoin (VIII) did not afford mesitil in the reaction with thionyl chloride. Ultraviolet spectra of the enediol sulfite (XIII) and its related compounds suggested that the enediol sulfite system could be regarded as a chromophore with an absorption maximum at 260 mμ.

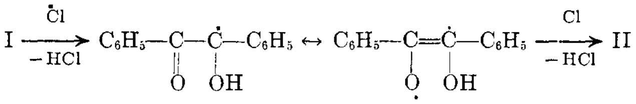
In the previous paper,[1b] it was reported that benzoin (I) reacted with thionyl chloride at room temperature and gave a mixture of benzil (II) and desyl chloride (III) containing a small amount of sulfur, and that sulfuryl chloride converted benzoin into benzil in almost quantitative yield.



The formation of benzil from benzoin could be accounted for by postulating three different reaction paths. (1) The chlorine atom of the chlorosulfite (IV) or the chlorosulfate (V) could abstract the α-hydrogen.

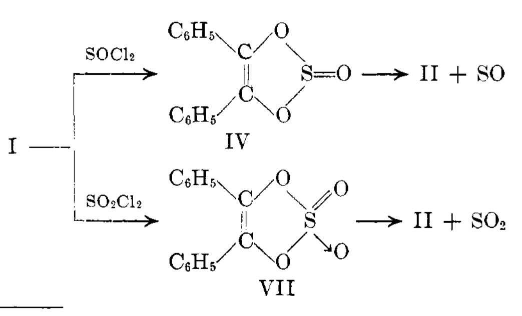


(2) The reaction (especially with sulfuryl chloride) could proceed through a process involving a semiquinone-type free radical like that in the oxidation of benzoin in alkaline alcoholic solution.[2]



$$I \xrightarrow[-HCl]{\dot{C}l} C_6H_5-\underset{O}{\overset{\|}{C}}-\underset{OH}{\dot{C}}-C_6H_5 \leftrightarrow C_6H_5-\underset{\dot{O}}{C}=\underset{OH}{C}-C_6H_5 \xrightarrow[-HCl]{Cl} II$$

(3) The reaction could proceed through *cis*-stilbene-α,α′-diol sulfite (VI) or sulfate (VII) as its intermediate.

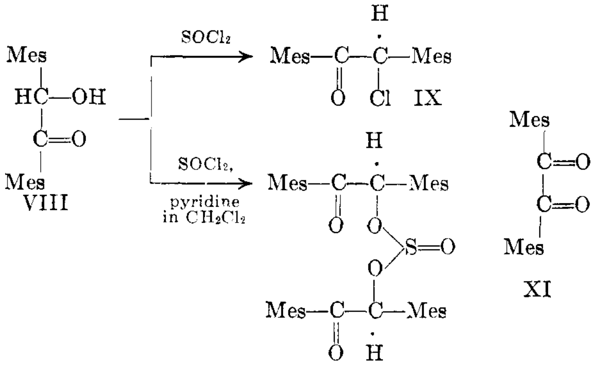


---

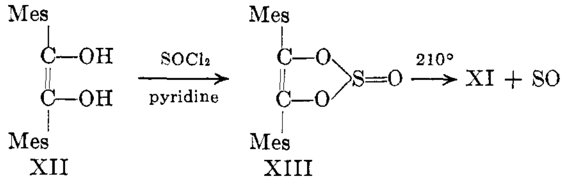
[1] (a) Recipient of a Fulbright travel grant on leave from Nagoya University Graduate School (1959–1961). Present address: Chemical Institute, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan. Reprints may be requested at this address. (b) Louis F. Fieser and Yasuaki Okumura, *J. Org. Chem.*, **27**, 2247 (1962).

[2] L. Michaelis and E. S. Fetcher, *J. Am. Chem. Soc.*, **59**, 1246 (1937); J. L. Ihrig and R. G. Caldwell, *ibid.*, **78**, 2097 (1956).

Mesitoin (VIII)[3] without a solvent reacts readily with thionyl chloride even under cooling in an ice bath and gives only 2,2′,4,4′,6,6′-hexamethyldesyl chloride (IX); but when treated with thionyl chloride and pyridine in methylene chloride at −20°, mesitoin gives bis(2,2′,4,4′,6,6′-hexamethyldesyl) sulfite (X). On the other hand, mesitoin, when treated with sulfuryl chloride, is converted into mesitil (XI) only in 5% yield, whereas benzoin is converted into benzil in almost quantitative yield. These facts would tend to eliminate the possibility of reaction paths 1 and 2. Reaction path 3 is, therefore, the most probable one, though neither intermediates VI nor VII could be isolated.

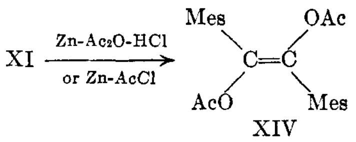


Mes = 2,4,6-trimethylphenyl



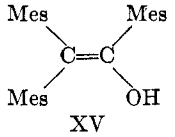
Since 2,2′,4,4′,6,6′-hexamethylstilbene-α,α'-diol exists in stable *cis*- and *trans*-forms in inert gases,[3] the *cis*-enediol (XII) should form the corresponding enediol sulfite (XIII). When the enediol (XII) prepared according to the method described by Fuson[3] was treated with thionyl chloride and pyridine in methylene chloride at −20°, it gave *cis*-2,2′,4,4′,6,6′-hexamethylstilbene-α,α'-diol sulfite (XIII) in 25.8% yield. This compound melted at 178–180° and decomposed at 210° into mesitil and sulfur monoxide.[4]

The fact that the desyl chloride (IX) is the sole product in the reaction of mesitoin with thionyl chloride at low temperature would indicate that steric hindrance due to the methyl groups in the *ortho* positions hampers the formation of the *cis*-enediol sulfite (XIII) by keeping two mesityl groups in the *trans* position. This assumption is supported also by the fact that reductive acetylation of mesitil (XI) afforded only *trans*-2,2′,4,4′,-6,6′-hexamethylstilbene-α,α'-diol diacetate (XIV) even when acetyl chloride was used instead of acetic anhydride–hydrochloric acid.[5] These facts would indicate that the formation of benzil from benzoin involves *cis*-stilbene-α,α'-diol sulfite (VI) or sulfate (VII) as its intermediate according to the use of the reagents.



The details of pyrolysis of the enediol sulfite (XIII) into mesitil (XI) can best be accounted for in the following manner. The pyrolysis of hydrobenzoin sulfite[6] gives desoxybenzoin from the *cis* isomer, and gives diphenylacetaldehyde from the *trans* isomer. In this pyrolysis, one of the C—O bonds of the sulfite ester group ionizes into a carbonium ion and a sulfite ion, and then migration of either hydride ion or phenyl group gives the product. In the pyrolysis of the enediol sulfite (XIII), however, since the C—C double bond, the two enolic oxygen atoms, and the sulfur atom lie in the same plane, and since the *p*-electrons on the oxygen atoms are conjugated with π-electrons of the C—C double bond, the mobility of electrons in the enediol sulfite system must be great and would facilitate splitting into the α-diketone and sulfur monoxide. Since the pyrolysis of perfluoro-4-octene-4,5-diol di(perfluorobutyrate) yields perfluoro-4,5-octanedione through a free-radical reaction path,[7] the enediol sulfite (XIII), likewise, may undergo decomposition through a free-radical process. The difference in stability between sulfur dioxide and sulfur monoxide would account for the fact that sulfuryl chloride converts benzoin into benzil in much better yield than does thionyl chloride.

Two mesityl groups in the molecule of the enediol sulfite (XIII) are not coplanar with the enediol sulfite group as the Stuart atomic models make clear. However, from ultraviolet spectral data, Rodebush and Feldman[8] have suggested that one mesityl group in the molecule of trimesitylvinyl alcohol (XV) must be coplanar with the vinyl alcohol group. The n.m.r. spectrum of XIII in carbon tetrachloride at 60 Mc. has three signals at 401 c.p.s. (a), 130 c.p.s. (b), and 124 c.p.s. (c), respectively (hexamethyldisiloxane, $\tau = 9.80$ p.p.m., as internal reference), and their area-ratio (a:b:c) is 2:3:6. They are assigned as follows: (a) ($\tau = 3.12$): four hydrogen atoms on the aromatic rings; (b) ($\tau = 7.63$): six hydrogen atoms on two methyl groups in the 4- and 4′-positions; (c) ($\tau = 7.73$): twelve hydrogen atoms on four methyl groups in the 2-, 2′-, 6- and 6′-positions. If XIII is in the same circumstances as were suggested for the vinyl alcohol (XV), the mesityl group coplanar with the enediol sulfite group would bring one methyl group in the *ortho* position very close to the oxygen atom, and the interaction between the methyl hydrogens and the oxygen atom would affect the n.m.r. spectrum of the methyl hydrogens. Therefore, both mesityl groups in the enediol sulfite (XIII) must be nearly perpendicular to the plane of the enediol sulfite group.



XV

---

[3] R. C. Fuson, C. H. McKeever, and J. Corse, *J. Am. Chem. Soc.*, **62**, 600 (1940).

[4] Sulfur monoxide is in equilibrium as expressed by the equation: $2\,SO \rightleftarrows SO_2 + {}^1/_2S_2$. This accounts for the origin of sulfur in the reaction mixture. H. Zeise, *Z. Physik. Chem.*, **B51**, 120 (1942).

[5] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., revised, D. C. Heath, Boston, Mass., 1957, p. 176. In this condition, benzil gives *cis*-stilbene-α,α'-diol diacetate exclusively.

[6] C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1211 (1954).

[7] J. J. Drysdale and D. D. Coffman, *ibid.*, **82**, 5111 (1960).

[8] W. H. Rodebush and I. Feldman, *ibid.*, **68**, 896 (1946).

The enediol sulfite (XIII) shows two very strong absorption bands in its infrared spectrum which are assigned to the enediol sulfite group at 1230 cm.$^{-1}$ (S=O) and 1211 cm.$^{-1}$ (enolic C—O), respectively. The shift of the sulfite absorption to a higher frequency[9] is analogous to the similar shift observed in the case of carboxylic enol esters.

The enediol sulfite(XIII) shows an ultraviolet absorption maximum at 261 mμ (ϵ = 10,650), and hydromesitoin(XVI) shows two absorption maxima at 269 mμ (ϵ = 585) and 276 mμ (ϵ = 485) (Fig. 1). On the other hand, hydrobenzoin[10] in ethanol shows two absorption maxima at 253 mμ (ϵ = 322) and 258 mμ (ϵ = 402), whereas *cis*-stilbene-α,α'-diol diacetate (XVII) in ethanol shows an absorption maximum at 265 mμ (ϵ = 12,800).[5] This bathochromic and hyperchromic shift of absorption observed in XVII can be attributed to the conjugation between the phenyl group and the C—C double bond of the enediol system. Since the aromatic rings in XIII are nearly perpendicular to the plane of the enediol sulfite group as the n.m.r. spectrum shows, conjugation between the aromatic ring and C—C double bond of the enediol sulfite group should be small, if at all. Therefore, the absorption–intensity differential curve for XIII—XVI with its maximum at 260 mμ (ϵ = 10,226) may be ascribed to the absorption by the enediol sulfite group. *trans*-2,2',4,4',6,6'-Hexamethylstilbene-α,α'-diol diacetate (XIV) shows an absorption maximum at 235 mμ (ϵ = 19,390) (Fig. 1). Since both the enediol sulfite (XIII) and *cis*-2,2',4,4',6,6'-hexamethylstilbene-α,α'-diol diacetate (XVIII) are esters of the same enediol, the comparison of their ultraviolet spectra should give some information about the absorption by the enediol sulfite group. However, the *cis*-enediol diacetate (XVIII) was not prepared. Since, in α,α'-disubstituted stilbenes, *cis* isomers absorb less strongly and at longer wave lengths than the *trans* isomers,[11] the *cis*-enediol diacetate (XVIII) would absorb less strongly and at a longer wave length than the *trans*-enediol diacetate (XIV), though the mesityl groups in both diacetates should be nearly perpendicular to the plane of the enediol C—C double bond as shown by the Stuart atomic models. The absorption–intensity of XVIII would, therefore, be lower than that of the enediol sulfite (XIII), even if XVIII absorbs around 260 mμ. On the basis of this assumption, the absorption–intensity differential curve with its maximum at 260 mμ may be regarded as absorption by the enediol sulfite group.

The *trans*-enediol diacetate (XIV) shows a higher carbonyl absorption (1770 cm.$^{-1}$) than that of *trans*-stilbene-α,α'-diol diacetate (1754 cm.$^{-1}$).[5] This difference in carbonyl frequency can be accounted for in the following manner. Since *trans*-stilbene-α,α'-diol diacetate has the phenyl groups in conjugation with the enediol C—C double bond, and since this conjugation could cancel the electron-attracting mesomeric effect of the C—C double bond on acetoxyl carbonyls, the carbonyl absorption occurs near the region of frequency shown by ordinary acetates. On the other hand, since XIV has the mesityl groups nearly perpendicular to the plane of the enediol C—C double bond, the mesomeric effect of this C—C double bond should remain effective. Therefore, the shift of the carbonyl absorption to a higher frequency can be attributed to the electron-attracting mesomeric effect of the enediol C—C double bond along with the negative inductive effect of the acetoxyl groups and the mesityl groups.

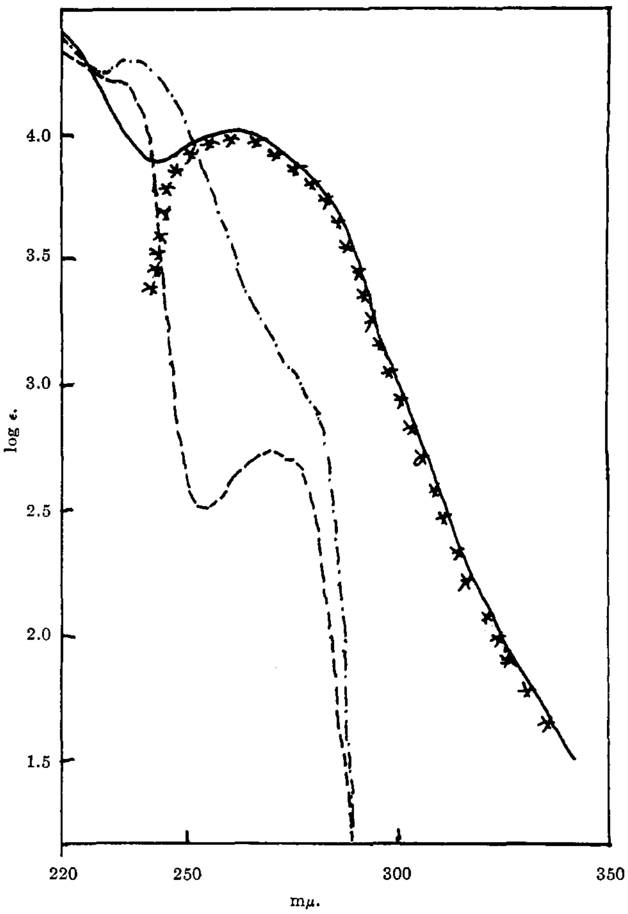


Fig. 1.—Ultraviolet spectra in ethanol of the enediol sulfite (XIII) (———); hydromesitoin (XVI) (- - - -), and the *trans*-enediol diacetate (XIV) (- · - · -); the intensity differential curve for XIII-XVI (* * * *).

As was reported in the previous paper,[1] the reaction mixture of benzoin with thionyl chloride–pyridine followed by treatment with sodium borohydride gave desoxybenzoin as its major product. This formation of desoxybenzoin could be accounted for by postulating that the attack of hydride at the C—C double bond of the intermediate VI could give the enol sulfite of desoxybenzoin which could be hydrolyzed into desoxybenzoin. But treatment of the enediol sulfite (XIII) with sodium borohydride in 95% ethanol produced not desoxymesitoin but mesitil, sulfur, and hydrogen sulfide. This result would, therefore, indicate that steric hindrance due to the *ortho*-methyl groups prevents hydride ion from attacking the enediol C—C double bond, and that sodium borohydride attacks only the sulfite group in a manner analogous to the reaction of cyclic sulfites with Grignard reagents.[12]

---

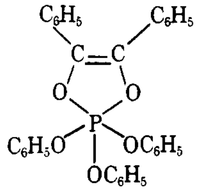
(9) S=O stretching vibrations in sulfites: 1220–1170 cm.$^{-1}$ (strong), A. D. Cross, "Introduction to Practical Infrared Spectroscopy," Butterworths Scientific Publications, London, 1960, p. 72; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., Methuen, London, 1958, p. 360.

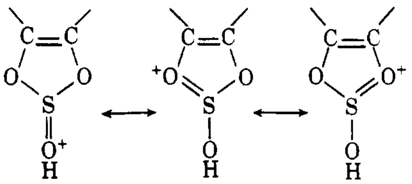
(10) M. J. Klaud-English, R. K. Summerbell, and I. M. Klotz, *J. Am. Chem. Soc.*, **75**, 3709 (1953).

(11) H. Suzuki, *Bull. Chem. Soc. Japan*, **25**, 145 (1952); M. Ballester, C. Molinet, and J. Rosa, *Tetrahedron*, **6**, 109 (1959).

(12) H. H. Szmant and W. Emerson, *J. Am. Chem. Soc.*, **78**, 454 (1956).

Ramirez, *et al.*,[13] reported that compound XIX in the reaction with hydrogen chloride in ether solution gave desyl chloride and triphenyl phosphate; therefore, the enediol sulfite (XIII) should undergo a similar reaction with hydrogen chloride and yield the corresponding desyl chloride (IX). However, when treated with anhydrous hydrogen chloride in chloroform, the enediol sulfite (XIII) was recovered unchanged. This fact would indicate that steric hindrance due to the *ortho*-methyl groups probably inhibits the access of chloride ion to the enediol C—C double bond, and that protonation on the S=O oxygen would give rise to a pseudo aromatic system in the enediol sulfite group.


XIX



Bis(2,2′,4,4′,6,6′-hexamethyldesyl) sulfite (X) shows its carbonyl absorption at 1712 cm.$^{-1}$ between the carbonyl frequencies of the desyl chloride (IX) (1727 cm.$^{-1}$) and mesitoin (VIII) (1698 cm.$^{-1}$). This relationship in carbonyl frequencies, parallel to the strength of the negative inductive effect of the substituent on the α-carbon atom, is also observed among desyl chloride (III) (1718 cm.$^{-1}$), didesyl carbonate[14] (1695 cm.$^{-1}$)[15] and benzoin (I) (1686 cm.$^{-1}$).

Experimental[16]

Bromomesitylene.—Bromomesitylene was prepared according to the procedure described by Smith and MacDougall[17a]; b.p. 109–111°/20 mm. (lit.,[17a] 105–107°/16–17 mm.).

Mesitoyl Chloride.—Mesitoyl chloride was prepared from bromomesitylene by a given method[17b]; b.p. 110–115°/20 mm.

2,2′,4,4′,6,6′-Hexamethylstilbene-α,α′-diol.—This enediol was prepared by the bimolecular reduction of mesitoyl chloride with magnesium–magnesium iodide.[3]

Mesitoin (VIII).—The hexamethylstilbenediol was isomerized into mesitoin with hydrogen chloride according to Fuson's method[3]; m.p. 129.5–130°, ν_{max} 1698 cm.$^{-1}$ (C=O).

2,2′,4,4′,6,6′-Hexamethyldesyl Chloride (IX).—(a) A mixture of 500 mg. of mesitoin and 0.5 ml. of thionyl chloride was warmed on the steam bath for 10 min., then the excess thionyl chloride was removed by evacuation at the water pump for 5 min. To the residue, 5 ml. of petroleum ether (b.p. 30–60°) was added and boiled off, and the flask was evacuated again at the pump for 10 min. Recrystallization of the residue from methanol gave 515 mg. (97%) of colorless needles, m.p. 110–111°, ν_{max} 1727 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{20}H_{23}OCl$ (314.84): C, 76.29; H, 7.36. Found: C, 76.07; H, 7.23.

(b) To 500 mg. of mesitoin placed in a 50-ml. round-bottomed flask, cooled in an ice bath, was added 0.5 ml. of thionyl chloride, and the flask was kept in the ice bath for 12 hr. Mesitoin dissolved in thionyl chloride rapidly with bubbling; then the mixture solidified. The residue after removal of the excess thionyl chloride by suction showed an infrared spectrum quite similar to that of the desyl chloride obtained in the experiment (a) described above. Recrystallization of this product from methanol afforded 513 mg. (96.6%) of needles, m.p. 110–111°, ν_{max} 1727 cm.$^{-1}$ (C=O). This compound was identified as the hexamethyldesyl chloride (IX) by mixture melting point and comparison of infrared spectra.

***cis*-2,2′,4,4′,6,6′-Hexamethylstilbene-α,α′-diol Sulfite (XIII).** To a solution of 6 g. of the preparation of the enediol (XII) in 30 ml. of methylene chloride containing 3.2 ml. of pyridine, was added dropwise 1.45 ml. of thionyl chloride in 10 ml. of methylene chloride, with stirring at −20° in nitrogen. After being stirred for 2 hr., the reaction mixture was transferred to a 250-ml. separatory funnel, and the washings of the reaction flask with methylene chloride were combined. The methylene chloride solution was shaken with 0.1 *N* hydrochloric acid, water, 5% sodium bicarbonate solution, and again with water, then dried with anhydrous magnesium sulfate. The solution was concentrated to dryness *in vacuo* at low temperature, and the residue was dissolved in a minimal volume of chloroform and let stand at room temperature. On slow evaporation of the solvent, the solution deposited colorless cubic crystals besides needles of mesitoin. Cubic crystals (m.p. 175–178°) were separated and recrystallized twice from benzene–petroleum ether, and gave colorless rods, m.p. 178–180° (fluffy needles from chloroform), λ_{max}^{EtOH} = 261 mμ (ϵ = 10,650), ν_{max} (cm.$^{-1}$): 2967, 2933, 2899, 1613, 1477, 1460, 1439, 1376, 1230, 1211, 1155, 1029, 993, 968, 949, 907, 851; yield, 1.8 g. (25.8%).

Anal. Calcd. for $C_{20}H_{22}O_3S$ (342.45): C, 70.14; H, 6.48; S, 9.36. Found: C, 70.39; H, 6.70; S, 9.38.

Pyrolysis of *cis*-2,2′,4,4′,6,6′-Hexamethylstilbene-α,α′-diol Sulfite (XIII).—In a 10-ml. Houben flask supplied with a gas inlet tube, was placed 341 mg. (9.96×10^{-4} mole) of the enediol sulfite (XIII). The side arm was connected to two absorption tubes containing 0.1 *N* sodium hydroxide under cooling in an ice bath. The system was flushed with nitrogen and the flask was heated in an oil bath at 240° for 1 hr. in a slow stream of nitrogen. The solution in each absorption tube was neutralized with 0.1 *N* hydrochloric acid at 0° and titrated iodimetrically. The total iodine consumption was 10.6×10^{-4} equiv., and this would correspond to iodine consumption by 5.3×10^{-4} mole (in total) of sulfites, sulfides, and thiosulfates derived from sulfur monoxide.[18] The solution immediately after iodimetric titration showed a turbidity due to a suspension of sulfur derived from the sulfides by the oxidation with iodine. The brown residue in the Houben flask was dissolved in 10 ml. of petroleum ether (b.p. 30–60°), and insoluble matter was removed by filtration. The filtrate was chromatographed on a column of silica gel (50 g.) and gave 5.7 mg. of crystalline sulfur, m.p. 117° (eluted with petroleum ether), 228 mg. (77.8%) of a compound, m.p. 118–119°, ν_{max} 1701 cm.$^{-1}$ (eluted with 2:3 benzene–petroleum ether), and 89 mg. of brown tar (eluted with 1:3 ether–benzene). The compound melting at 118–119° was identified as mesitil (XI) by infrared spectra and by mixture melting point with mesitil (m.p. 118–119°) derived from the preparation of the enediol (XII).

Anal. Calcd. for $C_{20}H_{22}O_2$ (294.38): C, 81.60; H, 7.53. Found: C, 81.80; H, 7.66.

Fuson reported m.p. 120–121° for mesitil.[19]

Reductive Acetylation of Mesitil. With Zinc and Acetic Anhydride–Hydrochloric Acid.—Reductive acetylation of 200 mg. of mesitil was carried out according to the method in the literature[5] and gave 254 mg. (98%) of *trans*-2,2′,4,4′,6,6′-hexametylstilbene-α,α′-diol diacetate (XIV)[20], m.p. 220°, λ_{max}^{EtOH} = 235 mμ (ϵ = 19,390), ν_{max} 1770 cm.$^{-1}$ (C=O).

With Zinc and Acetyl Chloride.—The treatment of mesitil (200 mg.) with zinc dust (200 mg.) and acetyl chloride (0.4 ml.) followed by column chromatography on silica gel gave 110 mg. (42.5%) of the *trans*-enediol diacetate (XIV), m.p. 220° (eluted

---

(13) F. Ramirez, R. B. Mitra, and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960).

(14) H. McCombie and J. W. Parkes, *J. Chem. Soc.*, **109**, 1689 (1914).

(15) Didesyl sulfite prepared by the treatment of benzoin with thionyl chloride and pyridine in methylene chloride at −20° shows its carbonyl absorption at 1698 cm.$^{-1}$ and an absorption due to the sulfite group at 1214 cm.$^{-1}$ in methylene chloride solution.

(16) Melting points are uncorrected. Infrared spectra were determined with a Perkin–Elmer Model 21 or Infracord Model 137 with a sodium chloride prism in carbon tetrachloride solutions. Ultraviolet spectra were taken with a Cary Model 11M with automatic recorder. N.m.r. spectrum was taken with a Varian Model V-4300-B.

(17) (a) L. I. Smith and F. H. MacDougall, *J. Am. Chem. Soc.*, **51**, 3002 (1929). (b) "Organic Syntheses," Coll, Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 555.

(18) Sulfur monoxide reacts with water at 0° to form hydrogen sulfide, sulfurous acid, and sulfur; with 5 *N* potassium hydroxide at 0° to form sulfites, sulfides, and thiosulfates; with alcoholic potassium hydroxide to form sulfites and sulfides. P. W. Schenk and H. Platz, *Z. anorg. allgem. Chem.*, **222**, 177 (1935).

(19) A. R. Gray and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 739 (1934).

(20) Ref. 3. Fuson, *et al.*, reported two diacetates, m.p. 164–165° and m.p. 218°, respectively. By the melting point rule, the *trans*-configuration can be assigned to the diacetate of higher melting point.

with chloroform) and a brown tar (eluted with 1:4-methanol-chloroform).

Anal. Calcd. for $C_{24}H_{28}O_4$(XIV) (380.46): C, 75.76; H, 7.42. Found: C, 76.04; H, 7.50.

Sodium Borohydride Treatment of the Enediol Sulfite (XIII).—To a colorless solution of 100 mg. of the enediol sulfite (XIII) in 7.5 ml. of 95% ethanol, was added 6 mg. of powdered sodium borohydride at room temperature. The solution turned yellow with evolution of hydrogen sulfide gas (detected with lead acetate paper). After complete solution of the borohydride, the solution was acidified with 1 *N* hydrochloric acid and extracted with ether. The ether layer was washed with water, 5% sodium bicarbonate solution, and again with water, then dried with anhydrous magnesium sulfate. After evaporation of the solvent, the residue (a yellow crystalline mass) was dissolved in petroleum ether (b.p. 30–60°) and chromatographed on 10 g. of silica gel. Elution with petroleum ether gave 80 mg. (93%) of mesitil and 5.4 mg. of crystalline sulfur. Mesitil resisted sodium borohydride reduction at room temperature, and gave hydromesitoin (XVI) smoothly only when boiled with sodium borohydride in 95% ethanol. Hydromesitoin (XVI), m.p. 205–206.5° (lit.,[21] 212–213°).

Anal. Calcd. for $C_{20}H_{26}O_2$ (298.41): C, 80.49; H 8.87. Found: C, 80.18; H, 8.55.

Bis(2,2′,4,4′,6,6′-hexamethyldesyl) Sulfite (X).—To a solution of 1.48 g. of mesitoin in 20 ml. of methylene chloride containing 0.8 ml. of pyridine, was added 0.35 ml. of thionyl chloride in 3 ml. of methylene chloride under agitation, at −20° in nitrogen. After being stirred for 2 hr., the reaction mixture was concentrated to dryness *in vacuo* at low temperature, and then extracted with dry benzene. The benzene solution was subjected to freeze-drying and gave a white powder, m.p. 200–202° (1.85 g.). Recrystallization of this powder from chloroform gave fluffy crystals, m.p. 202–204°, ν_{max} (cm.$^{-1}$): 1712 (C=O), 1205 (S=O).

Anal. Calcd. for $C_{40}H_{46}O_5S$ (638.83): C, 75.20; H, 7.26. Found: C, 77.96; H, 7.78.

On standing in the air for a long time, the color of this compound turned pale brown even in a refrigerator.

Reaction of Mesitoin with Sulfuryl Chloride.—To 400 mg. of mesitoin placed in a 50-ml. round-bottomed flask, cooled in an ice bath, was added 0.4 ml. of sulfuryl chloride, and the reaction mixture which was allowed to stand at 0° for 12 hr. solidified. After evacuation to remove the excess sulfuryl chloride, the mixture was dissolved in petroleum ether and chromatographed on 10 g. of silica gel. Elution with petroleum ether gave 11 mg. of colorless needles, m.p. 125°, and 20 mg. (5%) of mesitil, m.p. 118–119°. Elution with 1:9-benzene–petroleum ether gave 25 mg. of a colorless compound, m.p. 157–159°, ν_{max} (cm.$^{-1}$): 1704 (C=O), 1460, and 1168 (sulfate group ?).

Anal. Found: C, 65.0; H, 5.55.

Elution with 1:3 benzene–petroleum ether gave 186 mg. of a colorless compound, m.p. 159°, ν_{max} (cm.$^{-1}$): 3570 (OH), 1702 (C=O).

Anal. Found: C, 60.33; H, 5.48.

Crystalline products other than mesitil have not been identified yet, but the details of this reaction will be reported elsewhere.

Acknowledgment.—The author wishes to thank Professor Louis F. Fieser for the privilege and inspiration of working in his laboratory. This work was supported by grants from the National Cancer Institute of the National Institutes of Health (CY-1696) and the National Science Foundation.

---

[21] R. C. Fuson, J. J. Denton, and C. E. Best, *J. Org. Chem.*, **8**, 64 (1943).

Equilibration of Bicyclic Alcohols

Charles F. Wilcox, Jr., Maureen Sexton,[1] and Mary F. Wilcox

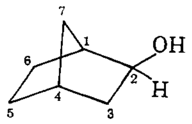
Department of Chemistry, Cornell University, Ithaca, New York

Received July 23, 1962

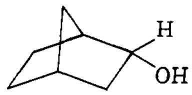
Equilibration under various conditions of *exo-* and *endo*-norborneol as well as isoborneol and borneol is reported. The equilibrium constants are linearly correlated with the relative rates of oxidation. A similar linear correlation is noted between the relative oxidation rates of epimeric cholestanols and their estimated relative stabilities.

In contrast to the extensive study of reactions of strained bicyclic systems there has been much less work on quantitative determination and analysis of this strain.[2] This paper is concerned with one aspect of the general problem, the measurement of the relative stability of *exo* and *endo* epimeric alcohols of [2.2.1]-bicycloheptane derivatives. These data are applied to the analysis of the rates of chromic acid oxidation of the bicyclic alcohols. As a result of this analysis and its extrapolation to the epimeric cholestanols an approximate but facile method for indirectly determining alcohol stability is developed.

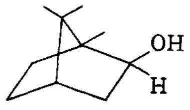
Results and Discussion



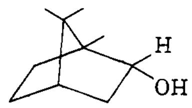
Ia



Ib



IIa



IIb

The relative stability of *exo-* and *endo*-hydroxyl group was determined at different temperatures for norborneol (Ia and Ib) and borneol (IIa and IIb) by equilibration of *exo–endo* mixtures with aluminum isopropoxide and analysis by gas–liquid chromatography.[3] In a series of control experiments it was determined that multiple ether extractions were required for representative sampling and it was shown that within our estimated error in composition (±1–3%) no molar response corrections were required for the chromatographic analyses. With borneol, which equilibrates more slowly than norborneol, the equilibrium composition was approached from both sides. The single

---

[1] This paper is based in part on the dissertation of M. Sexton submitted in September, 1961, to the Graduate School of Cornell University in partial completion of the requirement for the M.S. degree.

[2] An unpublished calculation and correlation of the available data by H. Dauben assigns a strain energy of about 10 kcal./mole to bicycloheptane (H. Dauben, private communication).

[3] The experimental procedure was patterned after that of C. H. De Puy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960). These authors did not specify the amount of extraction employed. We found that multiple extraction was required.