The Conformational Preference of Sulfur in Hemithioketals

MATHIAS P. MERTES

Department of Pharmaceutical Chemistry, School of Pharmacy, The University of Kansas, Lawrence, Kansas

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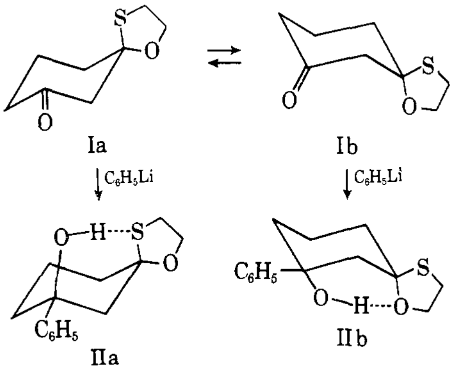
The addition of phenyllithium to an equilibrium mixture of the conformers of 1,4-oxathiospiro[4.5]-7-decanone (I) has been shown to give a ratio of 67:33 in favor of *cis*-7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (IIb). Assignment of configuration was based on infrared studies in the 3600–3400-cm.$^{-1}$ region where intramolecular OH–O and OH–S hydrogen bonding was observed. Evidence also is presented to show that product ratio in equilibration of hemithioketals using an acid catalyst depends on the size of the catalytic agent.

The conformational analysis of divalent sulfur recently has been studied by several investigators. Using infrared and Raman absorption assignments, Chiurdoglu[1] concluded the SH group preferred the axial orientation with a conformational free energy difference of -0.4 kcal./mole. More recently Eliel, Thill, and Gianni[2] have determined the conformational preference for divalent sulfur using nuclear magnetic resonance (n.m.r.) and calculated a value of 0.8 kcal./mole for C_6H_5S and 0.9 kcal./mole for SH in 4-*t*-butylcyclohexyl compounds indicating expected preference of sulfur for the less hindered equatorial position. In addition to the n.m.r. analysis Eliel and coworkers[3,4] have also recorded a value of 0.4 kcal./mole for divalent sulfur based on equilibration studies.

In a previous paper[5] evidence was presented for the presence of intramolecular hydrogen bonding from hydroxyl to divalent sulfur on the basis of infrared and near-infrared studies. At that time it was assumed from steric considerations that the greater size of the sulfur atom[6] compared to oxygen in the monohemithioketal of 1,3-cyclohexanedione (I) would give an equilibrium mixture with Ib predominating. Treatment with phenyllithium should give *cis*-7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (IIb) as the major product (*cis–trans* nomenclature is used in this discussion to refer to the relative positions of the oxygens).



Houlihan[7a] reported that the stereochemistry of the addition of alkyl- or aryllithium derivatives is influenced by the steric environment of the carbonyl. A preference for the slightly less hindered equatorial approach on addition of methyllithium to 4-*t*-butylcyclohexanone resulted in a 65:35 ratio of the equatorial *vs.* axial methyl product. Although no attempt to isolate the *cis* isomer was reported, Tomboulian[7b] found the addition of phenyllithium to 2-hydroxy-2-phenylcyclohexanone gave a 75% yield of *trans*-1,2-diphenyl-1,2-cyclohexanediol. Beckett and co-workers[7c] have studied the stereochemistry of the addition of aryllithium reagents to 1,2-disubstituted 4-piperidones and tropinone. In the former examples the preferred conformation of the ketone was presumed to be the chair form with the 3-alkyl group in the equatorial position. By variation of the size of the aryl group "steric approach control"[8] resulted in from 75% to essentially 100% equatorial addition. When a considerable increase in steric hinderance to approach due to 1:3 diaxial interactions is involved, such as that found in tropinone, they found the addition of phenyllithium gave 97% of the equatorial product.

In this study the addition of 1,4-oxathiospiro-[4.5]-7-decanone (I) to phenyllithium yielded between 65 and 84% of the alcohol (II). It is assumed that the addition is predominately equatorial and the ketone reacts in the chair form free from distortions caused by the hemithioketal ring. The reaction was run at room temperature, 0°, and $-70°$. Under these conditions the major product was the isomer with the sulfur equatorial, *cis*-7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (IIb). The *cis–trans* ratio at room temperature was 67:33. At 0° the yield was 82% with a 68:31 ratio. After cooling both the phenyllithium and ketone solutions to $-70°$ prior to mixing, the yield was 81%, of which 77% was the *cis* product.

The product ratio can only reflect the conformer ratio if either the energy of activation to the transition states (E_{Ia}^*, E_{Ib}^*) is less than the barrier to conformer interconversion or if the energies of activation to Ia* and Ib* are the same ($k_{Ia} \cong k_{Ib}$).[9] Both steric and electronic effects are operative in defining the E_a^* and E_b^* and the properties of oxygen and sulfur suggest that these are in opposition. Disregarding solvation effects, a dipole–dipole repulsion is present in the transition state leading to IIb, whereas the steric effect of sulfur must be considered in the transition state to IIa. The lack of kinetic data on this reaction prohibits serious consideration of the magnitude of the steric

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[1] G. Chiurdoglu, J. Reisse, and M. VanderStichelen Rogier, *Chem. Ind.* (London), 1874 (1961).

[2] (a) E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, **3**, 97 (1962); (b) E. L. Eliel and B. P. Thill, *Chem. Ind.* (London), 88 (1963).

[3] E. L. Eliel and L. A. Pilato, *Tetrahedron Letters*, **3**, 103 (1962).

[4] E. L. Eliel, L. A. Pilato, and V. G. Badding, *J. Am. Chem. Soc.*, **84**, 2377 (1962).

[5] M. P. Mertes, *J. Org. Chem.*, **26**, 5236 (1961).

[6] Chiurdoglu's value for sulfur was published while ref. 5 was in press.

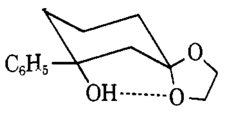
[7] (a) W. J. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962); (b) P. Tomboulian, *ibid.*, **26**, 2652 (1961); (c) A. H. Beckett, A. F. Casy, G. Kirk, and J. Walker, *J. Pharm. Pharmacol.*, **9**, 939 (1957).

[8] W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

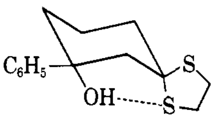
[9] For a further discussion of the "Curtin–Hammett" principle see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

and electronic effects.[10] It is interesting to note that, assuming the A value of divalent sulfur is 0.9 kcal./mole[2b] and oxygen is 0.6 kcal./mole, the calculated conformer ratio of the starting ketone (Ia:Ib) is in fair agreement with the product ratio (IIa:IIb). Further work is necessary to separate the electronic and steric effects and also to investigate the possibility of a low activation energy.

Conformational assignments were made by examination of the infrared absorption characteristics of IIa, IIb, III, and IV in the 3650–3400-cm.$^{-1}$ region. It was noted previously[5] that OH–O bonding in 7-phenyl-1,4-dioxaspiro[4.5]-7-decanol (III) gave a shift of 101 cm.$^{-1}$ from the unassociated OH stretching frequency assigned to 3604 cm.$^{-1}$ in a model 1,4 system. Compound IV had a shift of 158 cm.$^{-1}$ which was assigned to OH–S bonding and is in close agreement with previously reported shifts involved in hydrogen bonding to divalent sulfur.[11]



III



IV

The equatorial sulfur isomer, *cis*-7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (IIb) had a concentration independent peak at 3534 ± 2 cm.$^{-1}$, a shift of 70 cm.$^{-1}$ from the assigned unassociated hydroxyl.[12] The *trans* isomer (IIa) showed two concentration independent peaks: one at 3583 ± 2 cm.$^{-1}$ attributed to OH–π bonding[13] and the other at 3478 ± 2 cm.$^{-1}$ assigned to OH–S bonding. The former band, showing a shift of 21 cm.$^{-1}$, was also observed in compound IV where this peak appeared at 3581 ± 5 cm.$^{-1}$. The magnitude of the frequency shift due to intramolecular hydrogen bonding to sulfur, 126 cm.$^{-1}$, again is in fair agreement with a similar shift (158 cm.$^{-1}$) observed in compound IV.[14]

Eliel[3,4] tentatively has assigned the conformation of suitably substituted hemithioketals on the basis of n.m.r. spectra wherein a perceptible shift in the triplets of O–CH$_2$ and S–CH$_2$ to higher fields accompanies a change from the equatorial to the axial positions. Since the independent assignment of the conformations of IIa and IIb was made on the infrared absorption characteristics it appeared that inspection of the n.m.r. proton resonance signals would substantiate the reported assignments. A mixture of IIa and IIb showed overlaping of the triplets in both the CH$_2$–O and the CH$_2$–S region. The former appeared at −240 c.p.s. and −249 c.p.s., with both peaks split into triplets with J = 6 c.p.s. The CH$_2$–S triplets doubled at −175 and −178 c.p.s. (J = 6 c.p.s.). Examination of the pure isomers showed the O–CH$_2$ (equatorial) in IIa to appear at −240 c.p.s. and the axial S–CH$_2$ to appear at −175 c.p.s. The other peaks reported were found in the *cis* isomer IIb where the axial O–CH$_2$ is assigned to −249 c.p.s. and the equatorial S–CH$_2$ to −178 c.p.s. If the interpretation is correct that the axial X–CH$_2$ protons (X = S or O) should appear at a higher field than the corresponding equatorial isomer then the O–CH$_2$ protons in IIb should be at a higher field than IIa. This is contrary to the observed resonance signals where the axial O–CH$_2$ proton signal actually is shifted to a lower field. It is proposed that this shift is an effect of deshielding due to a decrease in the electron density of the α-CH$_2$ and a corresponding increase in the electron density of the oxygen caused by hydrogen bonding. Such an effect has been observed to lead to a shift to lower field. Lewin and Winstein[15] noted an analogous shift in 4-alkylcyclohexanols ranging from 2–6 c.p.s. in changing from a nonpolar to a polar solvent, the latter participating in intermolecular hydrogen bonding.

In contrast, no such shift has been reported for protons on carbon linked to divalent sulfur which participates in hydrogen bonding. The n.m.r. signals for the protons of CH$_2$S are in agreement with the reported shift to higher field in the axial SCH$_2$ isomer. While the shift is small (3 c.p.s.), it is of the same magnitude as the reported interpretation.[3,4] The absence of a significant shift of the hydrogen bonded S–CH$_2$ proton signal corresponding to that encountered in O–CH$_2$ is thought to be due to the lack of a significant change in the electron density of sulfur caused by participation in hydrogen bonding. An analogous observation was reported in comparing the electron densities of the hetero atoms in cyclic ethers and sulfides.[16] The effect of electron density change on the chemical shift of the CH$_2$X protons was greater when X = O than when X = S.

In connection with the study of monothioketals of substituted cyclohexanones, an effort was made to establish an equilibrium mixture of the hemithioketal of 3-methylcyclohexanone (V). The isomer ratio found was not in accord with that previously found on the equilibration of the hemithioketal of 4-*t*-butylcyclohexanone.[3,4,17] While this could be influenced by the nonrigidity of the ring system used, the increased hinderance of a 1,3-diaxial interaction would prevent the molecule from assuming any appreciable amount of the 3-methyl axial conformation at the temperatures encountered. Assuming the proposed mechanism of equilibration is correct,[3,4] that is, initial complexation of boron trifluoride to oxygen, ring opening with sulfur assuming the positive charge, followed by recyclization to the equilibrium mixture, it is possible that the final step involves a BF$_3^-$–O–R complex that is not representative of the conformational preference or size of a simple $^-$O–R group. On this basis further studies on the equilibration of hemithioketals were performed.

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(10) The addition of phenyllithium to Michler's ketone was shown [C. G. Swain and L. Kent, *J. Am. Chem. Soc.*, **72**, 518 (1950)] to be first order with respect to ketone and first order in phenyllithium with a half-life of 0.002 sec.

(11) P. von R. Schleyer and R. West, *ibid.*, **81**, 3164 (1959); A. W. Baker and A. T. Shulgin, *ibid.*, **80**, 5358 (1958); A. Luttringhaus, S. Kabuss, H. Prinzbach, and F. Langenbucher, *Ann.*, **653**, 195 (1962).

(12) The previously reported peak for IIb at 3519 ± 5 cm.$^{-1}$ in ref. 5 is believed to be due to contamination by isomer IIa and the fact that resolution on a prism instrument was not sufficient to detect both peaks.

(13) F. A. L. Anet and D. M. G. Bavin, *Can. J. Chem.*, **34**, 1756 (1956); D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

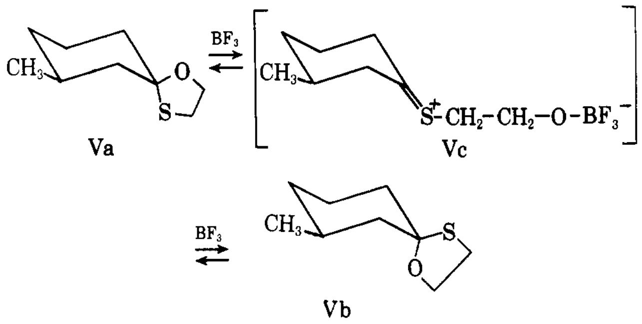
(14) Compound IV was equilibrated with deuterium oxide and base and both the 3581-cm.$^{-1}$ and the 3446-cm.$^{-1}$ peaks shifted to the O—D stretching frequency with a value of 1.33 for the OH/OD frequency ratio.

(15) A. H. Lewin and S. Winstein, *J. Am. Chem. Soc.*, **84**, 2465 (1962).

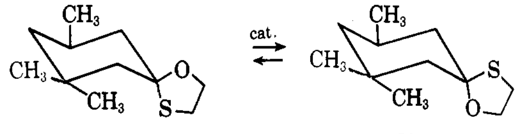
(16) H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *ibid.*, **76**, 4242 (1954).

(17) A difference in reactivities between 3- and 4-alkyl substituted cyclohexyl systems has been observed and attributed to deformation of the ring. J. C. Richer, L. A. Pilato, and E. L. Eliel, *Chem. Ind.* (London), 2007 (1961).

Starting with a mixture or either pure isomer of the hemithioketal of 3-methylcyclohexanone (V), it was found that excess boron trifluoride equilibration in refluxing ether resulted in all experiments in a mixture of 76% of the O-equatorial isomer (Va) and 24% of the S-equatorial isomer (Vb). Similarily a mixture of the isomers of the hemithioketal of 3,3,5-trimethylcyclohexanone (VI) and also the pure isomers were equilibrated with excess boron trifluoride. In these experiments the ratio converged toward 79% O-equatorial (VIa) and 21% S-equatorial (VIb).



Va Vc Vb

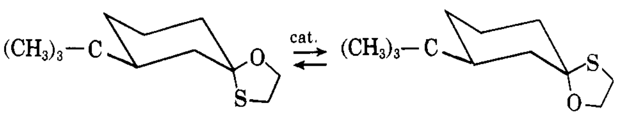


VIa VIb

The preferred conformation of the hemithioketals of 3-methylcyclohexanone (V) and 3,3,5-trimethylcyclohexanone (VI) is assumed to be the chair form with a minimum of diaxial interactions. Inspection of the equilibrium ratio from catalytic equilibration of hemithioketals reveals the O-equatorial isomer to be thermodynamically more stable than the S-equatorial isomer. The observed equilibrium ratio is not in accord with the reported *A* value of sulfur (0.9 kcal./mole) and that for oxygen (0.6 kcal./mole). Thus it would appear that the catalyst affects the ratio by complexing with oxygen and subsequently altering the size and the conformational preference.[18]

In an effort to examine the effect of the size of the catalyst, a catalytic quantity of *p*-toluenesulfonic acid in refluxing benzene was used in equilibrations of pure Va and of pure VIa. The former gave a 67:33 ratio with the O-equatorial isomer (Va) predominating and VIa gave an equilibrium mixture of 76% VIa and 24% VIb. While temperature and solvent affect the equilibrium, these results suggest that the size of the catalytic agent also influences the equilibration leading to a slightly higher proportion of the S-equatorial isomer in both examples when *p*-toluenesulfonic acid rather than boron trifluoride was used.

Previous interpretations[4,19] that the kinetically controlled product is the isomer with the equatorial sulfur were examined. The synthesis of VI was followed by chromatography at intervals from one minute after the addition of catalyst to the refluxing mixture to several hours. It was found that the initial product ratio became richer in the O-equatorial isomer to an equilibrium value which remained stable for the duration of the reaction, usually several hours after the last traces of water were collected. Analysis of the reaction mixture of VI after ten minutes showed 68% of the O-equatorial isomer (VIa) and this gradually increased to 76%. Synthesis of the hemithioketal of 3-*t*-butylcyclohexanone (VII) showed an initial concentration (one-minute reaction time) of 76% of VIIa which gradually increased to 82%. Thus, in accord with the reported mechanism, the equatorial sulfur is the product of the kinetic reaction.



VIIa VIIb

Experimental

The n.m.r. spectra were run on carbon tetrachloride or deuteriochloroform solutions at 60 Mc. using tetramethylsilane as an internal standard. The infrared spectra were obtained from carbon tetrachloride solutions using a Perkin-Elmer Model 421 grating infrared spectrophotometer. All melting points are corrected.

7-Phenyl-1,3-oxathiospiro[4.5]-7-decanol (II).—This was prepared by a modification of the previously reported procedure.[5] An ether solution of phenyllithium was prepared in a nitrogen atmosphere by the addition of 11 g. of bromobenzene (0.07 mole) to 1 g. of freshly cut lithium metal (0.14 g.-atom) in 100 cc. of ether. After several hours stirring, when most of the lithium had reacted, a solution of 0.500 g. of 1,4-oxathiospiro[4.5]-7-decanone (0.0029 mole) in 25 cc. of ether was added over a period of 1 hr. After stirring an additional 15 min. the mixture was decomposed by the slow addition of 30 cc. of water. The layers were separated and the aqueous layer extracted twice with 20-cc. portions of ether; the ether layers were combined, dried with anhydrous sodium sulfate, and evaporated to a thick oil weighing 2.074 g.

Separation of the *cis* and *trans* isomers was accomplished by placing 1.624 g. (78% of the total residue) on a 3 × 45 cm. column of neutral alumina (Merck, regular grade) and eluting the isomers with a 10:1 followed by a 4:1 hexane–ether solution. The first pass yielded 183 mg. of pure *cis*-7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (IIb) and 569 mg. of impure material. The latter was rechromatographed twice, the first yielding 85 mg. of pure *cis*- and the second giving an additional 50 mg. of pure *cis*- and 153 mg. of pure *trans*-7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (IIa). The total yield was 471 mg. (84%). The *cis* isomer (318 mg.) represented 67.5% of the total. After recrystallization from ether–hexane the product melted at 95–96°. Characteristic triplets were observed in the n.m.r. spectrum (carbon tetrachloride) at −178 c.p.s. ($S-CH_2$) and −249 c.p.s. ($O-CH_2$); $J = 6$.

Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; S, 12.80. Found: C, 66.81; H, 7.14; S, 13.05.

The *trans* isomer (153 mg.) represented 32.5% of the total; recrystallization from ether–hexane gave a product melting at 92–93°. Triplets in the n.m.r. spectrum (carbon tetrachloride) were at −175 c.p.s. ($S-CH_2$) and −240 c.p.s. ($O-CH_2$); $J = 6$.

Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; S, 12.80. Found: C, 66.95; H, 6.97; S, 13.00.

Cooling the phenyllithium solution and the ketone to 0° prior to mixing gave an 82% yield after column purification with 67.5% *cis*, 32.5% *trans*. At −70° an 81% yield of the alcohol was realized, of which 77% was the *cis* compound.

7-Methyl-1,4-oxathiospiro[4.5]decane (V).—A benzene solution of 3-methylcyclohexanone (44.8 g., 0.4 mole), mercaptoethanol (31.2 g., 0.4 mole), and 200 mg. of *p*-toluenesulfonic acid was refluxed for 10 hr. during which 7.0 cc. of water (97% theoretical) was collected in a Dean–Stark trap. After cooling, the

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[18] The hemithioketal of 4-*t*-butylcyclohexanone was reported to give a 50:50 mixture using an excess of boron trifluoride etherate (2.4 mole equivalents) (see ref. 3 and 4). These authors also noted that a shift of the equilibrium favored the O-equatorial isomer when a catalytic quantity of boron trifluoride etherate (0.2 mole equivalent) was used at room temperature.

[19] C. Djerassi, M. Shamma, and T. Y. Kan, *J. Am. Chem. Soc.*, **80**, 4723 (1958).

reaction mixture was neutralized with 20 cc. of a saturated solution of sodium carbonate, washed with water, dried over anhydrous sodium sulfate, and the solvent removed by distillation.

Gas chromatographic analysis of the residue on a diethylene adipate column[20] indicated the product was a 34:66 mixture of isomers. The residue was distilled and 49.5 g. (77%) of product was collected at 116–123° (19 mm.), $n^{25}\text{D}$ 1.5027.

Anal. Calcd. for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61. Found: C, 62.83; H, 9.86; S, 18.24.

The isomers were separated on a 3 × 45 cm. neutral alumina column by elution with hexane. The first fraction collected was the minor constituent and was shown to be the S-equatorial isomer (Vb) by n.m.r. analysis (deuteriochloroform) which showed triplets at −183 c.p.s. ($S\text{–}CH_2$) and −248 c.p.s. ($O\text{–}CH_2$). The second isomer collected (S-axial, Va) which represented 66% of the total product showed n.m.r. triplets (deuteriochloroform) at −181 c.p.s. ($S\text{–}CH_2$) and −252 c.p.s. ($O\text{–}CH_2$).

7,7,9-Trimethyl-1,4-oxathiospiro[4.5]decane (VI).—The procedure described in V was used starting with 3,3,5-trimethylcyclohexanone and mercaptoethanol in benzene with *p*-toluenesulfonic acid as the catalyst. The product was collected in 45% yield at 118–131° (19 mm.). The isomers were separated on neutral alumina using hexane for elution. The first isomer collected (VIa) showed n.m.r. triplets (deuteriochloroform) at −178 c.p.s. (axial $S\text{–}CH_2$) and −251 c.p.s. (equatorial $O\text{–}CH_2$). The second isomer (VIb) showed triplets at −180 c.p.s. (equatorial $S\text{–}CH_2$) and −248 c.p.s. (axial $O\text{–}CH_2$).

Anal. Calcd. for $C_{11}H_{20}OS$: C, 65.95; H, 10.06; S, 16.00. Found: C, 65.40; H, 9.93; S, 15.70.

The progress of the reaction was followed by withdrawing and immediately neutralizing samples of the reaction mixture. These were taken at 5-min. intervals starting with the addition of catalyst to the refluxing solution of ketone and mercaptoethanol. Gas chromatographic analysis revealed after 10-min. reaction time a ratio of 68:32 in favor of the O-equatorial isomer (VIa). This gradually changed (seven determinations until stabilizing at 76:24 after 100 min.) and remained unchanged for the next 20 hr.

7-*t*-Butyl-1,4-oxathiospiro[4.5]decane (VII).—This was prepared according to the procedure described in V from 3-*t*-butylcyclohexanone[21] and mercaptoethanol. The product was collected in 43% yield at 140–142° (11 mm.). Column chromatography yielded the O-equatorial isomer (VIIa) with n.m.r. triplets (carbon tetrachloride) at −176 ($S\text{–}CH_2$) and −246 c.p.s. ($O\text{–}CH_2$), while the S-equatorial isomer (VIIb) gave proton signals at −178 and −243 c.p.s., respectively.

Anal. Calcd. for $C_{12}H_{22}OS$: C, 67.25; H, 10.35; S, 14.93. Found: C, 67.25; H, 10.40; S, 14.90.

Analysis of the progress and equilibrium of the reaction was according to the procedure used in VI. The ratio changed from 76:24 in favor of the O-equatorial isomer (1-min. reaction time) to 82:18 after 18 hr. reflux. Gas chromatographic analysis was difficult due to overlap; in this case a retention time difference of about 2 min. was found, necessitating an approximation of the ratios.

Equilibrations.—The hemithioketals V and VI were refluxed with a 2.5 mol. equiv. of boron trifluoride in ether (100 parts) until equilibrium was reached as shown on gas chromatographic analysis. A mixture of the isomers of 7-methyl-1,4-oxathiospiro[4.5]decane (VI) and also an ether solution of the pure oxygen-equatorial isomer were both equilibrated to a 76:24 ratio in favor of the oxygen–equatorial isomer.

7,7,9-Trimethyl-1,4-oxathiospiro[4.5]decane (VI) and the pure isomer VIa were equilibrated to give in both cases a 79:21 ratio in favor of the O-equatorial isomer (VIa).

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[20] LAC-446 on Chromosorb P (F and M Scientific Corp.).

[21] C. Djerassi, E. Warawa, R. E. Wolff, E. J. Eisenbruan, *J. Org. Chem.*, **25**, 917 (1960).

Addition of Grignard Reagents to 1,3-Dimesitoylbenzene[1]

REYNOLD C. FUSON AND ROBERT J. SAUER

The Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

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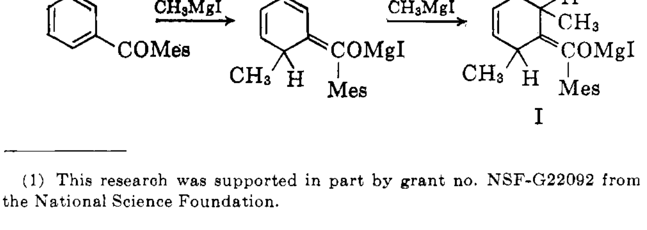
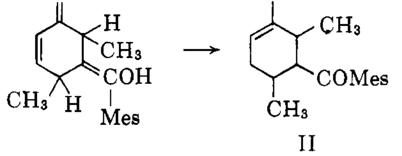
1,3-Dimesitoylbenzene reacts with two moles of methylmagnesium iodide; the product has been identified as a mixture of stereoisomeric 2,4-dimesitoyl-3,5-dimethylcyclohexenes.

Conjugate addition of Grignard reagents to hindered diaryl ketones involves nucleophilic attack on a benzene ring. It would be expected that vulnerability of the ring to such attack would be increased by a second ketone group, especially if it were in a position *meta* to the first. To test this idea we have studied the behavior of 1,3-dimesitoylbenzene toward the methyl and benzyl Grignard reagents. Reaction should occur initially at the 4-position; a second mole of the reagent would be expected to react readily with the adduct since the ring involved would have lost its aromatic character. Reaction with the methyl reagent would then take the following course.



I

Ketonization of the dienol produced by hydrolysis of adduct I might be expected to yield 2,4-dimesitoyl-3,5-dimethylcyclohexene (II).



II

The product, isolated in 59% yield, proved to be a mixture of stereoisomers of ketone II. It was not possible to isolate all of the isomers, but chromatography over alumina yielded a high melting, dimorphic isomer, m.p. 159–160° and 174.5–175.5°. Analyses of both the recrystallized mixture of isomers and the high melting isomer were consistent with the composition of $C_{28}H_{34}O_2$.

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