the DMSO concentrated in one layer, the reaction is difficult to control. The procedure given below, however, is easily reproducible.

Reaction of Potassium with Dimethyl Sulfoxide in a 2:1 Tetrahydrofuran-DMSO Mixture.—To a stirred mixture of 50 ml. of DMSO and 100 ml. of tetrahydrofuran (THF) at <10° was added 2.0 g. (0.05 g.-atom) of potassium (*ca.* 0.25-in. cubes). The reaction proceeded smoothly and was complete within an hour. The gas evolved (515 cc., 0.021 mole) was collected in a graduated cylinder by allowing it to displace water from the cylinder. When the reaction was complete, 10.0 g. (0.05 mole) of 1-iodopentane was added at room temperature and the reaction mixture was stirred for 3.5 hr. The THF was stripped off to leave a residue of 63.9 g., which still contained *ca.* 2.5 g. of THF and which was assumed to contain 8.4 g. (0.05 mole) of potassium iodide, since none had been recovered. Analysis by g.c. indicated that the residue contained 0.025 mole of pentyl methyl sulfoxide and 0.0276 mole of hexyl methyl sulfoxide. No attempt was made to recover dimethyl sulfide.

Reaction of Sodium Oxide with Dimethyl Sulfoxide.—To 100 ml. of DMSO was added 6.2 g. (0.1 mole) of sodium oxide (Alfa Inorganics, Inc.), and the mixture was heated at 50° for 18 hr. The mixture was cooled to room temperature, 15.1 g. (0.1 mole) of 1-bromopentane was added, and stirring was continued for 3 hr. The mixture was filtered to remove the unreacted sodium oxide, and the filtrate was poured into water, extracted with ethyl acetate, and dried over magnesium sulfate. The solvent was evaporated, and the residue was identified as being primarily hexyl methyl sulfoxide by g.c. analysis. The yield was around 25%. The low yield was probably due to the poor solubility of sodium oxide and/or to formation of a coating of sodium hydroxide on the surface of the sodium oxide.

Acknowledgment.—The authors are indebted to Dr. C. D. Broaddus for helpful critical comments on the manuscript and to Mr. A. L. Voegele and Mr. D. E. Weik for their excellent technical assistance.

Stereochemistry of the Addition of Dialkylalkylthiosulfonium Salts to Alkenes and Alkynes[1,2]

GEORGE K. HELMKAMP, BARBARA ANN OLSEN, AND JAMES R. KOSKINEN

University of California, Riverside, California

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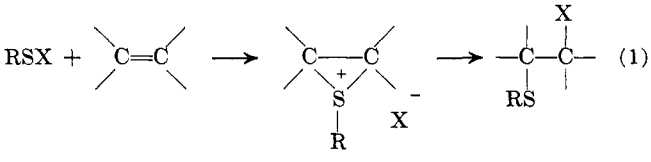
trans-2-Butene reacts with dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**) to form *dl-erythro*-1-dimethylsulfonio-2-methylthiobutane 2,4,6-trinitrobenzenesulfonate (**2**). Alkylation of **2** with trimethyloxonium trinitrobenzenesulfonate yielded 2,3-bis(dimethylsulfonio)butane 2,4,6-trinitrobenzenesulfonate (**3**). The direction of addition of **1** to the alkene was established as *trans* by comparing **3** with a product formed in the following sequence: (a) conversion of (*S,S*)-2-butene episulfide to (2*S*:3*R*)-3-methylthio-2-butanethiol (**5**); (b) monoalkylation of **5** to yield optically inactive (hence *meso*) 2,3-bis(methylthio)butane (**6**); and (c) exhaustive alkylation of either **5** or **6** to yield a compound identical with **3**. Similarly, the compound formed when **1** reacts with acetylene has n.m.r. and infrared spectra consistent with a *trans* arrangement of protons.

Dialkylalkylthiosulfonium salts react with alkenes and alkynes[3] in much the same way as do sulfenyl halides[4,5] to form 1:1 adducts. The proposed mechanism of addition of sulfenyl halides to olefins involves initial transfer of a sulfenium group to the double bond to form an episulfonium intermediate (eq. 1).[6]

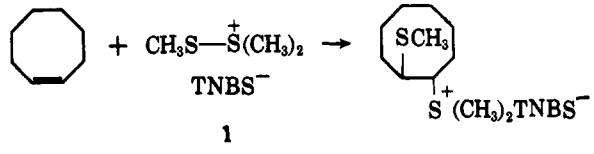


(1)

Nucleophilic attack by halide ion subsequently collapses the intermediate to produce the adduct. In dry acetic acid the reaction follows second-order kinetics.[6] In addition, observations of a positive salt effect and enhanced rates in polar solvents support a transition state that is more polar than the reactants.

The addition reaction between olefins and sulfenyl halides has been shown to be stereospecific. Addition to *cis* and *trans* olefin pairs gives nonidentical products.[7] The supposition that *trans* addition is involved is suggested by the nature of the products obtained from the solvolyses of the two butene adducts.[8] Assignment of stereochemistry is based on the reasonable assumption that the episulfonium intermediate opens *trans*.

Preliminary data on the reaction of alkylated disulfides with olefins indicated that the process was *trans* and stereospecific. Addition of dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate (**1**) to *cis*-cyclooctene affords the same product (eq. 2) as that



1

(TNBS = 2,4,6-trinitrobenzenesulfonate)

obtained by the reaction of cyclooctene S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate with dimethyl sulfide,[3] which indicates that the postulation of an episulfonium salt as a reaction intermediate is not unreasonable. The episulfonium salt of cyclooctene must have the *cis* configuration since it is prepared either by the reaction of *cis*-cyclooctene with methanesulfenyl 2,4,6-trinitrobenzenesulfonate[9] or by alkylation of *cis*-cyclooctene episulfide.[10] Furthermore, treatment of the salt with iodide or mercaptide ion regenerated *cis*-cyclooctene.[10] Thus, by analogy

(1) Supported in part by Grant GM 8185 from the National Institutes of Health, U. S. Public Health Service.

(2) Presented at the 1964 Pacific Southwest Regional Meeting of the American Chemical Society, Costa Mesa, Calif., Dec. 1964.

(3) G. K. Helmkamp, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 676 (1965).

(4) N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *J. Am. Chem. Soc.*, **69**, 1612 (1947).

(5) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

(6) W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

(7) N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953).

(8) A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956).

(9) D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **29**, 2702 (1964).

(10) D. J. Pettitt and G. K. Helmkamp, *ibid.*, **28**, 2932 (1963).

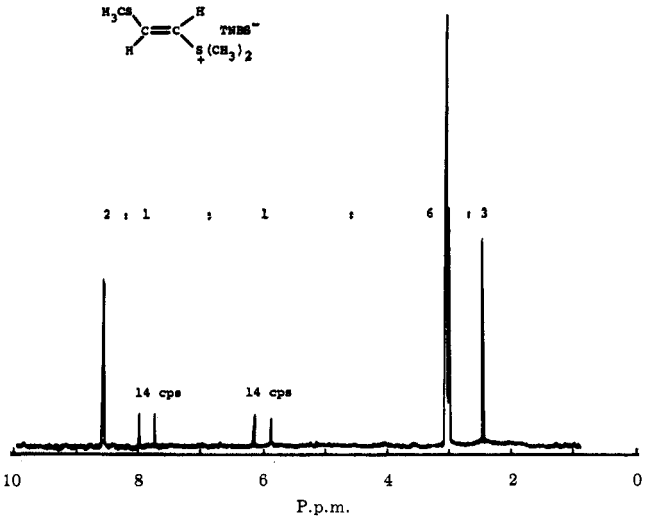
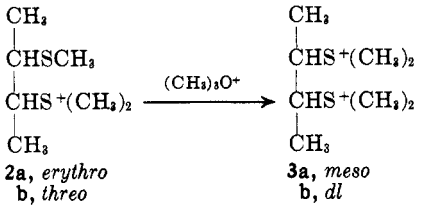


Figure 1.—Proton n.m.r. spectrum of the adduct formed from dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate and acetylene. Data for a nitromethane solution at 60 Mc.

with similar ring-opening reactions, it appears logical to assign the adduct the *threo* configuration.[11-13]

When the adduct from *cis*-2-butene and **1** was decomposed by iodide ion, *cis*-2-butene was regenerated. The *trans*-2-butene adduct similarly regenerated *trans*-2-butene. Although both salts have approximately the same melting point,[3] there is a mixture melting point depression, and the two compounds can be readily distinguished by their infrared spectra. Obviously, the addition reaction possesses stereochemical integrity, regardless of whether *cis* or *trans* addition is involved.

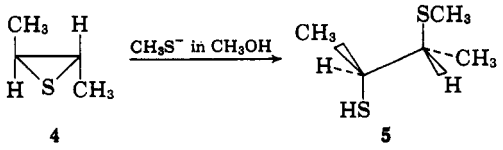
When the two nonidentical adducts of **1** and *cis*-2-butene and of **1** and *trans*-2-butene (**2a** and **b**) were alkylated to form the 2,3-bis(dimethylsulfonio)butane salts (**3a** and **b**), two different compounds were obtained (eq. 3). There was a melting point difference of ap-



(3)

proximately 30° between the two, and their infrared spectra could be readily distinguished. The higher melting **3** resulted from the *trans*-2-butene adduct.

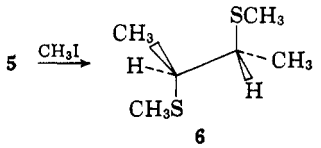
In order to prepare a model compound to serve in the identification of the stereoisomers of **3**, a synthetic sequence with an optically active starting material was used. (*S*,*S*)-2-Butene episulfide[14] (**4**) was treated



(4)

with methyl mercaptide ion to yield 3-methylthio-2-butanethiol (**5**) with a high degree of optical activity, $[\alpha]^{25}D$ +21.9° (eq. 4).

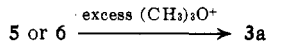
Treatment of **5** (presumably an *erythro* isomer) with 1 equiv. of methyl iodide in methanolic potassium hydroxide afforded 2,3-bis(methylthio)butane (**6**, eq. 5) which had negligible optical activity, $[\alpha]^{25}_{578}$ +0.02



(5)

± 0.01°. Since **6** produced in this manner was essentially devoid of optical activity, it must be assigned the *meso* configuration. If **6** is *meso*, then **5** must have had the *erythro* configuration which can result only from *trans* opening of the ring of compound **4**.

Both **5** and **6** could be exhaustively alkylated (eq. 6) to give the identical 2,3-bis(dimethylsulfonio)-

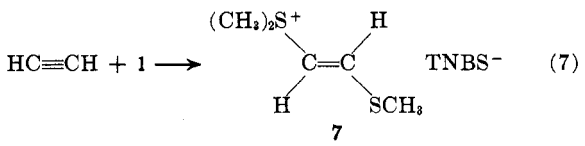


(6)

butane salt, $[\alpha]^{22}D$ 0.000 ± 0.002°. This salt, prepared *via trans* ring opening of the episulfide, must have had the *meso* configuration **3a**. The material was also identical (melting point, mixture melting point, infrared spectrum, n.m.r. spectrum) with **3** prepared by alkylation of the adduct **2a** formed from **1** and *trans*-2-butene. Hence, the addition of the dialkylalkylthiosulfonium ion to olefins is indeed stereochemically a *trans* process. If *cis* addition had been the case, *cis*-2-butene and **1** would have resulted in an adduct with the *erythro* configuration which could have been alkylated to yield **3a**.

An additional conclusion that can be drawn from the chemical comparisons is the definition of the elimination reaction of **2** (promoted by iodide ion) as a *trans* process.

Since dialkylalkylthiosulfonium salts add across alkenes in a *trans* manner, their addition to alkynes, by analogy, might also be *trans*. Previously, alkyl- and arylacetylenes were reported to react readily with **1**, but acetylene itself was sluggish.[3] The adduct **7** of the latter will form slowly in an uncatalyzed reaction (eq. 7).[15]



(7)

The n.m.r. spectrum of **7** is shown in Figure 1. There is a low-field singlet of weight 2 corresponding to the two protons on the 2,4,6-trinitrobenzenesulfonate anion. Two doublets corresponding to the vinyl protons, each of weight 1, are present midfield. Upfield are two sharp peaks, one of weight 3 attributable to the three methyl protons adjacent to the neutral sulfur and the other of weight 6 corresponding to the

(11) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

(12) G. K. Helmkamp and H. J. Lucas, *ibid.*, **74**, 951 (1952).

(13) G. K. Helmkamp, R. D. Clark, and J. R. Koskinen, *J. Org. Chem.*, **30**, 666 (1965).

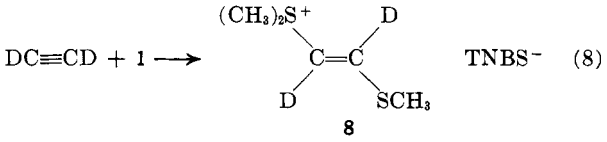
(14) Optically active compounds are described by the (*R*,*S*) system of R. S. Cahn, C. K. Ingold, and V. Prelog [*Experientia* **12**, 81 (1956)].

(15) The addition of 2,4-dinitrobenzenesulfenyl chloride to acetylene has been reported as occurring only in the presence of aluminum chloride as catalyst.[16] Aluminum chloride catalysis in this case did not afford **7**. With nitromethane as solvent, **1** reacted with aluminum chloride prior to reaction with acetylene.

(16) N. Kharasch and S. J. Assony, *J. Am. Chem. Soc.*, **75**, 1081 (1953).

six methyl protons on the positively charged sulfur. The large peak shows minor splitting. The coupling constant observed for the splitting of the vinyl protons is 14 c.p.s. In general, coupling constants of 6–14 c.p.s. are found for splitting between *cis*-ethylenic protons, while the range for *trans* splitting is 11–18 c.p.s.[17] The value observed for the protons in the acetylene adduct therefore lies at the uppermost extreme of the *cis* range and in the middle of the *trans* range. Thus, 14 c.p.s. is not an unreasonable value to observe in this instance for *trans* coupling. Without direct comparison between the values observed for **7** and its stereoisomer, the magnitude of the coupling constant does not conclusively eliminate the possibility of a *cis* arrangement of protons.

Two protons attached to a carbon–carbon double bond in a *trans* arrangement usually results in an infrared absorption peak near 965 cm.$^{-1}$, while a 675–730-cm.$^{-1}$ band is common for the *cis* structure.[18] However, the presence of large electronegative substituents decreases the frequency at which absorption occurs. In the infrared spectrum of **7**, several peaks are visible in the 840–1000-cm.$^{-1}$ range. Since **7** has two large substituents, one bearing a positive charge, assignment of one of these bands to a twist vibration without further evidence is virtually impossible. Therefore **1** was added to deuterated acetylene (eq. 8). Com-



(8)

parison of infrared spectra shows that a reasonably strong band present at 843 cm.$^{-1}$ in **7**, the protium compound, is absent in **8**, the deuterium compound. The shift of this peak must be the result of substitution of the hydrogen atoms in **7** by deuterium. Normally there is a decrease in the twist frequency (from 965 cm.$^{-1}$) when the molecule contains substituents having high inductive power. Since *trans*-dichloroethylene shows this mode at 892 cm.$^{-1}$, it is not unreasonable to assume that the 843-cm.$^{-1}$ band arises from a *trans* arrangement in **7**. Thus, the tentative conclusion is made that dialkylalkylthiosulfonium salts react toward alkynes stereochemically in the same manner as toward alkenes.

Experimental[19]

(*S,S*)-2-Butene Episulfide.—Optically active and (*R,S*)-episulfides were prepared from the corresponding epoxides by the thiourea method described by Bordwell and Andersen.[20] Results of the syntheses were comparable with those reported previously.[21]

(2*S*:3*R*)-3-Methylthio-2-butanethiol.—Excess methanethiol was bubbled into a cold sodium methoxide solution prepared from 16 g. (0.7 g.-atom) of sodium and 200 ml. of methanol. After the addition the solution was allowed to warm to room temperature. A solution of 13 g. (0.15 mole) of 2,3-dimethylthiirane in 50 ml. of methanol was added dropwise with stirring over a 5-hr. period. After standing overnight, the mixture was made slightly acidic with dilute hydrochloric acid. The resulting solution was extracted with four 25-ml. portions of pentane. The pentane solution was dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation. The product was isolated by vacuum distillation in a small Vigreux column: b.p. 56° (5 mm.), d^{25}_4 1.006, $[\alpha]^{25}_D$ 21.9°, yield 7.0 g. (0.051 mole), 34%.

Anal. Calcd. for $C_5H_{12}S_2$: C, 44.06; H, 8.88. Found: C, 43.73; H, 8.98.

***meso*-2,3-Bis(methylthio)butene.**—The *meso* isomer was prepared from both (*R,S*)- and (2*S*:3*R*)-3-methylthio-2-butanethiol. The yields were 85 and 78%, respectively. In both cases a solution of 1.7 g. (0.031 mole) of potassium hydroxide in 15 ml. of methanol were added to 2.2 g. (0.016 mole) of 3-methylthio-2-butanethiol in 25 ml. of methanol. Methyl iodide (2.3 g., 0.016 mole), diluted with about 5 ml. of methanol, was added with swirling over a period of about 2 min. The temperature of the reaction mixture reached about 45°. When it reached room temperature, 150 ml. of water were added. The product was extracted three times with 50-ml. portions of pentane and the organic phase was dried over sodium carbonate. The solvent was removed by distillation at 1-atm. pressure, and the residual material was distilled at reduced pressure. The physical properties and yield for the compound prepared from (2*S*:3*R*)-3-methylthio-2-butanethiol were b.p. 76.6–77.0° (6 mm.), n^{24}_D 1.5132, yield 1.7 g., 78%, $[\alpha]^{25}_{578}$ +0.02°.

Anal. Calcd. for $C_6H_{14}S_2$: C, 47.95; H, 9.39. Found: C, 48.01; H, 9.39.

2,3-Bis(dimethylsulfonio)butane 2,4,6-Trinitrobenzenesulfonate.—The isomer assigned the *meso* configuration was prepared *via* three routes.

A.—To 15 ml. of nitromethane was added 0.77 g. (0.0021 mole) of trimethyloxonium trinitrobenzenesulfonate and 1.00 g. (0.0021 mole) of the adduct formed from **1** and *trans*-2-butene. The mixture was warmed at about 50° for 4 hr. The white solid that formed was removed by filtration. Addition of ether to the filtrate precipitated a small amount of unreacted oxonium salt. The bisdimethylsulfonium salt was soluble in methyl sulfoxide and could be recrystallized from it by adding ether containing sufficient ethanol to keep the liquid phases homogeneous. The yield was nearly quantitative: m.p. 235–236° dec.

Anal. Calcd. for $C_{20}H_{24}N_6O_{18}S_4$: C, 31.41; H, 3.16; N, 10.99. Found: C, 31.67; H, 3.28; N, 10.67.

B.—To 15 ml. of nitromethane was added 4.5 g. (0.012 mole) of trimethyloxonium 2,4,6-trinitrobenzenesulfonate and 0.57 g. (0.0042 mole) of the optically active 3-methylthio-2-butanethiol. The mixture was warmed at about 50° for 4 hr., then treated as in the previous synthesis. The yield of product was almost quantitative: m.p. 233–234° dec., m.m.p. 234–235° dec. with product from A, $[\alpha]^{25}_D$ +0.10° (0.107 g. in 2 ml. of methyl sulfoxide). The infrared spectra of both products were identical.

C.—An almost quantitative yield was obtained by warming a mixture of 0.71 g. (0.0020 mole) of trimethyloxonium 2,4,6-trinitrobenzenesulfonate and 0.10 g. (0.0006 mole) of *meso*-2,3-bis(methylthio)butane in 10 ml. of nitromethane: m.p. 234–235° dec., m.m.p. 234–235° dec. with product from A.

2,3-Bis(dimethylsulfonio)butane 2,4,6-Trinitrobenzenesulfonate.—The isomer assigned the *dl*-configuration was prepared by alkylating the adduct of **1** and *cis*-2-butene as above: m.p. 199–200°.

1-Dimethylsulfonio-2-methylthioethene 2,4,6-Trinitrobenzenesulfonate.—Acetylene, purified with a train of four concentrated sulfuric acid scrubbers and a potassium hydroxide drying tube, was bubbled slowly into a suspension of 1.0 g. (0.0025 mole) of dimethylmethylthiosulfonium 2,4,6-trinitrobenzenesulfonate[22] in about 10 ml. of nitromethane for 6 hr. At the end of this time the reaction was considered essentially complete. The reaction solution had become clear after approximately 3 hr. An excess of anhydrous ether was added to cause precipitation, and the product mixture was chilled. The resultant pale yellow solid was isolated by filtration and dried under reduced pressure. Fractional recrystallization showed that the initial precipitate had at least two components, trimethylsulfonium 2,4,6-trinitrobenzenesulfonate (identified by comparing its melting point and infrared spectrum with those of an authentic sample) and the

(17) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 161.

(18) W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, **15**, 679 (1959).

(19) Microanalyses were by C. F. Geiger, Ontario, Calif.

(20) F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 4959 (1953).

(21) G. K. Helmkamp and N. Schnautz, *Tetrahedron*, **2**, 304 (1958).

(22) G. K. Helmkamp, H. N. Cassey, B. A. Olsen, and D. J. Pettitt, *J. Org. Chem.*, **30**, 933 (1965).

desired product. After several recrystallizations from nitromethane–ether, a small quantity of pure material was obtained, m.p. 131.5–133.5°.

Anal. Calcd. for $C_{11}H_{13}N_3O_9S_3$: C, 30.91; H, 3.07; N, 9.83. Found: C, 30.89; H, 3.10; N, 10.10.

1,2-Dideuterio-1-dimethylsulfonio-2-methylthioethene 2,4,6-Trinitrobenzenesulfonate.—Deuterated acetylene was prepared by adding deuterium oxide (99.5 mole % min.) to calcium carbide at a rate sufficient to maintain a constant slow flow of gas through a Drierite drying tube into a reaction vessel containing 2.0 g. (0.0050 mole) of **1** in approximately 15 ml. of nitromethane. Total reaction time was 8.5 hr. The reaction mixture was worked up as above to yield product, m.p. 128–129.5°, and trimethylsulfonium 2,4,6-trinitrobenzenesulfonate. A mixture melting point between the deuterated and undeuterated adducts showed no depression, and the n.m.r. of **8** was identical with that of **7** with the exception of the absence of the two doublets from the vinyl protons.

Synthesis of 1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6. Novel Lithium–Ammonia Reduction of the γ,δ-Diacetoxy α,β-Unsaturated Ketone System[1a]

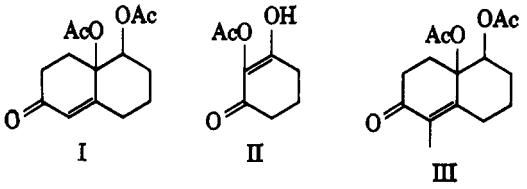
THOMAS A. SPENCER, KLAUS K. SCHMIEGEL,[1b] AND WALTER W. SCHMIEGEL

Department of Chemistry, Dartmouth College, Hanover, New Hampshire

Received December 12, 1964

1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (III) has been synthesized *via* careful, stepwise Robinson annelation of dihydropyrogallol acetate with ethyl vinyl ketone, in a sequence analogous to the previously reported preparation of 1,9-*cis*-diacetoxy-$\Delta^{5,10}$-octalone-6 (I). Treatment of III and I with lithium in ammonia converted these substances to 1-methyl-$\Delta^{9,10}$-octalone-2 (XII) and $\Delta^{9,10}$-octalone-2 (XIV), respectively. A mechanism for this novel reduction, involving successive carbanionic elimination of the two acetoxyl groups, is presented and discussed.

We have previously reported the synthesis of 1,9-*cis*-diacetoxy-$\Delta^{5,10}$-octalone-6 (I) by careful, stepwise Robinson annelation of dihydropyrogallol acetate (II) with methyl vinyl ketone.[2] In this paper the preparation of the ethyl vinyl ketone analog, 1,9-*cis*-diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (III), and the novel reduction of III and I with lithium in ammonia are described.



Synthesis of 1,9-*cis*-Diacetoxy-5-methyl-$\Delta^{5,10}$-octalone-6 (III).—The synthesis of III was undertaken as a continuation of our studies[2] of intermediates potentially useful for elaboration to diterpenoids of the rosenonolactone type and was accomplished by essentially the same path used for the synthesis of I. Michael addition of II to ethyl vinyl ketone smoothly afforded 80% of the adduct IV, m.p. 68.5–69.5°. Cyclization of IV with pyrrolidine and acetic acid was much slower than cyclization of the corresponding methyl vinyl ketone adduct.[2] However, upon treatment of IV with excess pyrrolidine and acetic acid at room temperature for 72 hr., a 67% yield of ketol V, m.p. 217–217.5°, was obtained. The hydronaphthalenic skeleton of the ketol was evident from its n.m.r. spectrum. It is assigned the *cis* ring fusion (as shown in V) by analogy to the corresponding ketol in the methyl vinyl ketone series, according to our postulate[2] of stereoselective cyclization of *cis*-fused ring systems when a bulky angular substituent is present.[3] Further work to substantiate this assignment is planned. No experimental evidence is available concerning the configuration of the C-5 methyl group.[4]

No bridged ketol isomeric to V was isolated, but 5% of a substance, m.p. 118–119°, with an analysis indicating a molecular formula $C_{11}H_{16}O_4$ was obtained. This material has been tentatively assigned the dioldione structure VI on the basis of its infrared and n.m.r. spectra, and its conversion, upon refluxing with *p*-toluenesulfonic acid in benzene, to 5-methyl-6-hydroxytetralone-1 (VII).[5] This structural assignment deserves to be the subject of further investigation. Although formation of VI from IV could result from displacement on the tertiary acetate carbonyl at any stage during the prolonged treatment with pyrrolidine and acetic acid, this result was not expected and is intriguing.

Dehydration of ketol V to the desired α,β-unsaturated ketone VIII proved to be the most troublesome step in the synthesis of III. An extended study of dehydration conditions was necessary in order to find those which would effect formation of VIII without causing subsequent aromatization to VII. Heating with *p*-toluenesulfonic acid in benzene, the conditions which effected the desired dehydration successfully in the methyl vinyl ketone series,[2] yielded only VII plus recovered starting material. Very brief treatment of V with dilute hydrogen chloride in methanol gave 88% of 5-methyl-6-methoxytetralone-1 (IX).[6] However,

(1) (a) A portion of this work was presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964. We wish to thank Dr. Morris Brown for making this presentation. (b) National Science Foundation Graduate Teaching Assistant Summer Fellow, 1963.

(2) T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963).

(3) J. A. Marshall and W. I. Fanta [*J. Org. Chem.*, **29**, 2501 (1964)] showed selective formation of a *cis*-fused ring system when the angular substituent was methyl, and selective formation of a *trans*-fused system when the angular substituent was hydrogen. These workers also presented n.m.r. evidence proving the hydronaphthalenic skeleton of a ketol previously prepared by McQuillin and assigned a *cis*-fused structure: R. Howe, F. J. McQuillin, and R. Temple, *J. Chem. Soc.*, 363 (1959), and references cited therein.

(4) Since V is a *cis*-decalin derivative, this methyl group can adopt an equatorial conformation in either configuration.

(5) A. J. Birch, J. A. K. Quartey, and H. Smith, *J. Chem. Soc.*, 1768 (1952); J. W. Ralls, W. C. Wildman, K. E. McCaleb, and A. L. Wilds, *Chem. Abstr.*, **49**, 1813 (1955).

(6) R. H. Martin and R. Robinson, *J. Chem. Soc.*, 491 (1943).