[Chem. Pharm. Bull.
13(6) 663～672 (1965)]

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86. **Issei Iwai and Junya Ide**: Studies on Acetylenic Compounds. XLI.[*1] The Reactions of Methylsulfinyl Carbanion with Diphenylacetylene or 1,4-Diphenyl-1,3-butadiyne.[*2]

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There have been only few reports concerning the reaction of carbanions with non-carbonyl or conjugated acetylenes. In this fields Mulvaney and his co-workers[1)] found that the reaction of diphenylacetylene with butyllithium yields *trans-α*-butylstilbene, while Eisch and Kaska[2)] obtained triphenylacrylic acid from phenyllithium and diphenylacetylene followed by carbonation. Furthermore, there has been another report[3)] which deals with the reaction of malonate anion with acetylene in the presence of zinc stearate as a catalyst. In our laboratory, we have found that *p*-nitrophenylacetylene reacted with 2-nitropropane in the presence of sodium ethoxide as a catalyst to give 1-(*p*-nitrophenyl)-3-methyl-3-nitro-1-butene but that further application of this reaction on phenylacetylene and active methylene compounds such as ethyl cyanoacetate, diethyl malonate[4)] was unsuccessful. This is in contrast with Grignard reagents which are generally unreactive toward 1,2-disubstituted acetylene at atmospheric pressure even under severe conditions.[5)] In a recent communication, however, Tsutsui[6)] has reported that phenylmagnesium bromide and diphenylacetylene reacted in high boiling solvents such as xylene to give two products; hexaphenylbenzene and octaphenyl derivative.

On the other hand, an increasing attention has been recently given to dimethyl sulfoxide which is very useful not only as a solvent but as an effective reagent. In

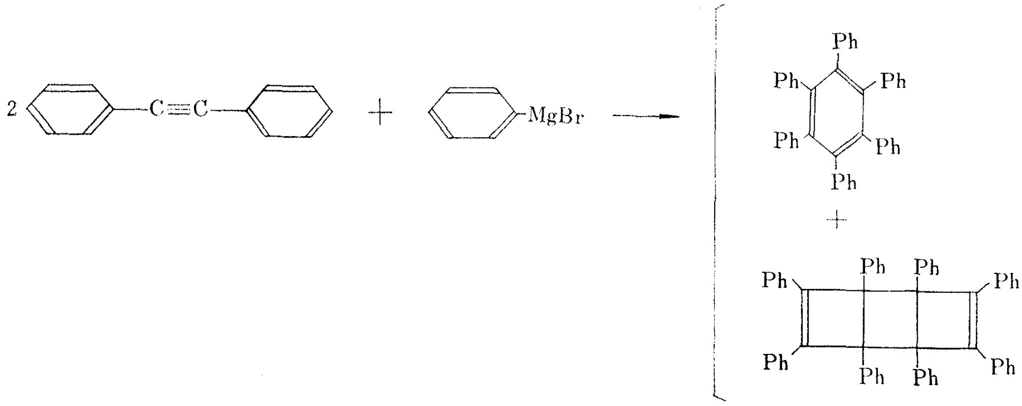

Chart 1.

[*1] Part XL: This Bulletin, **13**, 118 (1965).

[*2] In the course of this investigation, the authors have received a private communication from Dr. J.C. Craig, Professor of University of California, who had also investigated some parts of this work. The authors wish to express their gratitude for his valuable suggestion and for supplying us his sample for identification.

[*3] Hiromachi, Shinagawa-ku, Tokyo (岩井一成, 井手純也).

1) J.E. Mulvaney, Z.G. Gardlund, *et al.*: J. Am. Chem. Soc., **85**, 3896 (1963).

2) J.J. Eisch, W.C. Kaska: *Ibid.*, **84**, 1501 (1962).

3) M. Seefelder: Ann., **652**, 107 (1962).

4) Unpublished data in our laboratory.

5) M.S. Kharasch, O. Reinmuth: "Grignard Reactions of Nonmetallic Substances," Prentice Hall, New York, N.Y., 1954.

6) M. Tsutsui: Chem. & Ind. (London), **1962**, 780.

this respect, the methylsulfinyl carbanion, prepared from dimethyl sulfoxide and sodium hydride,[7] was proved to be a strongly basic reagent which reacts with triphenylmethane to produce a deep red solution of triphenyl carbanion. This fact indicates that methylsulfinyl carbanion has almost the same strong basicity as alkyllithium. Based on these facts, the present investigation was done with the reaction of methylsulfinyl carbanion and acetylenic derivatives in dimethyl sulfoxide. The treatment of diphenylacetylene (0.025 mole) with methylsulfinyl carbanion, which was prepared from sodium hydride (0.05 mole) and 25 ml. of dimethyl sulfoxide by stirring in nitrogen atmosphere, at 25~27° for one hour and then at 35~38° for three hours, gave a crystalline substance melted at 95~112° in 95% yield. This substance showed two spots by thin-layer chromatography on silica gel developed with a mixture of chloroform and ethanol (1:1). The fractional recrystallization from hexane-benzene afforded two compounds; I-a, m.p. 109~110° and I-b, m.p. 129~130°. The analytical data of both compounds agreed with the empirical formula corresponding to $C_{16}H_{16}OS$. The infrared spectra of both (I-a) and (I-b) showed absorption bands at 1031 cm^{-1} due to sulfoxide group.[8]

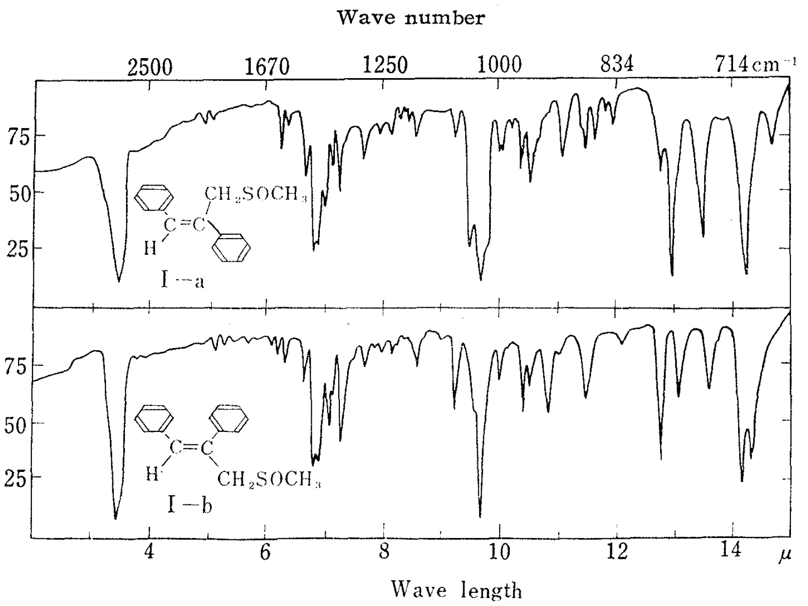

Fig. 1. Infrared Absorption Spectra of *cis* and *trans* Adducts of Methylsulfinyl Carbanion and Diphenylacetylene

The ultraviolet absorption spectrum of the sulfoxide (I-a) in ethanol showed an absorption maximum at 276 mμ (ε 17750) and that of I-b at 226.5 mμ (ε 19150) and 272 mμ (ε 14400). It is known that the *cis* isomer in olefins of type abC=Cbc, where the substituents a and c may undergo resonance interaction with the olefinic system, possess frequently its absorption maximum at a slightly shorter wave length and that the intensity is in all cases considerably weaker than that of the *trans* isomer. The major contributing factor to this situation seems to be the steric inhibition of resonance. Cram and his co-workers[9] have reported the ultraviolet spectra of *cis*- and *trans*-α-methylstilbene whose absorption maxima situated at 260 mμ (ε 11900) and 270 mμ (ε 20100) respectively. Therefore, our spectral analysis would suggest that the sulfoxides (I-a) and (I-b) are geometrical isomers to one another and have the *trans*- and *cis*-configuration respectively.

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7) E. J. Corey, M. Chaykovsky: J. Am. Chem. Soc., **84**, 866 (1962).

8) L. J. Bellamy: "The Infrared Spectra of Complex Molecules," p. 357 (1958), John Wiley & Sons, Inc., New York.

9) D. J. Cram, F. A. Abd Elhafez: J. Am. Chem. Soc., **74**, 5828 (1952).

The nuclear magnetic resonance spectra of the sulfoxide (I-a) in deuteriochloroform showed a multiplet pattern of aromatic protons at 2.1∼2.8 τ; a singlet peak at 2.86 τ assigned to a vinyl proton at α-position to the aromatic ring; AB type quartet at 5.68 τ and 5.91 τ (J_{AB}=13 c.p.s.) due to methylene protons adjacent to sulfoxide group; and the protons of methyl group at 7.60 τ as a singlet, and that of the sulfoxide (I-b) showed aromatic protons at 2.56∼2.93 τ; a singlet peak at 3.29 τ as a vinyl proton at α-position to the aromatic ring; AB type quartet at 6.03 τ and 6.24 τ (J_{AB}=12 c.p.s.) indicating the methylene protons adjacent to sulfoxide group; and the protons of methyl group at 7.46 τ as a singlet. Curtin and his co-workers[10] has observed that the vinyl proton occurs at a higher field for *cis*- than *trans*-stilbene in nuclear magnetic resonance spectra. In another report, the signals of the vinyl proton in *cis*- and *trans*-stilbene are located at 3.43 τ and 2.90 τ respectively.[11] In *trans* isomer each proton lies in the plane of two phenyl groups and is therefore deshielded, whereas, in *cis* isomer the aromatic rings are tilted and the deshielding of the olefinic protons is thereby reduced.

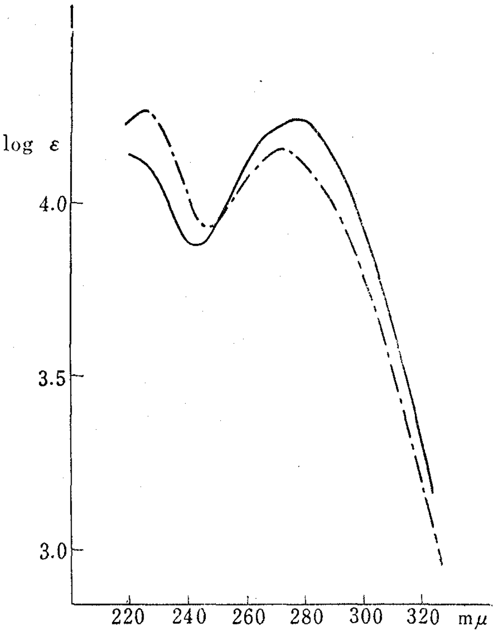
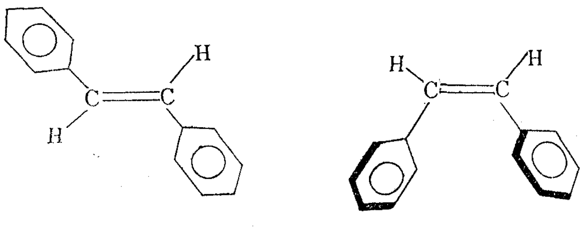


Fig. 2. Ultraviolet Absorption Spectra (in EtOH)

——— *trans*-3-Methylsulfinyl-1,2-diphenyl-1-propene (I-a)

------ *cis*-3-Methylsulfinyl-1,2-diphenyl-1-propene (I-b)

From these observations, the sulfoxides (I-a) and (I-b) are considered to be geometrical isomers to one another and I-a possessing the signal at 2.86 τ would be assigned as the *trans* and I-b at 3.29 τ as the *cis* isomer. This conclusion is consistent with the fact that both compounds have the same analytical values. The AB type patterns in both I-a and I-b are supposedly considered due to the system, -CH_2-SO-, in which the methylene group is adjacent to an asymmetric sulfur atom as in the case of the methylene group adjacent to an asymmetric carbon atom.[12]



trans *cis*

Fig. 3.

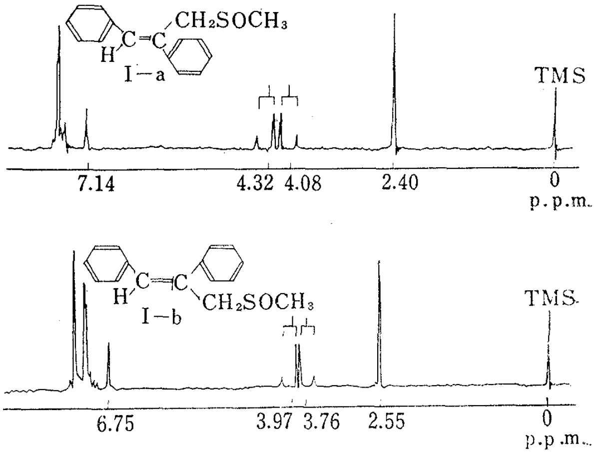


Fig. 4. Nuclear Magnetic Resonance Spectra (60 Mc.) of *trans*-3-Methylsulfinyl-1,2-diphenyl-1-propene and *cis*-3-Methylsulfinyl-1,2-diphenyl-1-propene in Deuteriochloroform using Tetramethylsilane as Internal Standard at 10 (τ-scale)

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10) D. Y. Curtin, H. Gruen, B. A. Shoulders : Chem. & Ind. (London), **1958**, 1205.

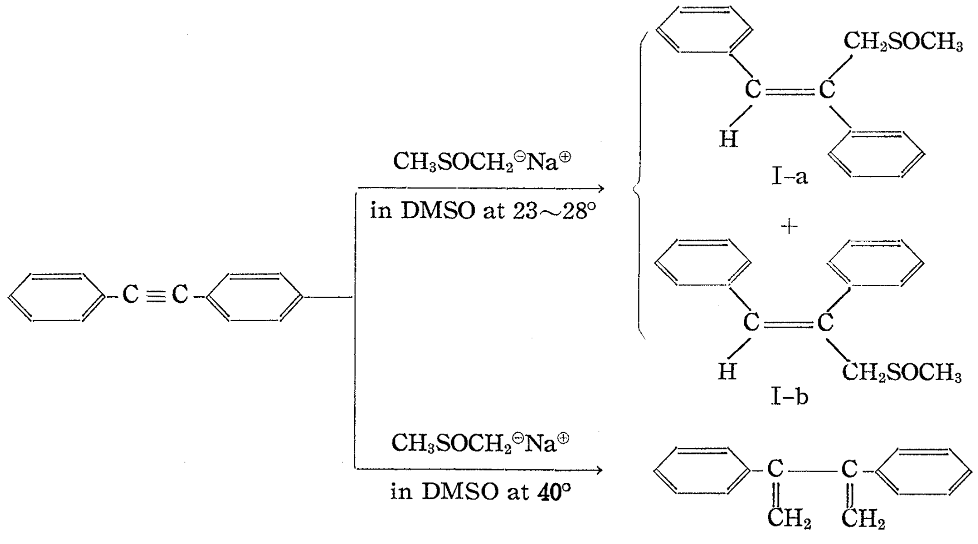
11) N. S. Bhacca, L. F. Johnson, J. N. Schoolery : "NMR Spectra Catalog," **1**, (1962), Varian Associates.

12) L. M. Jackman : "Application Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry." p. 101 (1959), Pergamon Press, London.

This pattern which is due to an asymmetric sulfur atom seems to be a rare and interesting example. From the results of ultraviolet, infrared,nuclea r magnetic resonance spectra and elemental analysis, I-a would be assigned to be *trans*-3-methylsulfinyl-1,2-diphenyl-1-propene and I-b *cis*-3-methylsulfinyl-1,2-diphenyl-1-propene.

The gas chromatographic method, for the determination of the ratio of *cis* and *trans* isomers in the reaction mixture, could not be applied on these compounds because of their high boiling points. The ratio, 88.5% of *trans* and 11.5% of *cis* was based on nuclear magnetic resonance spectra as evidenced by the peaks of methyl signals at 7.60 τ and 7.46 τ respectively.

On the other hand, however, treatment of diphenylacetylene (0.025 mole) with methylsulfinyl carbanion, prepared from sodium hydride (0.05 mole) in 25 ml. of dimethyl sulfoxide at 35∼38° in nitrogen atmosphere and then at 40° for three hours, afforded colorless prisms (II), m.p. 47∼48° in 28% yield after alumina chromatography, whose elemental analysis agreed with the empirical formula, $C_{16}H_{14}$. The infrared spectra of II revealed a characteristic terminal methylene band at 908 cm^{-1} and the nuclear magnetic resonance spectra showed a multiplet pattern of aromatic protons at 2.62∼2.90 τ and AB type quartet at 6.45 τ and 6.74 τ ($J_{AB}=3$ c.p.s.) which consisted of two equivalent AB type pattern due to the unequivalent protons of the terminal methylene group. The ultraviolet absorption maximum in ethanol was located at 242 mμ (ε 21500). From these data, the structure of II was supposed 2,3-diphenyl-1,3-butadiene, which was identical in melting point with that reported by K. von Auwers.[13] When the reaction was carried out at 75°, reaction temperature raised to 95∼100° after 15 minutes. In this case, the yield of the butadiene was very low (7% yield).



Chrat 2.

It would be considered that the reaction to afford butadiene derivative (II) consumed two moles of methylsulfinyl carbanion for one mole of acetylene. This reaction, however, was carried out from equimolecular amounts of the carbanion and diphenylacetylene to give almost the same yield (28.5% yield) as in the case of the reaction using two mole-equivalents of the anion. The yield in both cases is relatively low (28∼28.5%), therefore, it is uncertain whether this reaction requires either one or two moles of the anion. In each case, after the reaction was completed the solution of reaction mixture was poured into cold water. The aqueous solutions was neutral when

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[13] K. von Auwers: Ann., **499**, 123 (1932).

either one or two moles of the carbanion were used for each mole of diphenylacetylene. The proposed reaction mechanism affording the butadiene (II) would probably involve double addition of the anion to triple bond (-C≡C-), followed by elimination of two moles of CH_3SOH.

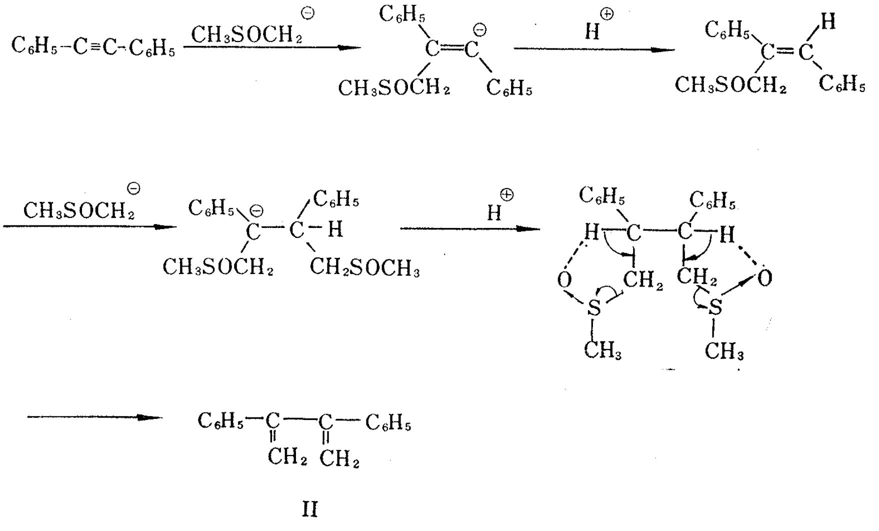

Chart 3.

The reaction using 1,4-diphenyl-1,3-butadiyne with methylsulfinyl carbanion was also carried out at room temperature for three hours and after the reaction mixture was chromatographed on alumina it afforded two crystalline compounds containing sulfur atom; pale yellow needles (A), m.p. 97.5~98.5° and colorless needles (B), m.p. 83~84° in 80% yield. The analytical data of both compounds agreed with the empirical formula, $C_{18}H_{16}OS$. Infrared absorption spectra of both compounds showed a characteristic sulfoxide band at 1042 cm^{-1} and a characteristic band for triple bond at 2198 cm^{-1}.

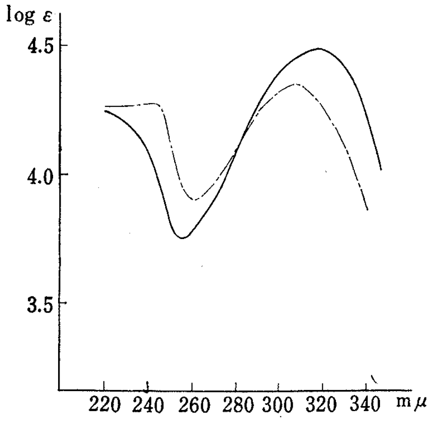

Fig. 5. Ultraviolet Absorption Spectra (in EtOH)

——— *trans*-1-Methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-a)
– – – – *cis*-1-Methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-b)

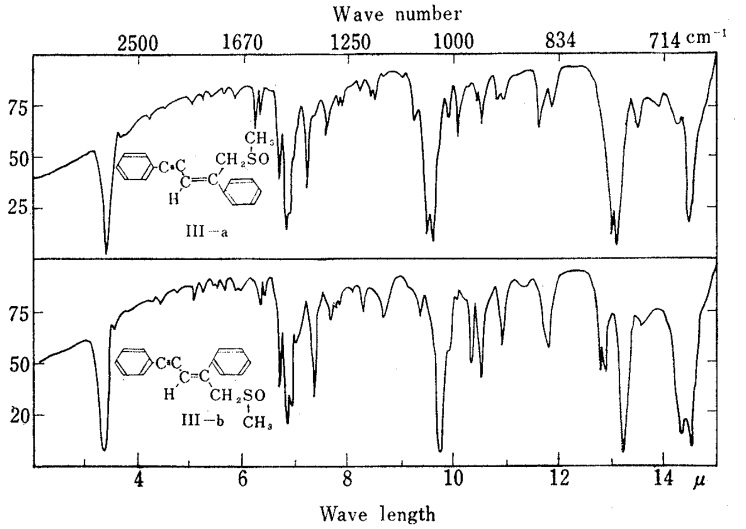

Fig. 6. Infrared Absorption Spectra of *cis* and *trans* Adducts of Methylsulfinyl Carbanion and 1,4-Diphenyl-1,3-butadiyne

The ultraviolet spectra of (A) exhibited an absorption maximum at 317 mμ (ε 31640) and those of (B) at 243 mμ (ε 19170) and 307 mμ (ε 22280). The pattern of ultraviolet spectra of (A) is very closely similar to that of *trans*-1,4-diphenyl-1-buten-3-yne[λ_{max}^{EtOH}

313 mμ (ε 39150)]. These observation suggested that both compounds (A) and (B) would be stereochemical isomers and the following two pairs of geometrical isomers will be considered.

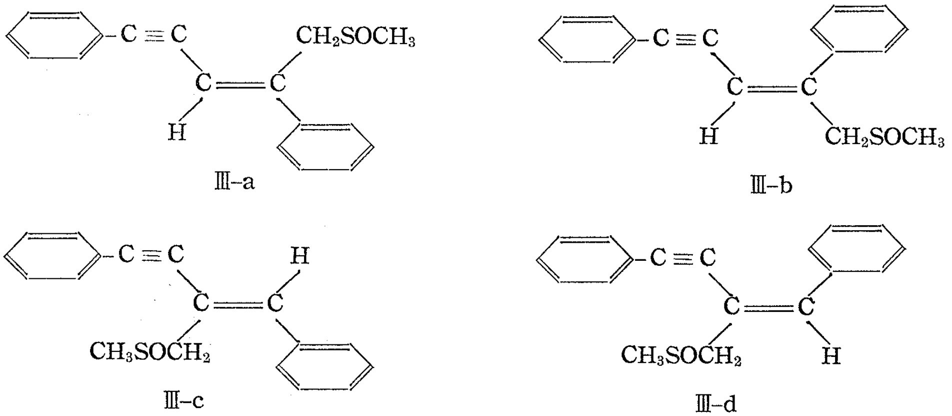
Ⅲ-a Ⅲ-b Ⅲ-c Ⅲ-d

Chart 4.

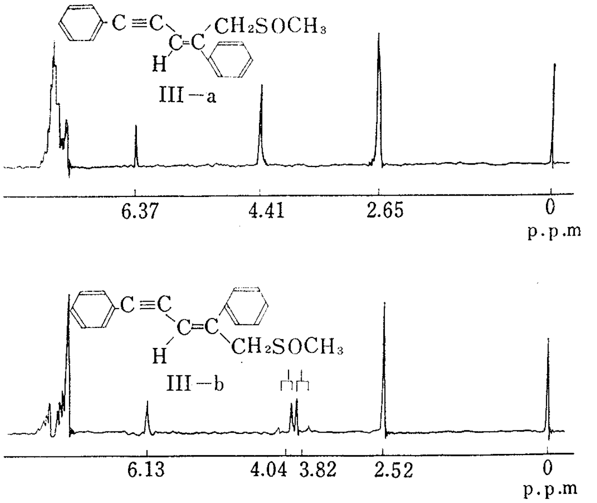

Fig. 7. Nuclear Magnetic Resonance Spectra (60 Mc.) of *trans*-1-Methylsulfinyl-2,5-diphenyl-2-penten-4-yne and *cis*-1-Methylsulfinyl-2,5-diphenyl-2-penten-4-yne in Deuteriochloroform using Tetramethylsilane as Internal Standard at 10 (τ-scale)

The nuclear magnetic resonance spectra of (A) and (B) were very closely similar to one another; each singlet signal at 7.35 τ and 7.48 τ in (A) and (B) were assigned to methylene group, and singlet peaks at 3.63 τ and 3.87 τ in (A) and (B) were due to olefinic proton conjugated with phenyl group respectively. In *trans*-1,4-diphenyl-1-buten-3-yne, AB type quartet at 2.92 τ and 3.59 τ ($J_{AB}=16.5$ c.p.s.) were revealed, the doublet at 3.59 τ were assigned to the proton on β-position from phenyl group and the doublet at 2.92 τ the proton on α-position because of anisotropic effect of phenyl ring. On the basis of these assignments, each singlet peak at 3.63 τ and 3.87 τ in (A) and (B) was assigned to the proton on β-position to phenyl group. Therefore, the tentative structure (Ⅲ-c) and (Ⅲ-d) were excluded and Ⅲ-a and Ⅲ-b were compatible with the structure (A) and (B).

The AB type at 5.95 τ and 6.18 τ ($J_{AB}=13$ c.p.s) of (B) was assigned to the methylene protons adjacent to an asymmetric sulfur atom. However, only singlet signal at 5.59 τ was observed in (A) for the methylene protons corresponding to that of (B). This fact would be caused by that the protons adjacent to sulfoxide group had incidentally the same chemical shift. The differences in chemical shift rather than coupling constant have been used[14] to differenciate *cis* and *trans* isomers of trisubstituted ethylenes of the type $CH_3aC_1=C_2Hb$. Since the protons of the methylene group on C_1 are close

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14) *a*) L. M. Jackman, R. H. Wiley: Proc. Chem. Soc., **1958**, 196. *Idem*: J. Chem. Soc., **1960**, 2881, 2886. *b*) D. Y. Curtin, H. Gruen, B. A. Shoulders: Chem. & Ind. (London), **1958**, 1205. *c*) R. Morris, C. A. Vernon, R. F. M. White: Proc. Chem. Soc., **1958**, 303. *d*) D. E. Jones, R. O. Morris, C. A. Vernon, R. F. M. White: J. Chem. Soc., **1960**, 2349.

enough to the *cis* substituent on C_2 that their observed chemical shift is influenced by the nature of this substituent[15,16] which may be either hydrogen or group b. Jackman and Wiley[14a)] have examined several pairs of *cis-trans* isomers of $\alpha\beta$-unsaturated esters and they observed that β-olefinic protons are specifically deshielded by 0.5~0.9 p.p.m. by a *cis* alkoxycarbonyl group and the protons of a β-methyl group are also deshielded by 0.25 p.p.m. as is shown in Table I:

TABLE I. Chemical-shift Data (τ values) for $\alpha\beta$-Unsaturated Esters

Esters	β-H	$\Delta^{a)}$	β-CH_3	$\Delta^{a)}$
Me_2 maleate	3.86	0.53		
Me_2 fumarate	3.33			
Me_2 citraconate	4.25	0.94	7.96	0.24
Me_2 mesaconate	3.31		7.72	
Me *cis*-crotonate	3.57	0.62	7.86	0.25
Me *trans*-crotonate	2.95		8.11	
Me *cis*-$\alpha\beta$-dimethylcinnamate			8.05	0.30
Me *trans*-$\alpha\beta$-dimethylcinnamate			7.75	

a) $\tau_{trans}-\tau_{cis}=\Delta$, where *cis* and *trans* refer to the relation of the proton(s) to the carboxylate group and not necessarily to the configuration of the ester.

This principle would be applied to the present work displacing phenylethynyl(Ph-C≡C-) and the methylene group (-$\underline{CH_2}$-$SOCH_3$) in place of alkoxycarbonyl and methyl group. In comparison of the methylene in both (A) and (B), the τ value (5.59 τ) of (A) was smaller than that of (B) (6.07 τ; average value of 5.96 τ and 6.18 τ of AB type), and therefore the compound A was assigned to *trans*, *trans*-1-methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-a), and the B *cis*-isomer, *cis*-1-methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-b). This assignment was in agreement with the results of ultraviolet spectra and analytical values.

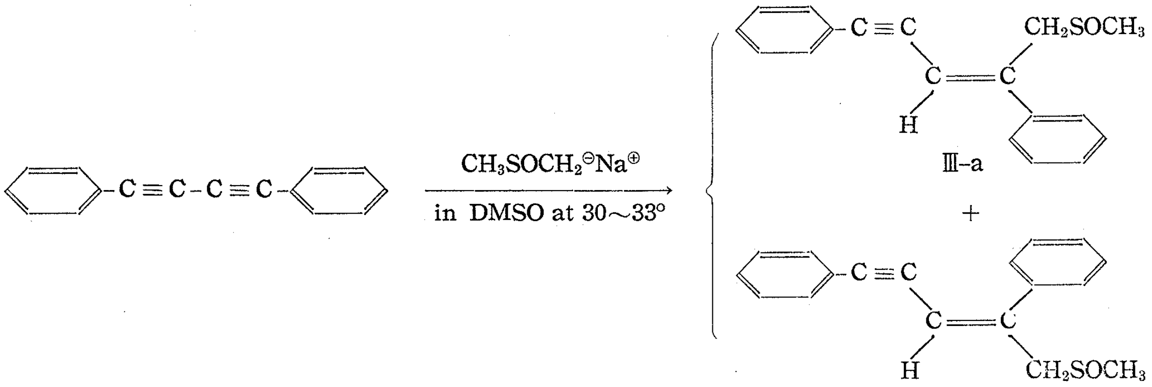

Chart 5. III-b

The ratio of III-a and III-b obtained from this addition reaction was 84% of *trans* and 16% of *cis* isomer as determined by column chromatography on alumina.

Strong bases, such as methoxide, and good nucleophiles such as mercaptides and thiophenoxides, add to acetylenes in nucleophilic fashion.[17] The stereochemistry of

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[15] E. L. Eliel: "Stereochemistry of Carbon Compounds," 335 (1962). McGraw-Hill, New York.

[16] L. M. Jackman: "Application Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry." p. 121 (1959), Pergamon Press, London.

[17] W.E. Truce: Nucleophilic Reactions of Thiols with Acetylenes and Chloroacetylenes, in N. Kharasch, ed., "Organic Sulfur Compounds," vol. 1. Pergamon Press, Ltd., London, (1961).

such nucleophilic addition is *trans*.[18] There is independent evidence that the base catalysed addition should be *trans*.[19] Thus the addition of sodium methoxide[18a] or sodium methylmercaptide[18b] to phenylacetylene has given *cis*-β-methoxystyrene or methyl *cis*-β-styryl sulfide respectively, *cis* isomers in both cases are formed by *trans* addition. This addition reaction of methylsulfinyl carbanion with diphenylacetylene or 1,4-diphenyl-1,3-butadiyne would be also believed to proceed in *trans* fashion. The *trans*-sulfoxide (Ⅲ-a) was treated with methylsulfinyl carbanion at room temperature to give *cis*-*trans* mixture with a ratio of 16% of *cis* and 84% of *trans* determined by protons of methyl group in nuclear magnetic resonance spectra. This ratio was in well agreement with the result of the addition of the anion to 1,4-diphenyl-1,3-butadiyne at room temperature. Therefore, the mechanism considered would be such that: The *trans*-isomer[19] was first produced by *trans* addition of methylsulfinyl carbanion to acetylenes, then it was transformed to an intermediate (Ⅶ) through an olefinic carbanion (Ⅵ). Thermodynamically controlled protonation of Ⅶ would give the *trans*- and *cis*-product in the ratio mentioned above.

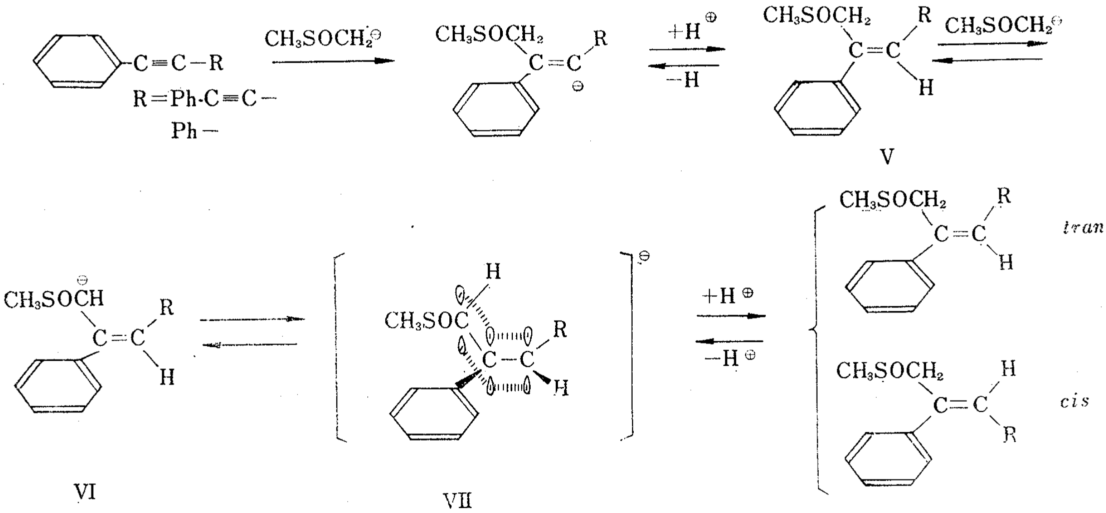

Chart 6.

Experimental[*4]

Commercially available dimethyl sulfoxide was treated with calcium hydride and distilled *in vacuo*.

***trans*-3-Methylsulfinyl-1,2-diphenyl-1-propene (I-a) and *cis*-3-Methylsulfinyl-1,2-diphenyl-1-propene (I-b)**——To a solution of methylsulfinyl carbanion which was prepared from 1.2 g. (0.05 mole) of sodium hydride and 30 ml. of dimethyl sulfoxide by stirring at 75° in N_2 gas and which was once cooled to room temperature, was added dropwise a solution of 4.45 g. (0.025 mole) of diphenylacetylene in 20 ml. of dimethyl sulfoxide in N_2 gas. The temperature during the addition was maintained within 25∼27° by cooling. After the addition was completed, the dark purple colored reaction mixture was stirred at room temperature for 1 hr. and then at 35∼37° for 3 hr. with continuous introduction of N_2 gas. After cooling, the reaction mixture was poured into 500 ml. of cold water and extracted with ether. The combined extracts were washed successively with water three times and then with satd. NaCl solution until neutral to litmus and dried over anhyd. Na_2SO_4. The ether was evaporated under reduced pressure to give

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[*4] All melting points are uncorrected.

18) *a*) S. I. Miller: J. Am. Chem. Soc., **78**, 6091 (1956). *b*) W. E. Truce, J. A. Simms: J. Am. Chem. Soc., **78**, 2756 (1956). *c*) F. Montanaro, A. Negrini: Gazz. chim. ital., **87**, 1061 (1957).

19) C. K. Ingold: J. Chem. Soc., **1954**, 2991; Ingold and King have reported that the first excited electronic state of acetylene has a flat *trans* structure. Ingold has suggested that this may provide a theoretical basis for well-known superiority of *trans* over *cis* addition or elimination in heterolytic reactions.

6.35 g. of solid substances which was crystallized from a mixture of hexane and benzene to afford colorless solid, m.p. 80～99°. This solid was recrystallized twice from hexane-benzene to give colorless needles, m.p. 109～110° (I-a) (3.6 g. yield). *Anal.* Calcd. for $C_{16}H_{16}OS$: C, 74.95; H, 6.29; S, 12.51. Found : C, 74.89; H, 6.40; S, 12.59. IRλ_{max}^{Nujol} cm^{-1} : 1031 (-SO-). UV λ_{max}^{EtOH} mμ (log ε) : 276 (4.25). The mother liquor of the first recrystallization was concentrated to afford crystalline substance which was recrystallized from hexane-benzene to give a small amount of I-a about 350 mg., the mother liquor of which was concentrated to leave solid substance, recrystallized from hexane-benzene to give a soft colorless needles, m.p. 124～128°. After two recrystallization, 300 mg. of colorless needles, I-b, m.p. 129～130° were obtained. *Anal.* Calcd. for $C_{16}H_{16}OS$: C, 74.95; H, 6.29; S, 12.51. Found : C, 74.73; H, 6.30; S, 12.51. UV λ_{max}^{EtOH} mμ (log ε) : 226.5 (4.28), 272 (4.16).

2,3-Diphenyl-1,3-butadiene——To a solution of methylsulfinyl carbanion which was prerared from 1.2 g. (0.05 mole) of sodium hydride and 30 ml. of dimethyl sulfoxide by stirring at 75° in N_2 gas and which was once cooled to room temperature, was added dropwise a solution of 4.45 g. (0.025 mole) of diphenylacetylene in 20 ml. of dimethylsulfoxide in N_2 gas. The temperature during the addition raised up to 31～39° without controlling. After the addition, the reaction mixture was warmed at 40° for 4 hr. in N_2 gas. The reaction mixture, after cooling, was poured into 500 ml. of cold water and extracted with ether. The combined extracts were washed successively with water three times and then with satd. NaCl solution until neutral to litmus and dried over Na_2SO_4. The solvent was evaporated to give 4.0 g. of brown colored liquid which was chromatographed on alumina (120 g.) (Woelm, grade I) and eluted with hexane-benzene (7:1) to afford 1.5 g. of Ⅱ. Recrystallization of crude Ⅱ from MeOH gave colorless needles, m.p. 47～48°. *Anal.* Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found : C, 92.80 : H, 6.88. IR λ_{max}^{Nujol} cm^{-1} : 908 (=CH_2). UUλ_{max}^{EtOH} mμ (log ε) : 242 (4.33).

***trans*-1-Methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-a) and *cis*-1-Methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-b)**——To a solution of methylsulfinyl carbanion prepared from 1.2 g. (0.05 mole) of sodium hydride and 30 ml. of dimethyl sulfoxide as described above was added dropwise a solution of 7.0 g. of (0.0346 mole) of 1,4-diphenyl-1,3-butadiyne in 40 ml. of dimethyl sulfoxide in N_2 gas at 30～33°. After the addition was completed the reaction mixture was stirred at room temperature for 6 hr. and then poured into 500 ml. of cold water and extracted with ether. The combined extracts were washed successively with water and satd. NaCl solution until neutral to litmus and dried over anhyd. Na_2SO_4. The solvent was removed under reduced pressure to leave 9.0 g. of solid which showed two spots by thin-layer chromatography on silica gel developed with EtOH-$CHCl_3$ (1:1). The residue (9.0 g.) was submitted to chromatography on alumina (120 g. Woelm, grade I) to give 6.25 g. of crude substance (Ⅲ-a), eluted with benzene-ether (1:1). Recrystallization from hexane-benzene (6:1) afforded pale yellow prisms (Ⅲ-a), m.p. 97.5～98.5°. *Anal.* Calcd. for $C_{18}H_{16}OS$: C, 77.10; H, 5.75; S, 11.43. Found : C, 76.95; H, 5.53; S, 11.40. UV λ_{max}^{EtOH} mμ (log ε) : 317 (4.50) and 1.581 g. of a mixture of Ⅲ-a and Ⅲ-b. This mixture was again chromatographed on alumina (90 g. Woelm, grade Ⅱ) to afford 1.252 g. of crude Ⅲ-b which was recrystallized from hexane-benzene to give colorless needles, m.p. 82～84°. Analytical sample was prepared by further recrystallizations : colorless needles (Ⅲ-b), m.p. 83～84°. *Anal.* Calcd. for $C_{18}H_{16}OS$: C, 77.10; H, 5.75; S, 11.43. Found : C, 76.89; H, 5.65; S, 11.64. UV λ_{max}^{EtOH} mμ (log ε) : 243 (4.28), 307 (4.35).

Isomerization of III-a into *cis* and *trans* Mixture——To a solution of methylsulfinyl carbanion prepared from 1.2 g. (0.05 mole) and 30 ml. of dimethyl sulfoxide as described above was added dropwise a solution of 2.0 g. (0.0071 mole) of Ⅲ-a in 10 ml. of dimethyl sulfoxide at room temperature. After addition, the reaction mixture was stirred for 7 hr. at room temperature and then poured into 400 ml. of cold water and extracted with ether. The combined extracts were washed successively with water and satd. NaCl solution until neutral to litmus. Evaporation of the solvent gave pale yellow solid which showed two spots corresponding to *cis* and *trans* isomers respectively on thin-layer chromatography of silica gel deveolped with EtOH-$CHCl_3$ (1:1). The ratio of *cis-trans* isomers obtained from reaction mixture was 16% of *cis* and 84% of *trans* determined by the protons of methyl group in NMR spectra.

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Summary

Treatment of diphenylacetylene with dimethylsulfinyl carbanion in dimethyl sulfoxide at room temperature gave two stereoisomeric compounds : *trans*-3-methylsulfinyl-1,2-diphenyl-1-propene (I-a) and *cis*-3-methylsulfinyl-1,2-diphenyl-1-propene (I-b) at a

ratio of 88.5% and 11.5% respectively, which were confirmed by ultraviolet, infrared, nuclear magnetic resonance spectra and elemental analyses. Analogously *trans*-1-methylsulfinyl-2,5-diphenyl-2-penten-4-yne (III-a) and *cis*-1-methylsulfinyl-3,1-diphenyl-2-pentin-4-yne (III-b) at a ratio of 84% and 16% respectively, were obtained from 1,4-diphenyl-1,3-butadiyne and the carbanion. Treatment of the *trans*-sulfoxide (III-a) with the carbanion at room temperature gave a *cis-trans* mixture at a ratio of 84% of *trans* and 16% of *cis* isomer. Furthermore, 2,3-diphenyl-1,3-butadiene (II) was given from diphenylacetylene and methylsulfinyl carbanion at relatively high temperature. The proposed reaction mechanism affording II would probably involve double addition of the anion to triple bond followed by elimination of two moles of methanesulfinic acid.

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87. **Yoshinobu Hirasaka and Isao Matsunaga**: Studies on the α(1,4) linked Polysaccharides of D-Glucuronic Acid and D-Glucose. VIII.[*1] Lactonization of the α(1,4) linked Disaccharides Containing Glucuronic Acid Residues.

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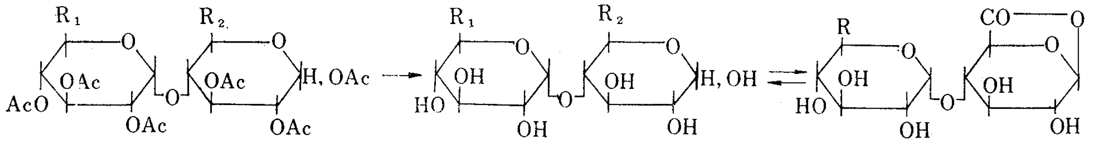
In the previous papers,1~4) the authors synthesized the three types of the α(1,4) linked disaccharides containing glucuronic acid residues: namely, 4-O-(α-D-glucopyranosiduronyl)-D-glucose (UG, VII), 4-O-(α-D-glucopyranosyl)-D-glucuronic acid (GU, VIII) and 4-O-(α-D-glucopyranosiduronyl)-D-glucuronic acid (UU, IX) by oxidation of the primary alcohols of 1,2,3,6,2′,3′,4′-hepta-O-acetylmaltose (I), 1,2,3,2′,3′,4′,6′-hepta-O-acetylmaltose (II) and 1,2,3,2′,3′,4′-haxa-O-acetylmaltose (III), followed by deacetylation, respectively (Chart 1).



I : R_1=-CH_2OH, R_2=-CH_2OAc
II : R_1=-CH_2OAc, R_2=-CH_2OH
III : R_1=R_2=-CH_2OH
IV : R_1=-CO_2H, R_2=-CH_2OAc
V : R_1=-CH_2OAc, R_2=-CO_2H
VI : R_1=R_2=-CO_2H

VII : R_1=-CO_2H, R_2=-CH_2OH (UG)
VIII : R_1=-CH_2OH, R_2=-CO_2H (GU)
IX : R_1=R_2=CO_2H (UU)

X : R=-CH_2OH (GUL)
XI : R=-CO_2H (UUL)

Chart 1.

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2) Y. Hirasaka, I. Matsunaga, K. Umemoto, M. Sukegawa: *Ibid.*, 83, 966 (1963).
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