BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2195—2198 (1970)

# The Stereoselectivity of the Methylcarbenoid of Zinc in the Reaction with Styrene, Indene, and Naphthalene

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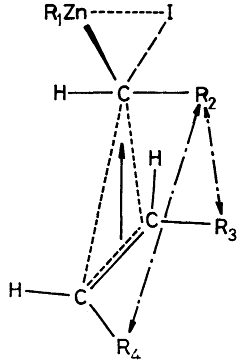
(Received January 7, 1970)

The stereoselectivity of the methylcarbenoid generated from diethylzinc and ethylidene iodide was investigated in the reactions with styrene, indene, and naphthalene. 1-Methyl-2-phenylcyclopropanes (*cis*/*trans*=4.1) were obtained from styrene in a 13% yield. Indene gave exclusively the *endo*-isomer of 6-methyl-2,3-benzobicyclo[3.1.0]hex-2-ene in a 28% yield. From naphthalene, three isomers of 5,8-dimethyl-2,3-benzotricyclo[5.1.0.0$^{4,6}$]oct-2-ene were obtained favorably to the *syn*-form, as in the cases with styrene and indene, but two isomers of 7-methyl-2,3-benzobicyclo[4.1.0]-hepta-2,4-diene were formed favorably to the *anti*-form. This *anti*-selectivity was explained by the step-by-step addition mechanism which had previously been proposed for the ring-expansion reaction of alkylbenzene by the methylcarbenoid.

The stereoselectivity of unsymmetrically-substituted carbenes and carbenoids in the reaction with olefins is an interesting problem. Alkyl-,[1] phenyl-,[2] halo-,[3] phenylthio-,[4] and phenylselenocarbenes[5] and their carbenoids generally exhibit *syn*-selectivity.[*2] On the other hand, alkoxy-,[6] phenoxy-,[7] carboalkoxy-,[8] and trimethylsilylcarbenes[9] and their carbenoids show *anti*-selectivity. The present authors have previously reported that the methylcarbenoid of zinc generated from diethylzinc and ethylidene iodide generally exhibits *syn*-selectivity.[1e] In general, a delicate balance of steric and electrostatic interactions among the substituents of olefins and of carbenoids in a three-centered transition state determines the stereoselectivity of the cycloaddition.[2c,d,3a,c,e]



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1) a) H. M. Frey, *J. Chem. Soc.*, **1962**, 2293; b) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 4876 (1964); c) H. E. Simmons, E. P. Blanchard and R. D. Smith, *ibid.*, **86**, 1347 (1964); d) G. Wittig and M. Jautelat, *Ann.*, **702**, 24 (1967); e) J. Nishimura, N. Kawabata and J. Furukawa, *Tetrahedron*, **25**, 2647 (1969).

2) a) G. L. Closs and L. E. Closs, *Tetrahedron Lett.*, **1960**, 26; b) U. Schöllkopf and M. Eisert, *Ann.*, **664**, 76 (1963); c) G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964); d) R. A. Moss, *J. Org. Chem.*, **30**, 3261 (1965); e) J. Furukawa, N. Kawabata and J. Nishimura, *Tetrahedron Lett.*, **1968**, 3495; f) S. H. Goh, L. E. Closs and G. L. Closs, *J. Org. Chem.*, **34**, 25 (1969);g) J. Furukawa, N. Kawabata and T. Fujita, *Tetrahedron*, **26**, 243 (1970).

3) a) G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.*, **87**, 4270 (1965); b) D. Seyferth, H. D. Simmons, Jr., and G. Singh, *J. Organometal. Chem.*, **3**, 337 (1965); c) R. A. Moss and R. Gestle, *Tetrahedron*, **23**, 2549 (1967). d) M. Schlosser and G. Heinz, *Angew. Chem.*, **80**, 849 (1968); e) C. W. Jefford and W. Wojnarowski, *Tetrahedron Lett.*, **1968**, 193.

4) a) U. Schöllkopf and G. J. Lehmann, *ibid.*, **1962**, 165; b) U. Schöllkopf, G. J. Lehmann, J. Paust and H.-D. Härtl, *Chem. Ber.*, **97**, 1527 (1964).

5) U. Schöllkopf and H. Küppers, *Tetrahedron Lett.*, **1963**, 105.

[*2] The terms *syn*- and *anti*-selectivity are used in the sense defined by Moss.[2d]

6) a) U. Schöllkopf and A. Lerch, *Angew. Chem.*, **73**, 27 (1961); b) U. Schöllkopf, A. Lerch and W. Pitteroff, *Tetrahedron Lett.*, **1962**, 241; c) U. Schöllkopf and J. Paust, *Angew. Chem.*, **75**, 670 (1963); d) U. Schöllkopf and W. Pitteroff, *Chem. Ber.*, **97**, 636 (1964); e) U. Schöllkopf, J. Paust, A. Al-Azrak and H. Schumacher, *ibid.*, **99**, 3391 (1966).

7) U. Schöllkopf, A. Lerch and J. Paust, *ibid.*, **96**, 2266 (1963).

8) a) R. R. Sauers, S. B. Schlosberg and P. E. Pfeffer, *J. Org. Chem.*, **33**, 2175 (1968); b) W. R. Moser, *J. Amer. Chem. Soc.*, **91**, 1135, 1141 (1969).

9) D. Seyferth, A. W. Dow, H. Menzel and T. C. Flood, *J. Amer. Chem. Soc.*, **90**, 1080 (1968).

Table 1. Results[a]

| Aromatic compound | Product | Yield[b] (%) | Isomer ratio | Bp (°C/mmHg) | $n_D^{25}$ | Anal. Calcd (Found) C; H |
|---|---|---|---|---|---|---|
| Styrene | *cis*- and *trans*-1-Methyl-2-phenylcyclopropane[c] | 13 | 4.1 : 1 | 64/16 | 1.5200 | 90.85 (90.86); 9.15 (9.24) |
| Indene | *endo*-6-Methyl-2,3-benzobicyclo[3.1.0]hex-2-ene | 28 | — | 62/3 | 1.5465 | 91.61 (92.30); 8.39 (8.47) |
| Naphthalene | *endo*- and *exo*-7-Methyl-2,3-benzobicyclo[4.1.0]hepta-2,4-diene | 14 | 1 : 3.5 | 99—100/10 | 1.5876 | 92.26 (92.52); 7.74 (7.85) |
| | *exo*, *exo*-, *exo*, *endo*- and *endo*, *endo*-5,8-Dimethyl-2,3-benzotricyclo[5.1.0.$0^{4,6}$]oct-2-ene | 7 | 1 : 9.6 : 3.9 | 110—112/11 | 1.5554 | 91.25 (91.51); 8.75 (8.73) |

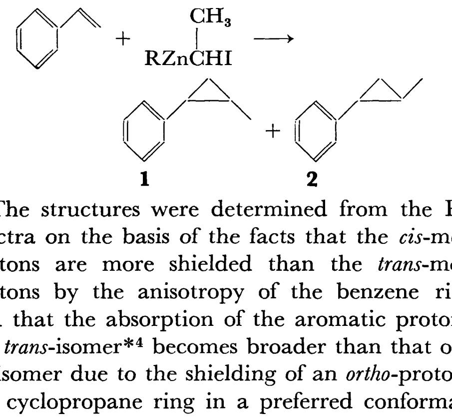
a) Reaction condition: Aromatic compound (0.20 mol), $Et_2Zn$ (0.25 mol) and $CH_3CHI_2$ (0.40 mol) in *n*-

b) Based on the aromatic compound.

c) Simmons and Smith (*J. Amer. Chem. Soc.*, **81**, 4256 (1959)) reported bp 78—79°C/20 mmHg and $n_D^{25}$

A highly polarizable group attached to olefin is expected to increase the *syn*-selectivity of the cycloaddition. In order to examine this effect, the reactions of the methylcarbenoid with styrene, indene and naphthalene were investigated. The results are summarized in Table 1.

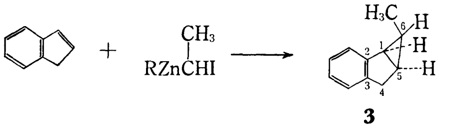
The reaction of styrene with twice as much of the methylcarbenoid in *n*-heptane at 80°C for 10 hours yielded a 4.1 : 1 mixture of *cis*- and *trans*-1-methyl-2-phenylcyclopropane. The *syn*-selectivity of the methylcarbenoid is higher in this reaction than in that with cyclohexene.[*3]



1 2 (1)

The structures were determined from the PMR spectra on the basis of the facts that the *cis*-methyl protons are more shielded than the *trans*-methyl protons by the anisotropy of the benzene ring[2b] and that the absorption of the aromatic protons of the *trans*-isomer[*4] becomes broader than that of the *cis*-isomer due to the shielding of an *ortho*-proton by the cyclopropane ring in a preferred conformation of the *trans*-isomer.[10] The difference in the chemical shift between *cis*- and *trans*-methyl protons is observed to be 0.40 Hz. The aromatic proton resonances of the *cis*-isomer form a narrow band with a half-width of 1.8 Hz centered at $\tau$ 2.89. The *trans*-isomer exhibits broad highly split aromatic proton resonances extending from $\tau$ 2.7 to 3.3.

The reaction of the methylcarbenoid with indene yielded exclusively the *endo*-isomer of 6-methyl-2,3-benzobicyclo[3.1.0]hex-2-ene (**3**)



(2)

**3**

The PMR absorption due to the methyl protons appeared as a doublet ($J=6.0$ Hz) at $\tau$ 9.43. This chemical shift is higher than those of methyl groups in 1-methyl-2-phenylcyclopropanes, which appear at $\tau$ 8.8—9.2. The result can be explained by the fixing of the methyl group in the shielding region of the anisotropy by the benzene ring. The absorption due to $H_1$ appeared at $\tau$ 7.60 as a triplet ($J=7.0$ Hz). This result indicates that $H_1$ couples with two equivalent protons, *i.e.*, $H_5$ and $H_6$ are placed in the *cis* position with respect to $H_1$. These PMR findings show that the product is the *endo*-isomer.

The reactions of the methylcarbenoid with styrene and indene gave methylcyclopropanes more favorably to the *syn*-form than that with cyclohexene.[*3] This result may be attributable to the large electrostatic interaction between the highly-polarizable phenyl group of olefin and the methyl group of the carbenoid. The highly *syn*-selective formation of 6-methyl-2,3-benzobicyclo[3.1.0]hex-2-ene from indene may be explained by a steric effect. The

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[*3] The reaction of cyclohexene with methylcarbenoid gave a 1.5 : 1 mixture of *endo*- and *exo*-7-methylnorcarane.[1e]

[*4] The structural assignment of the *trans*-isomer was also made by comparing its IR spectrum with that of the authentic sample, which was prepared in a *ca.* 50% yield by the reaction of *trans*-1-phenylpropene with diethylzinc and methylene iodide.[11]

10) a) G.L. Closs and H.B. Klinger, *J. Amer. Chem. Soc.*, **87**, 3265 (1965); b) F. R. Jensen and D. B. Patterson, *Tetrahedron Lett.*, **1966**, 3837.

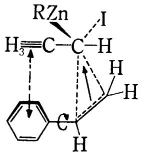
11) J. Furukawa, N. Kawabata and J. Nishimura, *Tetrahedron*, **24**, 53 (1968).

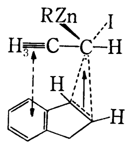
| IR<br>$\nu_{max}$ (cm$^{-1}$) | M+<br>*m/e* |
|---|---|
| (*cis*) 1604 (m), 1393 (w), 1028 (m), 694 ( s )<br>(*trans*) 1606 (m), 1380 (w), 1027 (m), 742 ( s ), 694 ( s ) | 132 |
| 1608 (w), 1393 (w), 1021 (m), 755 ( s ), 717 ( s ) | 144 |
| 1490 (m), 1456 (m), 1383 (w), 1038 (m), 771 ( s ) | 156 |
| 1493 ( s ), 1455 ( s ), 1383 (m), 1022 (m), 751 (vs) | 184 |

heptane (100 m*l*) at 80°C for 10 hr.

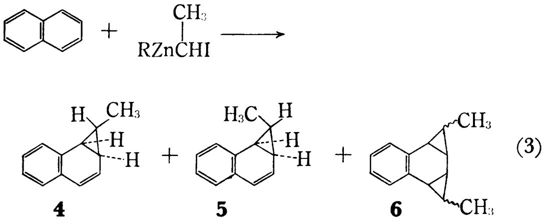
1.5204 for *cis*, *trans*-mixture.

steric interaction between the phenyl group of indene and the methyl group of carbenoid would be less than in the case of the reaction with styrene, and a strong electrostatic interaction between the phenyl group of indene and the methyl group of carbenoid can be expected at a sufficiently close range.





A high *syn*-selectivity of the methylcarbenoid in the reaction with naphthalene, as with indene, would be expected if the reactions proceeded in a concerted mechanism similar to that proposed for the Simmons-Smith reaction.[12] 7-Methyl-2,3-benzobicyclo[4.1.0]hepta-2,4-diene and 5,8-dimethyl-2,3-benzotricyclo[5.1.0.$0^{4,6}$]oct-2-ene were obtained by reaction (3).



(3)

Three kinds of 5,8-dimethyl-2,3-benzotricyclo[5.1.0.$0^{4,6}$]oct-2-ene (**6**) were isolated, and their structures were determined to be *exo,exo*-, *exo,endo*-, and *endo,endo*-dimethyl isomers by comparing the PMR absorption of methyl groups.[*5] The ratio of these isomers is given in Table 1. The ratio of the *syn*-methyl group to the *anti*-methyl group in these di-adducts (**6**) was calculated from the isomer ratios to be 1.9. This result indicates the *syn*-selective addition of methylcarbenoid to the mono-adducts (**4** and **5**). On the other hand, the mono-adducts (**4** and **5**) were not separated by glpc, although the two kinds of methyl groups were observed in the PMR spectrum (Fig. 1).[*6]

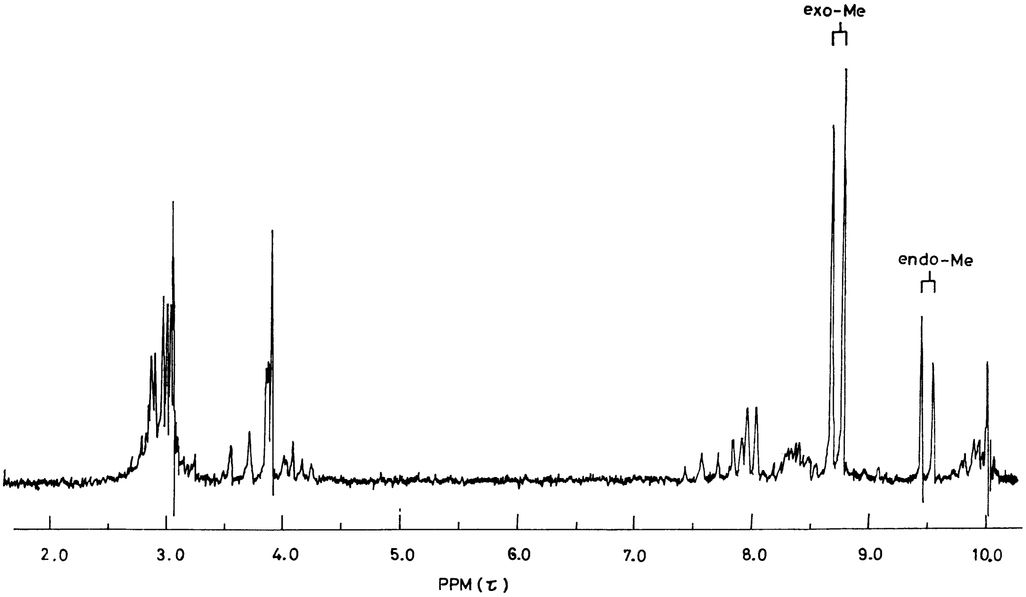


Fig. 1. The PMR spectrum of 7-methyl-2,3-benzobicyclo[4.1.0]hepta-2,4-diene (**4** and **5**).

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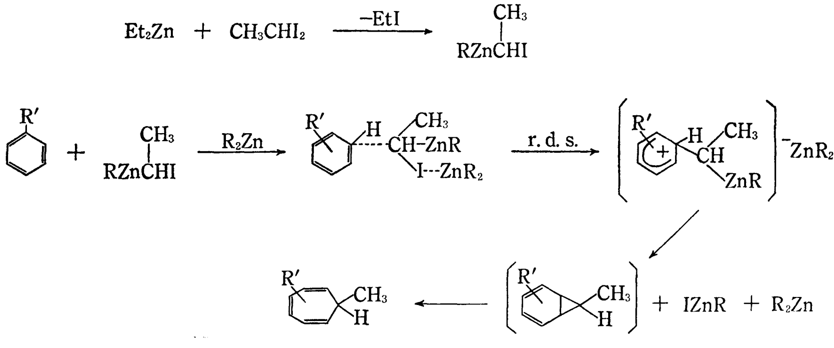
12) a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); b) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

[*5] See Experimental Section.

[*6] The spectrum is similar to that of 2,3-benzonorcaradiene-2,4-carboxylic acid reported by Huisgen *et al.* (*Chem. Ber.*, **94**, 2332 (1961)).

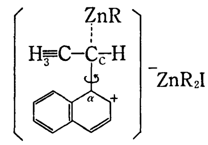


Scheme 1

One doublet peak ($J$=6.0 Hz), at $\tau$ 9.50, was assigned to an *endo*-methyl group, and the other one ($J$=6.0 Hz), at $\tau$ 8.73, to an *exo*-methyl group, by comparison with the chemical shift of the methyl group in compound (**3**). The *exo-/endo*-isomer ratio thus determined was 3.5, which suggests the *anti*-selective addition of methylcarbenoid to naphthalene, contrary to the above expectation.[*7] This difference in the selectivity of reaction (3) from reactions (1) and (2) suggests that the mechanism of reaction (3) is different from the concerted one which was proposed for the Simmons-Smith reaction.[12] Previously, the present authors have reported that the essential features of the cycloaddition of zinc carbenoid prepared from *gem*-diiodoalkane and diethylzinc to olefin are similar to that of the Simmons-Smith reaction.[11] On the other hand, the present authors have also reported the step-by-step mechanism (Scheme 1) for the ring expansion of alkylbenzenes by methylcarbenoid.[13]

Reaction (3) may proceed by a mechanism similar to that shown in Scheme 1. The *anti*-selectivity in reaction (3) may be due to free rotation around the $C_\alpha$—$C_c$ bond in a $\sigma$-complex (**7**), which may enhance the formation of the thermodynamically more stable *exo*-isomer.[*8]

In a previous paper, the $\sigma$-complex formation step was concluded to determine the rate of the ring expansion.[13] The formation of *endo*- and *exo*-7-methyl-2,3-benzobicyclo[4.1.0]hepta-2,4-diene



**7**

in reaction (3) may support the idea of the presence of a transient norcaradiene in the ring expansion reaction.

## Experimental

The analyses were performed at the Elemental Analysis Center of Kyoto University. The infrared and mass spectra were recorded on a Hitachi EPI-G spectrophotometer and a Hitachi mass spectrometer, Model RMS-4, respectively. The PMR spectra were taken on a Varian Model A-60, in carbon tetrachloride, using tetramethylsilane as the internal standard. The vapor-phase chromatograms were obtained on a Shimadzu GC-2C gas chromatograph. All the boiling points were uncorrected.

**Materials and Procedure.** The styrene and the indene were purified by distillation before use. Reagent-grade naphthalene was used without further purification. $n$-Heptane was purified by distillation over sodium metal. The other reagents and procedure are the same as have been described in previous papers.[1e,11]

The reactions with styrene and indene gave higher-boiling materials other than listed in Table 1 in a *ca.* 10% yield. The PMR spectra of the material showed the characteristic absorption for cycloheptatrienes at $\tau$ 3—5.

**5,8-Dimethyl-2,3-benzotricyclo[5.1.0.0$^{4,6}$]oct-2-ene (6).** The fraction (bp 110—112°C/11 mmHg) of the reaction mixture with naphthalene showed three peaks on glpc analysis conducted under these conditions: 2.25 m of Apiezon-L grease and 3.75 m of Silicone DC 550, 200°C. The ratio was 1 : 9.6 : 3.9, in the order of the retention times. These three isomers were isolated by glpc. The PMR spectra of these isomers showed two kinds of methyl groups. The peaks at $\tau$ 9.0—9.1 were assigned to the *endo*-methyl group, and those at $\tau$ 8.8—8.9 to the *exo*-one, on the basis of the effect by the anisotropy of the benzene ring. These three isomers were determined to be *exo,exo*-, *exo,endo*-, and *endo,endo*-isomers. The configurations of the tricyclo-ring were not confirmed.

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[*7] The *anti*-selective formation of the mono-adducts can be concluded even if only the *endo*-isomer (**4**) further reacts with methylcarbenoid to give three kinds of di-adducts, because the ratio of di-adducts to mono-adducts was 1 : 2 (Table 1).

13) J. Nishimura, J. Furukawa and N. Kawabata, The 22nd Annual Meeting of Chemical Society of Japan, Tokyo, 1969.

[*8] It is known that *exo*-phenylnorcarane is thermodynamically more stable than the *endo*-isomer.[10b,14]

14) G. L. Closs and J. J. Coyle, *J. Org. Chem.*, **31**, 2759 (1966).