

Transmethylation of olefin via *S*-methylsulfonium salts obtained by desulfurization of light oil

Yasuhiro Shiraishi*, Takayuki Hirai

Research Center for Solar Energy Chemistry and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Machikaneyama-cho 1-3, Toyonaka 560-8531, Japan

Received 17 September 2003; received in revised form 19 November 2003; accepted 21 November 2003

Abstract

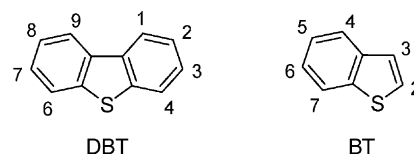
S-Methylsulfonium salts, obtained by a new desulfurization process for light oil based on methylation of sulfur-containing compounds using CH_3I and AgBF_4 , were used as a methyl-transfer agent for transmethylation of 2-methyl-2-octene. The sulfonium salts obtained from light oil showed higher transmethylation activity than the salts of dibenzothiophene (DBT) and benzothiophene (BT), used as model sulfonium salt. The salts obtained from light oil are derived from highly alkyl-substituted DBTs and BTs, of low nucleophilicity (low electron density on the sulfur atom), and release the methyl group easily, thus giving the higher transmethylation activity. The product distribution was almost the same as that obtained by the model sulfonium salts, suggesting that the salts obtained from light oil are a potential effective methyl-transfer agent.

© 2003 Elsevier B.V. All rights reserved.

Keywords: *S*-Methylsulfonium salts; Light oil; Desulfurization; Transmethylation; Olefin

1. Introduction

The transfer of an intact methyl group from a suitable donor to a suitable acceptor is a vitally important biological process, where the methyl donor (methyl-transfer agent) is in general *S*-adenosylmethionine, a *S*-methylsulfonium salt [1]. Based on the fundamental bioprocess, the use of *S*-methylsulfonium salts as a methyl-transfer agent for methylation of various kinds of nucleophilic substrates has been investigated, such as carboxylic acids, sulfonic acid, amines, alcohols [2], and olefins [3–5]. The transmethylation activity of the sulfonium salts depends strongly on the structure of the salts, where the salts, especially derived from diaryl sulfides, such as diphenyl sulfide and dibenzothiophene (DBT, **1a**), have been reported to show significantly high activity for transmethylation [3,4].



1a: nonsubstituted
1b: 4-methyl
1c: 4,6-dimethyl

2a: nonsubstituted
2b: 2-methyl
2c: 3-methyl

As is well known, DBT and benzothiophene (BT, **2a**) and their alkyl-substituted derivatives are main constituents of sulfur-containing compounds present in light oil, and their removal from the oil is urgently required for protection of environment against the contamination [6,7]. In our previous work [8,9], a new desulfurization process for light oil has been investigated based on methylation of DBTs and BTs using CH_3I and AgBF_4 and subsequent precipitation of the resulting *S*-methylsulfonium tetrafluoroborates. The DBTs and BTs in light oil are methylated by the reaction with the reagents to form the corresponding *S*-methylsulfonium tetrafluoroborates. The salts are highly polarized compounds and are insoluble in nonpolar light oil, so that the salts precipitate

* Corresponding author. Tel.: +81-6-6850-6271; fax: +81-6-6850-6273.

E-mail address: shiraish@cheng.es.osaka-u.ac.jp (Y. Shiraishi).

at the bottom of the flask, which can be removed easily by decantation. The process requires a large amount of CH_3I and AgBF_4 , the use of which must be reduced for industrial application. However, the reaction proceeds under conditions of room temperature and atmospheric pressure and the sulfur concentration of light oil is decreased successfully to less than 0.005 wt.%. The value of 0.005 wt.% is below the regulatory value that limited presently in Japan, US, and EU. The proposed process may therefore have a potential for effective and energy-efficient desulfurization of light oil. In this process, large amount of *S*-methylsulfonium salts of DBTs and BTs is obtained from light oil as the desulfurization product. In the present work, the sulfonium salts, obtained by desulfurization of light oil, were used as a methyl-transfer agent for transmethylation. The activity and behavior of the sulfonium salts were studied using 2-methyl-2-octene (**3**) as a substrate [3,4] and were compared with those of the sulfonium salts of pure DBTs (**1a–c**) and BTs (**2a–c**) as a model. The comparison of the product distribution of **3** was also carried out, and the applicability of the salts obtained from light oil to transmethylation was examined.

2. Experimental

2.1. Materials

1a, **2a**, and **3**, supplied by Wako, were used without further purification. **1b**, **1c**, **2b**, and **2c** were synthesized according to the procedure described previously [10]. The *S*-methylsulfonium tetrafluoroborates of **1a–c** and **2a–c** were synthesized by the reaction with CH_3I and AgBF_4 , according to the literature procedure [11]. The properties of the salts were summarized in a previous paper [8]. Light cycle oil, containing 0.132 wt.% sulfur, was used as a feedstock for investigations. The properties of the oil are summarized in the previous paper [8]. The desulfurization of the oil and the recovery of the sulfonium salts were also described previously [8], and a brief description is made here. The light oil (15 ml) was mixed with CH_2Cl_2 (15 ml) using a magnetic stirrer. The 20- and 2-fold molar excesses of CH_3I and AgBF_4 , based on the initial sulfur concentration of the light oil, were added to the above homogeneous solution under N_2 at 303 K. After 11 h of stirring, the byproduct AgI was recovered by filtration and CH_2Cl_2 was removed from the filtrate by evaporation. Upon cooling of the resulting light oil in an ice bath, the salts formed (0.857 g, containing 11.57 wt.% of sulfur) were recovered by decantation. The salts were recrystallized from acetonitrile/diethyl ether and then used for transmethylation experiments. The elemental composition of the salts was summarized in the previous paper [8], and the mole fractions of the salts of DBTs and BTs are summarized in Table 1(i).

Table 1

(i) Mole fraction of *S*-methylsulfonium salts of DBTs and BTs obtained by desulfurization of light oil^a and (ii) electron densities on sulfur atom for the corresponding DBTs and BTs obtained by MO calculation

Species ^b	DBTs		BTs	
	(i) (mol%)	(ii)	(i) (mol%)	(ii)
<C ₁	14.7 ^c	0.940 ^d	10.9 ^e	0.781 ^f
C ₂	9.4	0.913	6.1	0.745
C ₃	3.9	0.889	7.5	0.741
C ₄	1.6	0.876	5.1	0.732
C ₅	0.5	0.861	1.8	0.721
>C ₆	33.6	0.854 ^g	4.9 ^h	0.719 ⁱ
Total	63.7		36.3	

^a The mole fraction was determined by the analysis of the sulfur compounds remaining in the desulfurized light oil [8].

^b C_n denote the total number of carbon atoms of the alkyl group, substituted at any position of the DBT and BT molecules.

^c <C₁-DBTs contain also C₀-DBT.

^d Average of C₀- and C₁-DBTs.

^e <C₁-BTs contain also C₀-BT and alkyl and aryl sulfides.

^f Average of C₀- and C₁-BTs.

^g Obtained for C₆-DBTs.

^h >C₆-BTs contain also C₇- and C₈-BTs.

ⁱ Obtained for C₆-BTs.

2.2. Procedure and analysis

The transmethylation of **3** was carried out according to the procedure of literatures [3,4], as follows: **3** (0.5 g, 3.97 mmol) and a model sulfonium salt (2.65 mmol, containing 84.8 mg of sulfur) were mixed in a sealed tube, in the presence of 2,6-di-*tert*-butylpyridine (3.18 mmol) as a proton scavenger and *n*-undecane (0.53 mmol) as a standard. The mixture was heated for 24 h at 413–443 K under N_2 . The sulfonium salts obtained from light oil (0.734 g, containing 84.8 mg of sulfur) were also used as a methyl-transfer agent. The resulting solution was analyzed by GC-FID (Shimadzu GC1700 equipped with DB-1 capillary column). The product yield was determined based on the percentage of the methyl group transferred to the product from the sulfonium salt. Differential thermal analysis (DTA) of the sulfonium salts was carried out in a flow of N_2 on a DTG-50H analyzer (Shimadzu), with a heating rate of 10 K/min from ambient temperature. Theoretical calculations of the electron density on sulfur atom for DBTs and BTs were performed with the PM3 semiempirical method within the WinMOPAC version 3.0 software (Fujitsu, Inc), as described previously [8].

3. Results and discussion

3.1. Activity of sulfonium salts of DBTs and BTs

The behavior of the sulfonium salt of **1a** toward transmethylation of **3** has been studied in detail in the literature [3], but the behavior of the salt of **2a** has scarcely been

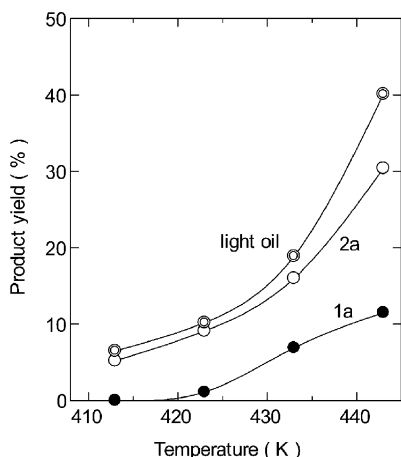


Fig. 1. Product yield in the transmethylation of **3** at various temperatures, using the salts of **1a** and **2a** and the salts obtained by desulfurization of light oil.

studied. The behavior of the salt of **2a** was studied first, comparing with that of the salt of **1a**. Fig. 1 shows the product yield in the transmethylation of **3** using the salt of **1a** or **2a**, as a function of the reaction temperature. When the salt of **1a** is used, almost no methylation takes place at <math> < 420 \text{ K}</math>, but the methylation is accelerated with an increase in the reaction temperature, as described previously [3]. For the salt of **2a**, the methylation is also accelerated with an increase in the temperature. The salt of **2a** gives significantly higher product yield than does the salt of **1a**, at every temperature. The transmethylation is initiated by the elimination of the methyl group from the sulfonium salts [3]. Therefore, the sulfonium salts, which release the methyl group easily, show high transmethylation activity. The S–CH₃ bond strength of the sulfonium salts depends on the nucleophilicity of the sulfur atom for the corresponding sulfur compounds [12,13], and the salt derived from less nucleophilic sulfur compounds release the methyl group more easily. By semiempirical MO calculations, electron densities on the sulfur atom for **1a** and **2a** were estimated to be 0.955 and 0.813, respectively, suggesting that the sulfur atom for **2a** has lower nucleophilicity than that for **1a**. The methyl group on the salt of **2a** is therefore eliminated more easily, thus demonstrating the higher transmethylation activity. The reason for the higher activity for the salt of **2a** was further studied by DTA. As shown in Fig. 2, both the salts of **1a** and **2a** demonstrate a strong endothermic peak, owing to the elimination of the methyl group from the salts [14]. The peak temperature of the salt of **2a** is found to be lower than that of the salt of **1a**. This suggests that the methyl group on the salt of **2a** is eliminated more easily against thermal stimulation.

The desulfurization product obtained from light oil contains various types of sulfonium salts of DBTs and BTs, having alkyl substituents on various positions of the molecules [8], as shown in Table 1. The transmethylation activity of the salts of methyl-substituted DBTs (**1b** and **1c**) and BTs (**2b** and **2c**) was therefore studied. Fig. 3 shows the relationship

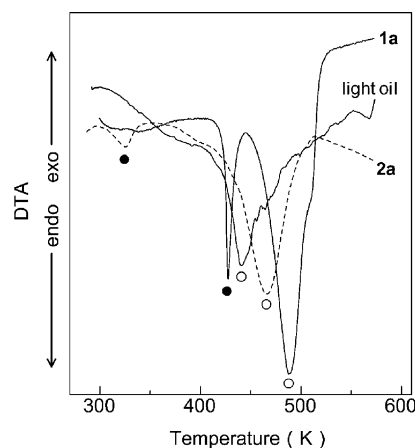


Fig. 2. DTA chart for the salts of **1a** and **2a** and the salts obtained by desulfurization of light oil (open circle symbol: peak attributable to elimination of the methyl group from the salts, closed circle symbol: peak attributable to melting of the salts).

between the product yield and the electron density on the sulfur atom for the corresponding DBTs and BTs, as estimated by MO calculations. The product yield is clearly shown to increase with a decrease in the electron density for the corresponding DBTs and BTs. It was found that the salts especially derived from the BTs of lower electron density show rather higher activity than the salts of DBTs. Fig. 4 shows the relationship between the product yield and the peak temperatures for the respective sulfonium salts, as estimated by DTA. The product yield is shown to increase with a decrease in the peak temperature of the sulfonium salt. The above findings, therefore, reveal that the sulfonium salts derived from sulfur compounds of low electron density on the sulfur atom release the methyl group very easily, thus showing higher transmethylation activity.

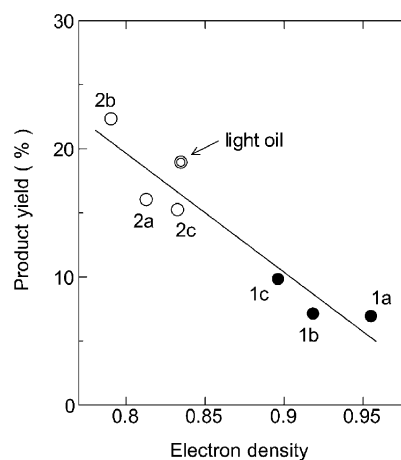


Fig. 3. Correlations between the product yield in the transmethylation of **3** during reaction at 433 K using the salts of DBTs (**1a–c**) and BTs (**2a–c**) and the salts obtained by desulfurization of light oil, and electron density on the sulfur atom on HOMO orbital for the corresponding DBTs and BTs.

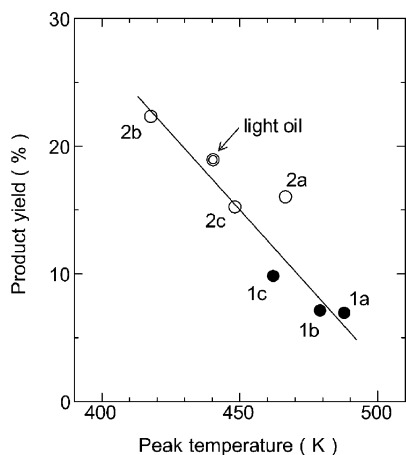


Fig. 4. Correlations between the product yield in the transmethylation of **3** during reaction at 433 K using the salts of DBTs (**1a–c**) and BTs (**2a–c**) and the salts obtained by desulfurization of light oil, and the peak temperature corresponding to the elimination of the methyl group from the salts, as estimated by DTA.

3.2. Sulfonium salts obtained by desulfurization of light oil

As shown in Fig. 1, for the salts obtained by desulfurization of light oil, the methylation of **3** is accelerated with an increase in the reaction temperature, as is also the case for the salts of **1a** and **2a**. It is noted that the salts obtained from light oil show significantly higher transmethylation activity than the salts of **1a** and **2a**. As shown in Table 1(i), the desulfurization products contain various types of sulfonium salts, derived from DBTs and BTs, having alkyl substituents of carbon number C_0 – C_6 present on various positions of the molecules [8]. To clarify the reason for the higher activity of the salts obtained from light oil, the electron densities on sulfur atoms of the respective alkyl-substituted DBTs and BTs were estimated by MO calculations. The average values obtained are summarized in Table 1(ii), as a function of carbon number of the alkyl substituents. The electron density on sulfur atoms of both DBTs and BTs is clearly shown to decrease with an increase in the carbon number of the alkyl substituents. The average electron density on sulfur atoms

Table 2

The product yield and the product distribution in the transmethylation of **3** using the salts obtained from light oil and the salts of **1a** and **2a**^a

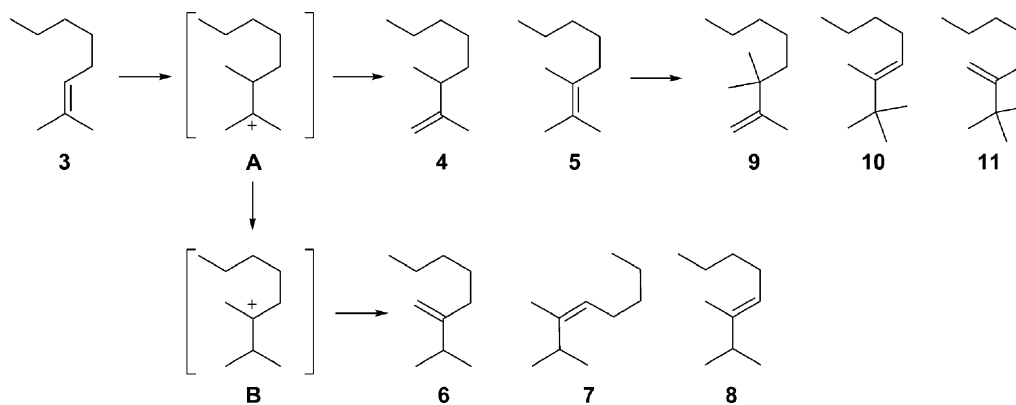
Entry	Methyl-transfer agent	Product yield (%)	Mole percentage (%)							
			4	5	6	7	8	9	10	11
1	Salt of 1a	11.5	10	53	4	4	12	3	13	1
2	Salt of 2a	30.4	9	35	5	4	13	7	24	3
3	Salt of light oil	40.1	11	21	5	3	13	9	33	5

^a Reaction temperature: 443 K.

of the DBTs and BTs, consisting of sulfonium salts obtained from light oil, was estimated to be 0.835. The value of 0.835 is lower than that for the DBTs used in the present study, as shown in Fig. 3, and a good correlation is observed between the electron density and the product yield. As shown in Fig. 2, the sulfonium salts obtained from light oil show a strong endothermic peak in DTA, as is also observed for the salts of **1a** and **2a**. As shown in Fig. 4, the peak temperature of the salts obtained from light oil is lower than that of the salts of **1a** and **2a**, and a good correlation is observed between the peak temperature and the product yield. The higher transmethylation activity for the salt, obtained from light oil, results since the salts are derived from highly alkyl-substituted DBTs and BTs of low electron density and release the methyl group very easily. The above findings suggest that the sulfonium salts obtained by desulfurization of light oil may be a potential effective methyl-transfer agent.

3.3. Product distribution

The product distribution in the transmethylation of **3**, obtained by using the salts from light oil, was compared with that obtained by using the salts of **1a** and **2a**. The results are summarized in Table 2. As shown in entry 1, the use of the salt of **1a** gives rise to five monomethylated olefins (**4–8**), including *cis-trans* isomers of 2,3-dimethyl-3-octene (*Z*: **7** and *E*: **8**), and three dimethylated olefins (**9–11**). As shown in Scheme 1 and described earlier [3,4], the transmethylation



Scheme 1. Schematic representation of transmethylation pathway for **3**.

of **3** by the salt of **1a** proceeds in the Markovnikov direction forming a carbonium ion (**A**). The proton on **A** is then transferred to 2,6-di-*tert*-butylpyridine, a proton scavenger, which leads to the formation of **4** and **5**. The intermediate **A** is converted by 1,2-hydride shift into another carbonium ion (**B**), which also loses a proton and gives rise to the other monomethylated olefins (**6–8**). The tetrasubstituted olefin (**5**) is a highly nucleophilic molecule, so that **5** is further methylated by the salt of **1a** to produce the dimethylated olefins (**9–11**).

When the salt of **2a** was used (entry 2), GC analysis exhibited the same eight products as those obtained with the salt of **1a**. The compound **5** is the main product, as is also the case for the salt of **1a**, but the mole percentage of **5** (35%) is lower than that obtained using the salt of **1a** (53%). In this case, sum of the percentage of dimethylated olefins (**9–10**) is 34%, which is twice as high as that obtained using the salt of **1a** (17%). These findings suggest that **5** is further methylated by the salt of **2a**, owing to the higher activity of **2a**, producing large amount of dimethylated olefins. Among the dimethylated olefins, the percentage of **10** is rather higher than that of **9** and **11**, as is also the case for the salt of **1a**. GC analysis did not show any other methylation products than the eight compounds shown in Table 2. Therefore, the transmethylation by the salt of **2a** proceeds in the same way as that for the salt of **1a**. As shown in entry 3, the use of the salts obtained from light oil also produced the same eight products as those obtained with the salts of **1a** or **2a**. It was found that the mole percentage of **5** is lower than that obtained with the salts of **1a** or **2a**, and the sum of the percentages for the dimethylated olefins (47%) is higher than that obtained with the salts of **1a** or **2a**. This indicates that the subsequent methylation of **5** is accelerated by the salts obtained from light oil compared to the case for the salt of **1a** and **2a**. The mole percentage of **10** in the dimethylated olefins is found to be also higher than that of **9** or **11**. The above results therefore suggest that the salts obtained from light oil accelerate the transmethylation of **3** in the same way as that for the case with the salt of **1a**, without producing any undesirable materials. Therefore, the sulfonium salts obtained from light oil are a potential effective methyl-transfer agent for transmethylation.

4. Conclusion

The *S*-methylsulfonium salts, obtained by desulfurization process for light oils based on the methylation of

sulfur-containing compounds using CH₃I and AgBF₄, were used as a methyl-transfer agent for the transmethylation of 2-methyl-2-octene. The sulfonium salts are derived from highly alkyl-substituted dibenzothiophenes and benzothiophenes of low electron density on the sulfur atom and release the methyl group very easily, thus demonstrating significantly high transmethylation activity. The use of the salts showed almost the same product distribution as that obtained using model sulfonium salts and did not produce any undesirable products. The sulfonium salts obtained from light oil as the desulfurization products are recyclable, and therefore, potential effective methyl-transfer agents for transmethylation.

Acknowledgements

The authors are grateful to Mr. Kenya Tachibana for his experimental help. The authors are also grateful for financial support by Grant-in-Aid for Scientific Research (No. 12555215) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and to the Division of Chemical Engineering, Osaka University for the Lend-Lease Laboratory System. Y.S. acknowledges the financial support by Showa Shell Sekiyu Foundation for Promotion of Environmental Research.

References

- [1] M. Akhtar, C. Jones, *Tetrahedron* 34 (1978) 813.
- [2] B. Badet, M. Julia, M. Ramirez-Munoz, *Synthesis* (1980) 926.
- [3] M. Julia, C. Marazano, *Tetrahedron* 41 (1985) 3717.
- [4] M. Julia, B. McDonald, M.C. Rezende, *Tetrahedron* 47 (1991) 6939.
- [5] J.D. Winkler, M. Finck-Estes, *Tetrahedron Lett.* 30 (1989) 7293.
- [6] Y. Shiraishi, Y. Taki, T. Hirai, I. Komasaawa, *Chem. Commun.* (1998) 2601.
- [7] Y. Shiraishi, T. Naito, T. Hirai, I. Komasaawa, *Chem. Commun.* (2001) 1256.
- [8] Y. Shiraishi, Y. Taki, T. Hirai, I. Komasaawa, *Ind. Eng. Chem. Res.* 40 (2001) 1213.
- [9] Y. Shiraishi, K. Tachibana, Y. Taki, T. Hirai, I. Komasaawa, *Ind. Eng. Chem. Res.* 40 (2001) 1225.
- [10] Y. Shiraishi, T. Hirai, I. Komasaawa, *Ind. Eng. Chem. Res.* 38 (1999) 3300.
- [11] R.M. Acheson, D.R. Harrison, *J. Chem. Soc. C* (1970) 1764.
- [12] B.M. Trost, L.S. Melvin Jr., *Sulfur Ylides*, Academic Press, New York, 1975 (Chapter 2).
- [13] P.A. Lowe, in: C.J.M. Stirling (Ed.), *The Chemistry of the Sulphonium Group. Part 1*, Wiley, New York, 1981 (Chapter 11).
- [14] O. Shimomura, I. Tomita, T. Endo, *J. Polym. Sci., Part A: Polym. Sci.* 39 (2001) 868.