by the Ministry of Education of Korea as a Free Research Project is gratefully acknowledged.

References and Notes

1. Present address: Korea Research Institute of Chemical Technology, Daedeog-Danji, Daejeon.
2. (a) C. A. Brown, *J. Am. Chem. Soc.*, **95,** 4100 (1973). (b) *idem., J. Org. Chem.*, **39,** 3913 (1974). (c) C. A. Brown and S. Krishnamurthy, *J. Organomet. Chem.*, **156,** 111 (1978). (d) S. Krishnamurthy, *Aldrichimica Acta,* **7,** 55 (1974). (e) S. Krishnamurthy and H. C. Brown, *J. Am. Chem. Soc.*, **98,** 3383 (1976). (f) *idem., J. Org. Chem.*, **41,** 3064 (1976). (g) H. C. Brown and S. C. Kim, Synthesis, 635 (1977). (h) H. C. Brown, A. Khuri, and S. C. Kim, *Inorg. Chem.*, **16,** 2229 (1977). (i) H. C. Brown, S. Krishnamurthy, and J. L. Hubbard, *J. Am. Chem., Soc.*, **100,** 3343 (1978).
3. (a) C. A. Brown, S. Krishnamurthy, and S. C. Kim, *J. Chem. Soc. Chem. Commun.*, 391 (1973). (b) H. C. Brown, J. S. Cha, B. Nazer, S. C. Kim, S. Krishnamurthy, and C. A. Brown, *J. Org. Chem.*, **49,** 885 (1984).
4. (a) H. C. Brown, J. S. Cha, and B. Nazer, *J. Org. Chem.*, **49,** 2073 (1984). b) H. C. Brown, J. S. Cha, B. Nazer, and C. A. Brown, *J. Org. Chem.*, **50,** 549 (1985).
5. H. C. Brown, W. S. Park, J. S. Cha, B. T. Cho, and C. A. Brown. *J. Org. Chem.*, **51,** 337 (1986).
6. J. S. Cha, M. S. Yoon, K. W. Lee, and J. C. Lee, *Heterocycles,* **27,** 1455 (1988).
7. J. S. Cha, M. S. Yoon, Y. S. Kim, and K. W. Lee, *Tetrahedron Lett.*, **29,** 1069 (1988).
8. H. C. Brown, G. W. Kramer, and M. M. Midland, "Organic Syntheses via Boranes," Wiley-Interscience, New York, 1975.
9. H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *J. Org. Chem.*, **41,** 1778 (1976).
10. H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc,* **94,** 7159 (1972).
11. Preliminary experiments revealed that in the competitive reaction between benzonitrile and caprylonitrile with a limiting amount of the reagent a yield of 85% of benzaldehyde was formed and a 99% yield of caprylonitrile was recovered.

Synthesis and Reactions of Benzimidazoline-2-thione Derivatives

Tae Ryong Lee and Kyongtae Kim*

Department of Chemistry, Seoul National University, Seoul 151-742. *Received October 4, 1988*

Two properties of sodium naphthalenide (2), i.e. a strong base and a good electron donor were utilized for one pot synthesis: 2-alkylthiobenzimidazoles were synthesized in excellent yields from the reactions of benzimidazoline-2-thione (1) with an equimolar amount of alkyl halides in the presence of 2. Continueous addition of a different alkyl haldie without the isolation of 2-alkylthiobenzimidazoles afforded 1-alkyl-2-alkylthiobenzimidazoles having different alkyl goups at N and S atoms in excellent yields. Further addition of 2 to 1-alkyl-2-alkylthiobenzimidazoles gave excellent yields of 1-alkylbenzimidazoline-2-thiones. When 2 in THF was added to a suspension of 1-alkyl-2-alkylthiobenzimidazoles in THF, a bond cleavage between N and C of alkyl group as well as S and C of alkyl group occurred. This is in contrast to the observation in which only cleavage between S and C of alkyl group takes place in the homogeneous solution.

Introduction

It has been well known that a number of benzimidazoline-2-thione derivatives have significant biological activity such as fungicidal, virucidal, and antitumor activity.[1] This stimulated us to study the development of new synthetic methods of benzimidazoline-2-thione derivatives.

Synthesis of 1-alkyl-2-alkylthiobenzimidazoles has been achieved by the several methods. The most widely used method consists of the reactions of 2-alkylthiobenzimidazoles with excessive amounts of alkyl halides. Thus formed 1-alkyl-2-alkylthiobenzimidazolium halides were treated under basic conditions to give 1-alkyl-2-alkylthiobenzimidazoles in 80% yields.[2] Similarly reactions of benzimidazoline-2-thione (**1**) with alkyl halides in saturated sodium bicarbonate solution of isopropanol afforded 1,2-dialkylated compounds of **1** as minor products.[3]

Apart from these methods, there have been some reports for the synthesis of 1,2-dialkylated compounds of **1** which appear to be of limited usefulness.[4]

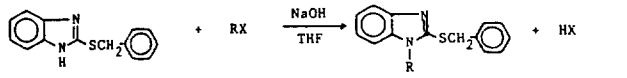
The characteristic of these methods lies in the two step processes, i.e., the formation of 2-alkylthiobenzimidazoles, followed by a alkylations at N-1 in aqueous alcohol to give low yields or the formation of 1-alkyl-2-alkylthiobenzimidazolium halides, followed by the removal of halogen acid using a base such as pyridine or potassium hydroxide.

We have developed one pot syntheses of 1-alkyl-2-alkylthio-benzimidazoles with two different alkyl groups and 1-alkylbenzimidazoline-2-thiones in dried THF using sodium naphthalenide (**2**) possessing two fundamental properties, i.e. a strong base and a good electron donor.

Results and Discussion

It has been shown that dialkylations at both N and S atoms of **1** can be readily achieved in almost quantitative

Table 1. Yields of 1-Alkyl-2-benzylthiobenzimidazoles



3 **4**

RX	Stirring time (h)	**4**(%)
CH_3CH_2I	1	**a**, 100
$CH_3CH_2CH_2I$	1	**b**, 99
$CH_2=CHCH_2Br$	1	**c**, 100
$CH_2=CHCH_2CH_2I$	3	**d**, 98

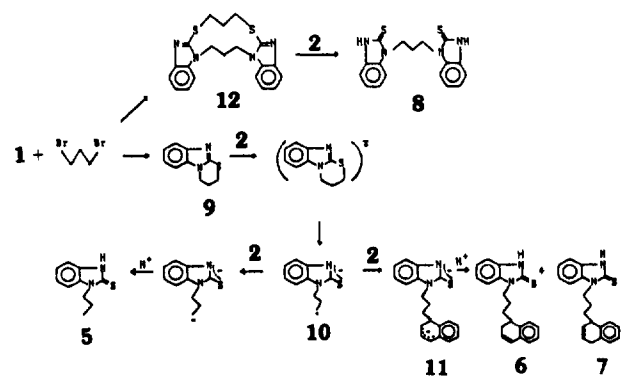
yields using **2** and excessive amounts of primary alkyl halides in THF,[5] which appear to be by far superior to any other methods reported for the preparation of 1-alkyl-2-alkylthiobenzimidazoles.[2-4] Since **2** acts as a strong base,[6] it is not surprising that **2** can be used in place of other base such as NaOH in aqueous solution.

By adding **2** in dry THF to **1** in dry THF, the green color of **2** disappears immediately. The addition was continued until pale green color persisted for few seconds. By this time an equimolar amount of benzyl bromide with **1** was added. Stirring for 3 to 4h, followed by the addition of ethyl iodide afforded 88% yield of 1-ethyl-2-benzylthiobenzimidazole (**4a**) and 5% of 1-benzyl-2-benzylthiobenzimidazole (**4**, R = CH_2Ph). When 2-benzylthiobenzimidazole was reacted with various alkyl halides in the presence of solid NaOH in THF, excellent yields of 1-alkyl-2-benzylthiobenzimidazoles were obtained as shown in Table 1.

The reaction of **1** with 1,3-dibromopropane in the presence of solid NaOH in THF, followed by the treatment with **2** gave the compounds **5**(61%), **6**(16%), **7**(2%), and **8**(7%), which were identified by the spectroscopic and mass spectral data.

The differentiation between **6** and **7** was based on the chemical shifts of benzylic and allylic protons of hydronaphthyl moiety of **6** in which a broad signal due to 3H appeared at δ2.15-3.00 ppm whereas three benzylic protons of hydronaphthyl moiety of **7** exhibited a broad signal at δ 3.18-3.65 ppm. The ratio of **6** to **7** in the mixture, based on the NMR signals, was 8:1.

The vinyl protons of **6** exhibited a multiplet between δ 5.63 and 6.54 ppm but those of **7** showed the corresponding peak between δ5.63 and 6.02 ppm. Other proton signals of **6** and **7** were unable to be distinguished from each other. The mechanism of formations of these compounds can be explained as shown in Scheme 1.



Scheme 1

Independent synthesis of **9**,[5] followed by the treatment with **2** also gave **5**, **6**, and **7**. Since it has been well known that anion radicals of aryl alkyl sulfides undergo a cleavage, yielding arylthiolates and alkyl radicals,[7] the formation of **10** from **9** is highly expected.

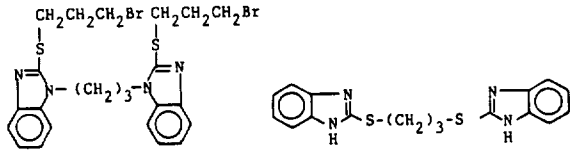
Compound **5** is believed to be formed by single electron transfer from **2** to **10**, yielding a carbanion, followed by protonations.[5]

Compounds **6** and **7** may be formed by a radical coupling between anion radicals **10** and **2** to give dianions (**11**), followed by protonations. Trapping of radicals by **2** and the basicity of thus formed hydronaphthalene carbanion have been well documented.[8]

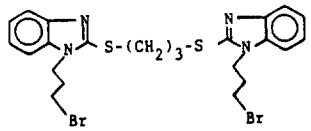
The formation of **8** suggests possible formation(s) of **12**, and/or **13** as intermediate(s) because any of these is exto give **8** by the reaction with **2** (vide infra).

In order to synthesize compound **12**, 1,3-bis(benzimidazolythio)propane (**14**) was treated with 1,3-dibromopropane in the presence of NaOH in THF. However, it was unsuccessful to separate the reaction mixture by column chromatography and each fraction showed four spots on tlc, exhibiting almost identical ^1H NMR spectra with each other. Treatment of the reaction mixture with **2** as described in the previous reaction gave a mixture from which **8** was isolated in 27% yield (based on **14**). In addition, 20 mg of a mixture containing **5** in view of R_f value was separated.

The isolation of **8** indicates that **12** is indeed formed. The formation of **5** suggests the presence of 1,3-bis(N-bromopropylbenzimidazolylthio)propane(**15**) in the reaction mixture obtained from the reaction of **14** with 1,3-dibromopropane since bond cleavages between C-Br of bromopropyl groups as well as sulfur-propyl groups by **2** are expected to occur readily according to the similar mechanism to the formation mechanism of **5** from **9**.

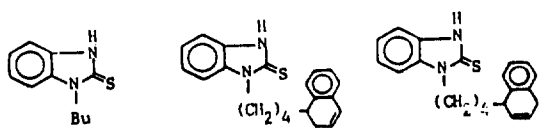


13 **14**

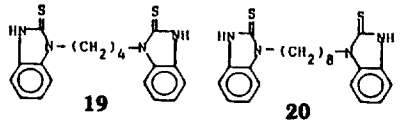


15

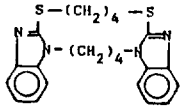
When 1,4-dibromobutane was used in place of 1,3-dibromopropane, compound **16**(53%), a mixture of **17** and **18**(22%), and a mixture of **19** and **20** were obtained. The first four compounds are analogues of the compounds, **5**, **6**, **7**, and **8**, respectively.



16 **17** **18**



19 **20**



21

The proton NMR spectrum of a mixture of **17** and **18** showed the same fashion as that of **6** and **7**. That is, the benzylic and allylic protons of **17** appeared at δ 2.10-3.00 ppm whereas three benzylic protons of **18** exhibited a broad signal at δ 3.18-3.58 ppm. The ratio of **17** to **18** in the mixture was calculated to be 8:1. The vinyl protons of **17** and **18** appeared at δ 5.67-6.59 and 5.67-6.03 ppm, respectively.

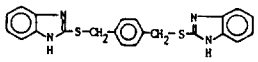
Compounds, **19** and **20**, in the mixture were unable to be separated by column chromatography and showed almost identical ^{1}H NMR spectra. However, tlc showed different R_f values, which were confirmed by those of the authentic samples. Pure compound **19** was obtained in 60% yield by the treatment of **21** with **2**. This result suggests that **21** may be a strong candidate for a precursor of **19**. However, the involvement of other intermediate such as analogue of **13** cannot be ruled out.

The formation of 1,8-bis(2'-mercapto-1'-benzimidazoyl) octane (**20**), of which analogous compounds was not detected in the reaction with 1,3-dibromopropane, indicates the formation of an anion radical analogous to **10**.

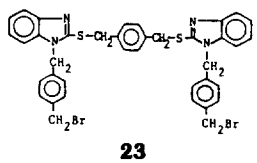
When one half moles of α,α'-dibromo-p-xylene was reacted with one mole of **1** under the same conditions as in the previous reactions, **22** was isolated in 97% yield whereas when more than one mole of α,α'-dibromo-p-xylene was used, **23** and **24** were isolated in 2% and 35% yields, respectively. The structures of **23** and **24** were identified based on ^{1}H NMR and mass spectral data.

Compounds **22** and **24** are rather insoluble in THF. Suspension of **22** in THF was treated with **2** to give **1** along with 1,2-p-ditolylethane in 61% yield. By the same treatment as in the reaction with **22**, compound **24**, however, afforded 1-(p-tolylmethyl)benzimidazoline-2-thione (**25**) in 32% yield in addition of **1** and 1,2-p-ditolylethane. No **26** was detected.

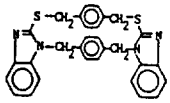
This result is in contrast to that obtained from the reaction with **21** where only bonds between S and C of alkyl group were cleaved and no **1** was isolated. The discrepancies in the results between two reactions may be attributable to the marked difference in the solubilities of **21** and **24** where **21** was soluble in THF and **24** seemingly insoluble. The validity as to the explanation mentioned above will be investigated.



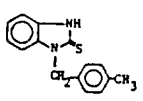
22



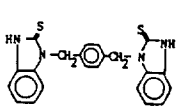
23



24



25



26

Experimental Section

Materials. Benzimidazoline-2-thione (**1**), naphthalene, all alkyl halides and sodium were obtained from Aldrich-Chemie, Germany. Synthetic methods of 2-benzylthiobenzimidazole (**3**), 1-propylbenzimidazoline-2-thione (**5**), and 1-butylbenzimidazoline-2-thione (**16**) were described in the previous report.[5] Sodium naphthalenide (**2**) was prepared according to the method described in the previous paper.[5] Tetrahydrofuran (THF) was dried over calcium hydride. Column chromatography was performed using silica gel(Merck, 70-230 mesh, ASTM). ^{1}H NMR spectra were recorded on a Varian EM 360A NMR spectrometer using tetramethylsilane as an internal standard and solvents were specified in each case. Mass spectra were obtained using a Hewlett packard 5985 B mass spectrometer. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected.

Typical Produre for the Preparation of 1-alkyl-2-benzylthiobenzimidazoles from 1. To a stirred solution of **1**(600 mg, 3.99 mmoles) in 20 m*l* of THF at room temperature under N_2 atmosphere were added **2** until green color of **2** had persisted for ca. 10 sec, followed by the addition of benzyl bromide (769 mg, 4.50 mmoles) in 30 m*l* of THF for 4h. Then ethyl iodide (1,950 mg, 12.5 mmoles) was added to the solution, which was additionally stirred for 3 h. After the solvent was removed, the residue was chromatographed on silica gel column (2 × 20 cm). Elution with *n*-hexane (140 m*l*) gave a mixture of naphthalene and 1,4-dihydronaphthalene. Elution with chloroform (200 m*l*) gave a mixture (1,013 mg) of 1-benzyl-2-benzylthiobenzimidazole[3] (**4**, R = CH_2Ph, 71 mg, 0.21 mmoles, 5%) and 1-ethyl-2-benzylthiobenzimidazole (**4a**, 942 mg, 3.51 mmoles, 88%).

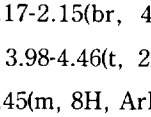
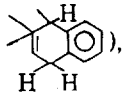
Typical Procedure for the Preparation of 1-alkyl-2-benzylthiobenzimidazoles from 3. To a stirred solution of **3**(200 mg, 0.83 mmoles) in 10 m*l* of THF at room temperature were added solid NaOH(200 mg, 5 mmoles) and ethyl iodide (975 mg, 6.25 mmoles). After the mixture was stirred for 1h, the solvent was evaporated and the residue was extracted with $CHCl_3$(40 m*l*). The $CHCl_3$ layer was dried over $MgSO_4$ and evaporation of $CHCl_3$ afforded 223 mg (0.83 mmoles, 100%) of 1-ethyl-2-benzylthiobenzimidazole (**4a**): liquid; ^{1}H NMR($CDCl_3$) δ 1.21(t, 3H, Me, J = 7 Hz), 3.91(q, 2H, CH_2N, J = 7 Hz), 4.59(s, 2H, CH_2S), 7.00-7.42(m, 8H, ArH), 7.55-7.78(m, 1H, = NArH); MS *m/e* 268(M^+).

Similarly, the following 1-alkyl-2-benzylthiobenzimidazoles were synthesized: 1-propyl-2-benzylthiobenzimidazole (4b): Liquid; 1 h stirring, 99% yield; ^{1}H NMR($CDCl_3$) δ 0.81(t, 3H, Me, J = 7 Hz), 1.31-1.97(m, 2H, CH_2), 3.84(t, 2H, CH_2N, J = 7 Hz), 4.59(s, 2H, CH_2S), 7.00-7.45(m, 8H, ArH), 7.53-7.70(m, 1H, = NArH); MS *m/e* 282(M^+).

1-Allyl-2-benzylthiobenzimidazole (4c): liquid; 1h Stirring, 100% yield; ^{1}H NMR($CDCl_3$) 4.33-4.60(m, 4H, CH_2S, CH_2N), 4.64-5.17(m, 2H = CH_2), 5.30-5.98(m, 1H, -CH =), 6.95-7.40(m, 8H, ArH), 7.50-7.75(m, 1H, = NArH); MS *m/e* 280(M^+).

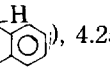
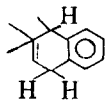
1-(3-Butenyl)-2-benzylthiobenzimidazole (4d): liquid; 3h stirring, 98% yield; ^{1}H NMR($CDCl_3$) δ 2.31(q, 2H, CH_2, J = 7 Hz), 3.89(t, 2H, CH_2N, J = 7 Hz), 4.57(s, 2H, CH_2S), 4.67-5.07(m, 2H, = CH_2), 5.25-5.95(m, 1H, -CH =), 6.96-7.41(m, 8H, ArH), 7.52-7.95(m, 1H, = NArH); MS *m/e* 294(M^+).

Reaction of 1 with 1,3-Dibromopropane, Followed by 2. To a mixture of **1**(1,010 mg, 6.72 mmoles) and NaOH(1g) in 40 m*l* of THF at room temperature under N_2 atmosphere was added 1,3-dibromopropane(1,360 mg, 6.73 mmoles) in 30 m*l* of THF for 5 min, followed by stirring for 10h, by this time no spot corresponding to **1** was observed on tlc. The mixture was treated with **2** and worked up as before.

Elution with *n*-hexane (200 m*l*) gave naphthalene. Elution with a mixture (70 m*l*) of *n*-hexane and ethyl acetate(3:1, v/v) gave 61 mg of unknown mixture. Eltuion next with a mixture(160 m*l*) of *n*-hexane and ethyl acetate(2:1, v/v) afforded 1-propylbenzimidazoline-2-thione[9](**5**, 794 mg, 4.13 mmoles, 61%) and a mixture(389 mg, 1.21 mmoles, 18%) of **6**(16%) and **7**(2%). ^{1}H NMR($CDCl_3$) of **6**: δ1.17-2.15(br, 4H, CH_2CH_2), 2.15-3.00(br, 3H, ), 3.98-4.46(t, 2H, CH_2N), 5.63-6.54 (m, 2H, vinyl H), 6.77-7.45(m, 8H, ArH), 12.14(s, 1H, NH); MS *m/e* 320(M^+). ^{1}H NMR($CDCl_3$) of **7**: δ1.17-2.15(br, 4H, CH_2CH_2), 3.18-3.65(br, 3H, ), 3.98-4.46(t, 2H, CH_2N), 5.63-6.02(m, 2H, vinyl H), 6.77-7.45(m, 8H, ArH), 12.14(s, 1H, NH). Elution next with the same solvent mixture (1:1, v/v, 110 m*l*) gave **1**(84 mg, 0.56 mmoles, 8%) and 1,3-bis(2-mercaptobenzimidazolyl) propane (**8**, 85 mg, 0.25 mmoles, 7%) (vide infra).

Preparation of 1,3-Bis(benzimidazolylthio)propane (14). To a stirred solution of 1,3-dibromopropane (2,753 mg, 13.62 mmoles) in THF(150 m*l*) containing solid NaOH(2,000 mg, 50 mmoles) was added **1**(2,206 mg, 13.49 mmoles) for 10 min. The mixture was stirred at room temperature overnight. Extractions of the reaction mixture with $CHCl_3$, followed by ethyl acetate afforded **9**(1,977 mg, 10.39 mmoles, 77%) and **14**(228 mg, 0.67 mmoles, 5%): mp 203.5-205 °C (ethyl acetate); ^{1}H NMR(DMSO-d_6-$CDCl_3$, 1:3, v/v) δ 1.95-2.60(m, 2H, CH_2), 3.54(t, 4H, $2SCH_2$, J = 7 Hz), 6.90-7.80(m, 8H, ArH), 11.3(s, 2H, 2NH); MS *m/e* 340(M^+).

Reaction of 14 with 1,3-Dibromopropane, Followed by 2. To a stirred solution of **14**(113 mg, 0.33 mmoles) in 10 m*l* of THF were added NaOH(100 mg, 2.5 mmoles) and 1,3-dibromopropane(68 mg, 0.34 mmoles). The mixture was stirred at room temperature for 3 days and worked up as usual. Elutions were carried out successively by using a mixture of *n*-hexane and ethyl acetate(1:1, v/v), the same solvent mixture (1:2, v/v), and ethyl acetate. Each fraction showed four spots on tlc but ^{1}H NMR spectrum was almost identical with each other. Total weight of the residue after removal of the solvent was 73 mg. The mixture was dissolved in 20 m*l* of THF followed by the addition of **2** until green color persisted. This reaction mixture was worked up as usual. Naphthalene was removed by the elution with *n*-hexane. Next elution with a mixtue of *n*-hexane and ethyl acetate (2:1, v/v, 25 m*l*) afforded 20 mg of a mixture, consisting of **5** as a major compound in view of R_f value. Elution next with a mixture of *n*-hexane and ethyl acetate(1:2, v/v, 90 m*l*) afforded **8**(29 mg, 0.09 mmoles, 27%): mp 277-280 °C; ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 5:1, v/v) δ2.00-2.80 (m, 2H, CH_2), 4.45(t, 4H, $2NCH_2$, J = 7 Hz), 6.92-7.50(m, 8H, ArH), 12.03(s, 2H, 2NH); MS *m/e* 340(M^+).

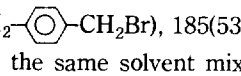
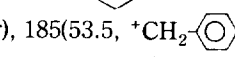
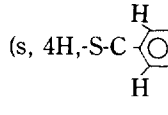
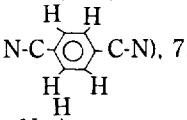
Reaction of 1 with 1,4-Dibromobutane, Followed by 2. To a stirred solution of **1**(525 mg, 3.50 mmoles) in 40 m*l* of THF were added solid NaOH(500 mg, 12.5 mmoles) and 1,4-dibromobutane(798mg, 3.70 mmoles). After the mixture was stirred for 5h at room temperature under N_2 atmosphere, **2** was added and then the reaction mixture was worked up as usual. Naphthalene was removed by elution with benzene. Elution next with chloroform(250 m*l*), followed by a mixture of *n*-hexane and ethyl acetate(1:1, v/v, 15 m*l*) afforded 1-butylbenzimidazoline-2-thione[5,10] (**16**, 382 mg, 1.85 mmoles, 53%) and a mixture(256 mg, 0.77 mmoles, 22%) of **17** and **18**. ^{1}H NMR($CDCl_3$) of **17**: δ 1.10-2.10(br, 6H, $CH_2CH_2CH_2$), 2.10-3.00(br, 3H ), 4.25(t, 2H, NCH_2, J = 7 Hz), 5.67-6.59(m, 2H, vinyl H), 6.80-7.35(m, 8H, ArH), 12.06(s, 1H, NH); MS *m/e* 334(M^+). ^{1}H NMR($CDCl_3$) of **18**: δ1.10-2.10(br, 6H, $CH_2CH_2CH_2$), 3.18-3.58 (br, 3H, ), 4.25(t, 2H, NCH_2, J = 7 Hz), 5.67-6.03(m, 2H, vinyl H), 6.80-7.35(m, 8H, ArH), 12.06(s, 1H, NH). Continuous elution with the same solvent mixture(50 m*l*) gave a mixture(115 mg) of 1,8-bis[2′-mercapto-1′-benzimidazoyl]octane (**20**)[5] and 1,4-bis[2′-mercapto-1′-benzimidazoyl]butane (**19**) (vide infra).

Synthesis of 21. To a stirred solution of 1,4-dibromobutane(2,875 mg, 13.31 mmoles) in THF(150 m*l*) at room temperature was added solid NaOH(2,000 mg, 50 mmoles), followed by the addition of **1**(2,000 mg, 13.32 mmoles) in THF (100 m*l*) for 10 min. The mixture was stirred overnight and worked up as usual. Elution with a mixture (450 m*l*) of *n*-hexane and ethyl acetate (1:1, v/v) afforded an unknown (97 mg) and 2,3,4,5-tetrahydro-1,3-thiazepino[3,2-a]benzimidazole[5] (2,215 mg, 10.84 mmoles, 81%). Eluiton next with ethyl acetate(200 m*l*) afforded **21**(205 mg, 0.50 mmoles, 8%): mp 215.5-217 °C(benzene); ^{1}H NMR($CDCl_3$) δ 1.70-2.07(m, 8H, $2CH_2CH_2$), 3.25-3.51(m, 4H, $2SCH_2$), 3.85-4.20(m, 4H, $2NCH_2$), 7.10-7.35(m, 6H, ArH), 7.48-7.77(m, 2H); MS *m/e* 408(M^+).

Reaction of 21 with 2. To a stirred solution of **21**(102 mg, 0.25 mmoles) in 10 m*l* of THF at room temperature was added **2** under N_2 atmosphere until green color persisted. The reaction mixture was worked up as before. Naphthalene was removed by the elution with *n*-hexane. Elution with chloroform afforded 1,4-bis[2′-mercapto-1′-benzimidazoyl] butant (**19**, 54 mg, 0.15 mmoles, 60%): mp 276-278 °C; ^{1}H NMR($CDCl_3$-DMSO-d_6, 5:1, v/v) δ1.81-2.13(m, 4H, $2CH_2$), 4.23-4.56(m, 4H, $2NCH_2$), 7.15-7.40(m, 8H, ArH), 12.5(s, 2H, NH); MS *m/e* 354(M^+).

Reaction of 1 with α,α'-dibromo-p-xylene. (a) To a stirred solution of **1**(2,020 mg, 13.4 mmoles) in 50 m*l* of THF at room temperature was added solid NaOH(2,000 mg, 13.4 mmoles), followed by the addition of α,α'-dibromo-p-xylene (2,030 mg, 7.69 mmoles). The reaction mixture was worked up as before and **22**(2,610 mg, 6.48 mmoles, 97%) was obtained. mp 274-277 °C(aq. DMSO); ^{1}H NMR ($CDCl_3$ + DMSO-d_6, 1:1, v/v) δ 4.56(s, 4H, $2CH_2$), 7.06-7.70(m, 12H, ArH), 12.5(s, 2H, 2NH); MS *m/e* 402(M^+).

(b) According to the same procedure as described in (a), **1**(2,030 mg, 13.5 mmoles) and NaOH(2,000 mg, 50 mmoles) in 50 m*l* of THF were reacted with α,α'-dibromo-p-xylene (3.830 mg, 14.5 mmoles) in 100 m*l* of THF. The reaction mixture was worked up as before. Elution with *n*-hexane,

followed by CH_2Cl_2 afforded unreacted α,α'-dibromo-p-xylene. Elution with a mixture of *n*-hexane and ethyl acetate(2:1, v/v, 85 m*l*) gave an unknown compound(11 mg). Elution with the same solvent mixture(1:1, v/v, 60 m*l*) gave **23**(112 mg, 0.15 mmoles, 2%); ^{1}H NMR($CDCl_3$) δ 4.45(s, 4H), 4.64(s, 4H), 5.26(s, 4H, $2NCH_2$), 7.00-7.50(m, 18H, ArH), 7.66-7.94(m, 2H, ); MS *m/e*(Rel. int) 183(58.1, ), 185(53.5, ). Elution with the same solvent mixture (1:2, v/v, 100 m*l*) gave **24** (1,191mg, 2.36 mmoles, 35%): ^{1}H NMR($CDCl_3$ + DMSO-d_6, 5:1, v/v) δ 4.50(s, 4H, $2SCH_2$), 5.23(s, 4H, $2NCH_2$), 6.61 (s, 4H, ), 6.94(s, 4H, ), 7.13-7.44 (m, 6H, ArH), 7.58-7.90 (m, 2H, ); MS *m/e* 540 (M^+).

Reaction of 22 with 2. Sodium naphthalenide (**2**) was added to a suspension of **22** (1,433 mg, 3.56 mmoles) in 30 m*l* of THF at room temperature under N_2 atmosphere until green color of **2** persisted. The reaction mixture was quenched with water, followed by the extraction with ethyl acetate. After the solvent was evaporated, the residue was chromatographed. Elution with chloroform(130 m*l*) afforded a mixture of naphthalene and 1,2-di-p-tolylethane[11] (228 mg, 1.08 mmoles, 61%). Elution with acetone(80 m*l*) gave **1**(869 mg, 5.79 mmoles, 81%).

Reaction of 24 with 2. As in the reaction of **22, 2** was added to a suspension of **24**(965 mg, 1.91 mmoles) in 30 m*l* of THF. The reaction mixture was worked up as in the previous reaction. Elution with *n*-hexane(150 m*l*) gave a mixture of naphthalene and 1,2-di-p-tolyethane. Elution with a mixture(90 m*l*) of *n*-hexane and ethyl acetate(3:1, v/v) gave 1-(*p*-tolylmethyl) benzimidazoline-2-thione(**25**, 155 mg, 0.61 mmoles, 32%): mp 201-202 °C (ethyl acetate-n-hexane, 1:10, v/v); ^{1}H NMR($CDCl_3$-DMSO-d_6, 3:1, v/v) δ 2.24(s, 3H, Me), 5.49(s, 2H, CH_2), 6.88-7.34(m, 8H, ArH), 12.60(s, 1H, NH); MS *m/e* 254(M^+). Elution next with the same solvent mixture(2:1, v/v, 170 m*l*) gave an unknown (157 mg) and **1**(282 mg, 1.88 mmoles, 49%).

Acknowledgement. Support of this work by Korea Science and Engineering Foundation is gratefully acknowledged.

References

1. (a) J. A. Vida, *Tetrahedron Letts.*, 3921 (1972).
(b) C. Rovnyah, V. L. Narayana, R. D. Haugwitz, and C. M. Cimarusti, U.S. Patent 3,927,014 (1975); *Chem. Abstr.*,**84** , 105596m (1976).
2. (a) R. J. Badger and G. B. Barlin, *J. Chem. Soc.* Perkin II. 1176 (1976).
(b) E. Hoggarth, *J. Chem. Soc.*, 3311 (1949).
3. O. P. Suri, R. K. Khajuria, D. B. Saxena, N. S. Rawat, and C. K. Atal, *J. Heterocyclic Chem.*,**20,** 813 (1983).
4. (a) B. Stanovnik, M. Tisler, A. Hribar, G. B. Barlin, and D. J. Brown, *Aust. J. Chem.*,**34,** 1729 (1981).
(b) E. V. Logachev, M. V. Povstanyanoi, P. M. Kochergin, Yu.I. Beilis, *Izv. Vyssh. Uchebn.* Zaved. *Khim. Khim. Tekhnol,* **19,** 1039 (1976); *Chem. Abstr.,* **85,** 159984a (1977).
(c) N. P. Bednyagina and I. Ya. Postovskii, Nauch. Doklady Vysshei, Shkoly, Khim. Khim. Tekhnol, No. 2, 333 (1959); *Chem. Abstr.*,**54,** 510b (1960).
(d) K. V. Ananeva, N. K. Rozhkova, *Uzb. Khim. Zh.* **17,** 56 (1973); *Chem. Abstr.,* **62**, 13140f(1965).
5. A manuscript has been submitted to *J. Heterocyclic Chem.*
6. N. L. Holy, *Chem. Rev.*, **74**(2), 243 (1974); References are cited therein.
7. J. F. Bunnett, *Accounts Chem. Res.*, **11,** 413 (1978).
8. (a) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **93,** 430 (1971).
(b) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).
9. K. Futaki, *J. Pharm. Soc. Jap.*,**74,** 1365 (1954).
10. G. N. Tyurenkova, E. I. Silina, and I. Ya. Postovskii, *Zhur. Priklad. Khim.* **34,** 2327 (1961); *Chem. Abstr.*, **56,** 7303d (1962).
11. S. Kunichika, S. Oka, and T. Sugiyama, *Bull. Inst. Chem. Res., Kyoto Univ.* **43**(3), 250(1965); *Chem. Abstr.*, **64,** 4972c (1966).

Topological Approach to the Rubber Elasticity of Polymer Networks

Jung Mo Son and Hyungsuk Pak*

Department of Chemistry, Seoul National University, Seoul 151-742. *Received October 4, 1988*

Applying the topological theory of rubber elasticity which was suggested by K. Iwata to the newly devised body-centered cubic lattice model, the authors calculated the values of four terms of the free energy to form polymer networks. Finding the projection matrix of the BCL model, and comparing this with the values of the simple cubic lattice (abbreviated to SCL hereafter) model of K. Iwata, the authors obtained the stress versus strain curves and found that the curves are in good agreement with the experimental results of poly(dimethyl siloxane) networks.

Introduction

Rubber elasticity theories are classified into two categories. One is the phantom network theories (PNT)[1-12] and the other the topological ones (TNT)[13-15]. In the former, the stress of networks is regarded as coming from the entropic