

macrocyclic complexes by using Fe(II) ion as a metal template. In addition, this study also shows that oxidation of Fe(II) to Fe(III) as well as the oxidative dehydrogenation of the macrocyclic ligand occur during the template reactions in the presence of base and a trace of oxygen.

**Acknowledgment.** This work was supported by Seoul National University DeWoo Research Fund.

### References

1. J. B. Harrowfield, A. J. Herit, P. A. Lay, A. M. Sargeson, and A. M. Bond, *J. Am. Chem. Soc.*, **105**, 5503 (1983).
2. M. P. Suh, W. Shin, D. Kim, and S. Kim, *Inorg. Chem.*, **23**, 618 (1984).
3. M. P. Suh, D. Kim, and S. Kim, *Inorg. Chem.*, **24**, 3712 (1985).
4. M. P. Suh, W. Shin, H. Kim, and C. H. Koo, *Inorg. Chem.*, **26**, 1846 (1987).
5. M. P. Suh and S.-G. Kang, *Inorg. Chem.*, **27**, 2544 (1988).
6. M. P. Suh, W. Shin, S.-G. Kang, M. S. Lah, and T.-M. Chung, *Inorg. Chem.*, **28**, 1602 (1989).
7. M. P. Suh, S.-G. Kang, and T.-M. Chung, *Bull. Korea Chem. Soc.*, **11**, 206 (1990).
8. M. P. Suh, S.-G. Kang, V. L. Goedken, S.-H. Park, *Inorg. Chem.*, **30**, 365 (1991).
9. O. Barton, and W. D. Ollis, *Comprehensive Organic Chemistry*, Pergamon press, Oxford, England, Vol. 2, p 83 (1979).
10. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", 2nd ed., Pergamon, Headington Hill Hall, Oxford, London, England, (1980).
11. J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).
12. J. Yarwood, "Spectroscopy and Structure of Molecular Complexes", Plenum, N. Y., pp. 141-145 (1973).
13. P. H. Smith, and K. N. Raymond, *Inorg. Chem.*, **24**, 3469 (1985).
14. V. L. Goedken, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 7355 (1972).
15. J.C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, **14**, 1881 (1975).
16. M. P. Suh, S. G. Kang, and K. W. Woo, *J. Chem. Soc.*, **28**, 384 (1984).
17. V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 3397 (1972).

### A Synthesis of the Pheromone of Mouse *Mus Musculus*

Jong-Gab Jun\*, Dong Gyun Shin, and Hyun Shun Shin

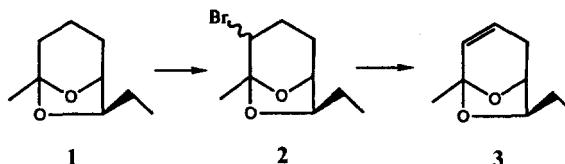
*Department of Chemistry, Hallym University,  
Chuncheon 200-702*

*Received August 17, 1991*

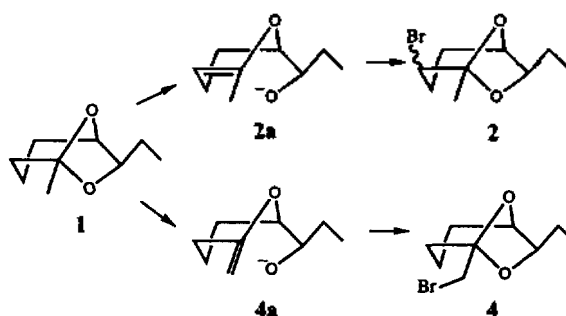
The mouse pheromone, exo-7-ethyl-5-methyl-6,8-dioxabicyclo-

clo[3.2.1]oct-3-ene (3), has been isolated from urine of the male mouse of the species *Mus musculus*<sup>1</sup> and synthesized in a low yield.<sup>2</sup>

In the course of our continuing study on bicyclic ketal compounds,<sup>3</sup> we developed the stereoselective synthesis of exo and endo bicyclic ketal and utilized this method to the brevicomin synthesis.<sup>4</sup> We now report a synthesis of the pheromone 3 from exo brevicomin 1 which is synthesized from methyl vinyl ketone dimer in high yield.



Bromination of acyclic acetals is known to occur on the carbon atom  $\alpha$  to the functional group.<sup>5</sup> Accordingly, 1 was brominated with one equiv. of bromine in carbon tetrachloride for 7 hrs stirring at room temperature to obtain mono-brominated ketal 2 in 88% yield. With the addition of  $\text{Na}_2\text{CO}_3$ , the reaction was completed within 1 hr in quantitative yield. In our bicyclic ketal system, there are two carbon atoms  $\alpha$  to the ketal and regiospecific bromination has been achieved via enolate 2a without any evidence of 4 as a product. But the product showed two peaks on the capillary gas-liquid chromatogram, indicative of the presence of 1:1 mixture of axial and equatorial isomers, however, dibromination was occurred with excess bromine.



The mono-brominated ketal 2 was subjected to dehydrobromination with various basic conditions using methoxide, *t*-butoxide, LDA, NaH and *n*-BuLi etc. Best result was achieved with *t*-butoxide at reflux in 71% yield.

### Experimental

**Exo-4-bromo-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane (2).** To a 0.18 g of exo-brevicomin 1 in 8 ml of anhydrous carbon tetrachloride was added 0.39 g of  $\text{Na}_2\text{CO}_3$  and 0.058 ml of  $\text{Br}_2$ . The reaction mixture was stirred for 1 hr at room temperature and filtered, followed by extraction with methylene dichloride (20 ml  $\times$  4). The organic layer was dried ( $\text{MgSO}_4$ ), filtered and evaporated to give 0.27 g of oily products (quantitative yield) which are 1:1 mixture of axial and equatorial isomers.

<sup>1</sup>H-NMR ( $\text{CDCl}_3$ ):  $\delta$  4.23 (m, 1H), 4.08-3.96 (m, 1H), 3.90 (t, 1H), 2.40-1.60 (m, 6H), 1.59 (s, 3H), 0.91 (t, 3H); IR (neat): 2958, 1459, 1381, 1330, 1235, 790  $\text{cm}^{-1}$ .

**Exo-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]oct-3-ene (3).** To a refluxed solution of *t*-butoxide (0.54 g) in *t*-butyl alcohol (8 ml) was added 0.23 g of **2** and refluxed overnight. After cooling, *t*-butyl alcohol was removed and H<sub>2</sub>O (10 ml) was added to this reaction mixture which was then extracted with diethyl ether (20 ml×4) and dried (MgSO<sub>4</sub>), followed by filtration, evaporation and chromatography gave 0.095 g of the product **3** (63% yield).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 5.77 (br, s, 2H), 4.20 (br, s, 1H), 3.82 (m, 1H), 2.8-1.3 (m, 4H), 1.60 (s, 3H), 0.90 (t, 3H); IR (neat): 2934, 1664, 1459, 1391, 1317, 1251, 720 cm<sup>-1</sup>.

**Acknowledgement.** The present studies were supported by the Program of Local University Promotion, Ministry of Education, 1991.

### References

1. D. P. Wiesler, F. J. Schwende, M. Carmack, and M. Novotny, *J. Org. Chem.*, **49**, 882 (1984).
2. B. P. Mundy and W. G. Bornmann, *J. Org. Chem.*, **49**, 5264 (1984).
3. J.-G. Jun, S. Suh, and D. G. Shin, *J. Chem. Soc. Perkin Trans. I*, 1349 (1989); J.-G. Jun and B. P. Mundy, *Bull. Korean Chem. Soc.*, **9**, 135 (1988); M. Bjorklund, J.-G. Jun, and B. P. Mundy, *Tetrahedron Lett.*, **26**, 3895 (1985).
4. J.-G. Jun and D. G. Shin, *J. Chem. Soc. Perkin Trans. I*, 956 (1991).
5. S. M. McElvain, R. L. Clarke, and G. D. Jones, *J. Am. Chem. Soc.*, **64**, 1966 (1942); W. H. Hartung and H. Adkins, *J. Am. Chem. Soc.*, **49**, 2517 (1927).

### A Facile Synthetic Route to 1,2-Dicarbomethoxy-1,2-dicyanocyclopropanes

Ju-Yeon Lee\*, Sung-Ok Cho, and Gil-Soo Mun

Department of Chemistry, Inje University,  
Kimhae 621-749

Received October 10, 1991

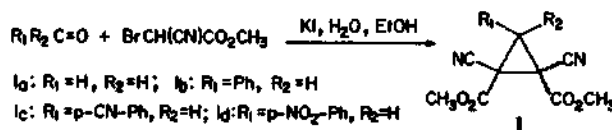
Although there are several reports on the synthesis of 1,1,2-trior, 1,1,2,2-tetracyanocyclopropanes, examples on the preparation of 1,2-dicyanocyclopropanes are rare. 1,1,2-Tricyanocyclopropanes can be prepared from bromomalononitrile and ylidenecyanoacetate.<sup>1</sup> 1,1,2,2-Tetracyanocyclopropanes can be prepared by the reaction of formaldehyde and malononitrile,<sup>2</sup> tetracyanoethylene and diazomethane,<sup>3</sup> or tetracyanoethylene with bromoketene acetals.<sup>4</sup> A large number of substituted 1,1,2,2-tetracyanocyclopropanes are available by the Wideqvist reaction,<sup>5,6</sup> in which a carbonyl compound reacts with 2 equiv of bromomalononitrile. Hart and his coworkers reported a similar cyclopropanation procedure.<sup>7,8</sup>

In the present report, we extended the Wideqvist reaction to prepare 1,2-dicarbomethoxy-1,2-dicyanocyclopropanes. A series of aldehydes and ketones were condensed with methyl bromocyanoacetate in the presence of potassium iodide.<sup>9</sup> The

**Table 1.** Synthesis of 1,2-Dicarbomethoxy-1,2-dicyanocyclopropane (**1<sub>a-d</sub>**)<sup>a</sup>

Compd	R <sub>1</sub>	R <sub>2</sub>	temp, °C	time, hr	yield, %	mp, °C
<b>1<sub>a</sub></b>	H	H	25	60	21	119-120
<b>1<sub>b</sub></b>	Ph	H	25	10	45	135-136
<b>1<sub>c</sub></b>	<i>p</i> -CN-Ph	H	25	10	50	114-115
<b>1<sub>d</sub></b>	<i>p</i> -NO <sub>2</sub> -Ph	H	25	10	54	116-117
	<i>p</i> -CH <sub>3</sub> O-Ph	H	25	10	†	
	<i>p</i> -OH-Ph	H	25	10	†	
	CH <sub>3</sub>	H	25	48	†	
	CCl <sub>3</sub>	H	25	10	†	
	CH <sub>3</sub>	CH <sub>3</sub>	25	10	†	
	-(CH <sub>2</sub> ) <sub>5</sub> -		25	10	†	
	Ph	CH <sub>3</sub>	25	10	†	
	Ph	CH <sub>2</sub> CN	25	10	†	
	<i>p</i> -CN-Ph	CH <sub>3</sub>	25	10	†	
	<i>p</i> -Cl-Ph	CH <sub>3</sub>	25	10	†	

<sup>a</sup>All the cyclopropanes were mixtures of *cis*- and *trans*-isomers, which was confirmed by <sup>1</sup>H-NMR and IR spectra. <sup>†</sup>Small amount of methyl cyanoiodoacetate was formed.



results are summarized in Table 1. As shown in Table 1, formaldehyde, benzaldehyde, and substituted benzaldehydes react readily with methyl bromocyanoacetate to give mixtures of *cis*- and *trans*-1,2-dicarbomethoxy-1,2-dicyanocyclopropanes (**1<sub>a-d</sub>**) in a moderate yield. Most of the common ketones such as acetone, cyclohexanone, benzophenone, and 4-acetylbenzophenone are inert to the condensation. In the case of *p*-substituted benzaldehydes, electron-withdrawing on benzene ring accelerated the reaction. However, benzaldehydes with electron-releasing group such as -OCH<sub>3</sub> failed to give cyclopropanes. These results are reasonable in view of the electrophilicity of carbonyl carbon. Chemical structures of the resulting cyclopropanes **1<sub>a-d</sub>** were identified by <sup>1</sup>H-NMR, IR, and elemental analysis data.<sup>10</sup> All the spectral and elemental analysis data confirmed the expected structures.

**Acknowledgement.** This work was supported by the Inje Research and Scholarship Foundation.

### References

1. Y. C. Kim and H. Hart, *J. Chem. Soc.(C)*, 2409 (1969).
2. R. M. Scribner, G. N. Sausen, and W. W. Prichard, *J. Org. Chem.*, **25**, 1440 (1960).
3. J. Bestus and J. Castells, *J. Proc. Chem. Soc.(London)*, 216 (1962).
4. J.-Y. Lee and H. K. Hall, Jr., *J. Org. Chem.*, **55**, 4963 (1990).
5. L. Ramberg and S. Wideqvist, *Arkiv Kemi*, **12A(22)**, (1937).
6. L. Ramberg and S. Wideqvist, *ibid.*, **14B(37)**, (1947).
7. H. Hart and F. Freeman, *J. Org. Chem.*, **28**, 1220 (1941).
8. H. Hart and Y. C. Kim, *ibid.*, **31**, 2784 (1966).