crocyclic 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.

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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

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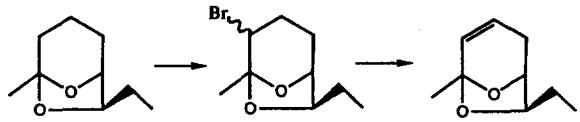
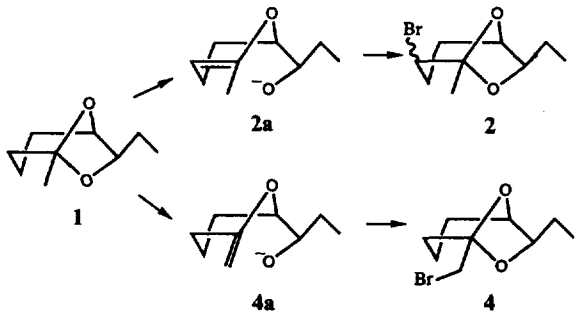
The mouse pheromone, exo-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]oct-3-ene (**3**), has been isolated from urine of the male mouse of the species Mus musculus[1] and synthesized in a low yield.[2]

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



Bromination of acyclic acetals is known to occur on the carbon atom α to the functional group.[5] Accordingly, **1** was brominated with one equiv. of bromine in carbon tetrachloride for 7 hrs stirring at room temperature to obtain monobrominated ketal **2** in 88% yield. With the addition of Na_2CO_3, the reaction was completed within 1 hr in quantitative yield. In our bicyclic ketal system, there are two carbon atoms α 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 m*l* of anhydrous carbon tetrachloride was added 0.39 g of Na_2CO_3 and 0.058 m*l* of Br_2. The reaction mixture was stirred for 1 hr at room temperature and filtered, followed by extraction with methylene dichloride (20 m*l*×4). The organic layer was dried ($MgSO_4$), filtered and evaporated to give 0.27 g of oilish products (quantitative yield) which are 1 : 1 mixture of axial and equatorial isomers.

^{1}H-NMR ($CDCl_3$): δ 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 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 m*l*) was added 0.23 g of **2** and refluxed overnight. After cooling, *t*-butyl alcohol was removed and H_2O (10 m*l*) was added to this reaction mixture which was then extracted with diethyl ether (20 m*l*×4) and dried ($MgSO_4$), followed by filtration, evaporation and chromatography gave 0.095 g of the product **3** (63% yield).

^{1}H-NMR ($CDCl_3$): 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^{-1}.

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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

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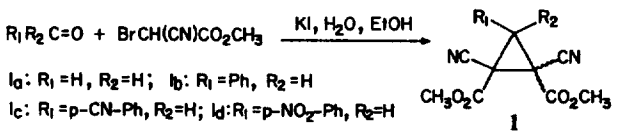
Although there are several reports on the synthesis of 1,1,2-trior 1,1,2,2-tetracyanocyclopropanes, examples on the preparation of 1,2-dicyanocyclopropanes are rare. 1,1,2-Tricyanocyclopropanes can be prepared from bromomalononitrile and ylidenecyanoacetate.[1] 1,1,2,2-Tetracyanocyclopropanes can be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

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.[9] The 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 ($\mathbf{1}_{a-d}$) in a moderate yield. Most of the common ketones such as acetone, cyclohexanone, benzophenone, and 4-acetylbenzonitrile 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 $-OCH_3$ failed to give cyclopropanes. These results are reasonable in view of the electrophilicity of carbonyl carbon. Chemical structures of the resulting cyclopropanes $\mathbf{1}_{a-d}$ were identified by ^{1}H-NMR, IR, and elemental analysis data.[10] All the spectral and elemental analysis data confirmed the expected structures.

Table 1. Synthesis of 1,2-Dicarbomethoxy-1,2-dicyanocyclopropane ($\mathbf{1}_{a-d}$)[a]

Compd	R_1	R_2	temp, ℃	time, hr	yield, %	mp, ℃
$\mathbf{1}_a$	H	H	25	60	21	119-120
$\mathbf{1}_b$	Ph	H	25	10	45	135-136
$\mathbf{1}_c$	*p*-CN-Ph	H	25	10	50	114-115
$\mathbf{1}_d$	*p*-NO_2-Ph	H	25	10	54	116-117
	p-CH_3O-Ph	H	25	10	[b]	
	p-OH-Ph	H	25	10	[b]	
	CH_3	H	25	48	[b]	
	CCl_3	H	25	10	[b]	
	CH_3	CH_3	25	10	[b]	
	$-(CH_2)_5-$		25	10	[b]	
	Ph	CH_3	25	10	[b]	
	Ph	CH_2CN	25	10	[b]	
	p-CN-Ph	CH_3	25	10	[b]	
	p-Cl-Ph	CH_3	25	10	[b]	

[a] All the cyclopropans were mixtures of *cis*- and *trans*-isomers, which was confirmed by ^{1}H-NMR and IR spectra. [b] Small amount of methyl cyanoiodoacetate was formed.



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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).