was washed with diethyl ether. Product nitroarenes were isolated by careful distillation of the filtrate. The solid catalyst, after being washed with ether, was dried in air and could be reused.

Acknowledgment. Support of our work by the U.S. Army Office of Research is gratefully acknowledged.

Registry No. Benzene, 71-43-2; nitrobenzene, 98-95-3; toluene, 108-88-3; 1-methyl-2-nitrobenzene, 88-72-2; 1-methyl-3-nitrobenzene, 99-08-1; 1-methyl-4-nitrobenzene, 99-99-0; ethylbenzene, 100-41-4; 1-ethyl-2-nitrobenzene, 612-22-6; 1-ethyl-3-nitrobenzene, 7369-50-8; 1-ethyl-4-nitrobenzene, 100-12-9; acetophenone, 98-86-2; *tert*-butylbenzene, 98-06-6; 1-(1,1-dimethylethyl)-2-nitrobenzene, 1886-57-3; 1-(1,1-dimethylethyl)-3-nitrobenzene, 23132-52-7; 1-(1,1-dimethylethyl-4-nitrobenzene, 3282-56-2; 1,2-dimethylbenzene, 95-47-6; 1,2-dimethyl-3-nitrobenzene, 83-41-0; 1,2-dimethyl-4-nitrobenzene, 99-51-4; 1,3-dimethylbenzene, 108-38-3; 1,3-dimethyl-2-nitrobenzene, 81-20-9; 1,3-dimethyl-4-nitrobenzene, 89-87-2; chlorobenzene, 108-90-7; 1-chloro-2-nitrobenzene, 88-73-3; 1-chloro-3-nitrobenzene, 121-73-3; 1-chloro-4-nitrobenzene, 100-00-5; bromobenzene, 108-86-1; 1-bromo-2-nitrobenzene, 577-19-5; 1-bromo-4-nitrobenzene, 586-78-7; naphthalene, 91-20-3; 1-nitronaphthalene, 86-57-7; 2-nitronaphthalene, 581-89-5; isopropylbenzene, 98-82-8; 1-isopropyl-2-nitrobenzene, 6526-72-3; 1-isopropyl-3-nitrobenzene, 6526-74-5; 1-isopropyl-4-nitrobenzene, 1817-47-6; fluorobenzene, 462-06-6; 1-fluoro-2-nitrobenzene, 1493-27-2; 1-fluoro-3-nitrobenzene, 402-67-5; 1-fluoro-4-nitrobenzene, 350-46-9; mercuric nitrate, 10045-94-0; Nafion-H, 63937-00-8.

Communications

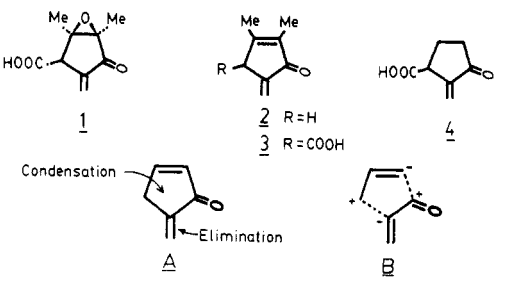
Novel Route to α-Methylene Cyclopentenones. High-Yield Synthesis of Methylenomycin B

Summary: α-Methylenecyclopentenones were conveniently synthesized from the methyl acrylate–anthracene adduct, an α-methylene carbonyl equivalent.

Sir: Methylenomycin A (1) and B (2)[1] deepoxy-4,5-didehydromethylenomycin A (3)[2], and the related sarkomycin (4)[3] (see Chart I) were isolated from the culture broth of *Streptomyces* species and belong to a family of "cyclopentenoid antibiotics".[4] As a result of their interesting biological activities, total syntheses of these compounds have been accomplished.[5] These syntheses invariably involve two compulsory steps: the construction of the cyclopentenone ring and subsequent formation of the *exo*-methylene group via an elimination reaction (structure A). We now report a new approach to a short and high overall yield synthesis of α-methylenecyclopentenones as depicted in structure B. Construction of the desired bonds, a three-carbon annelation program, was achieved by reacting a propene unit with a masked α-methylene carbonyl function as illustrated in Scheme I. (See Table I for melting point and yield data).

The anion derived from the known ester adduct **5**[6] was alkylated with allyl halide [LDA, in THF/HMPA (10:1)] to give directly the product **6** (78–98% isolated yield).[7]

Chart I



Scheme I

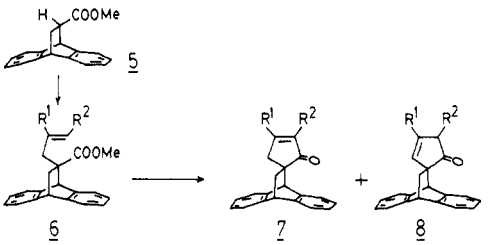


Table I

	substituents	mp, °C 7	mp, °C 8	ratio of 7/8	% yield
a	$R^1 = R^2 = Ph$	213[a]		1:0	92
b	R^1 = Me; R^2 = Ph	226.5[b]		1:0	93
c	R^1 = H; R^2 = Ph	210[a]		1:0	68
d	R^1 = H; R^2 = *m*-OMe-C_6H_4	157–158[c]		1:0	70
e	$R^1 = R^2$ = Me	148[b]	see text		
f	R^1 = Me; R^2 = H	156–157[b]	159[b]	1:1	87
g	$R^1 = R^2$ = H	170–171[b]	132–133[b]	1:1.2	82

[a] From EtOH. [b] From CH_2Cl_2/hexane. [c] From CCl_4.

The allylic ester was then cyclized[8] by using LDA in THF/TMEDA (4:1) at room temperature overnight.[9]

(1) Haneishi, T.; Kitihara, N.; Takiguchi, Y.; Arai, M.; Sugawara, S. *J. Antibiot.* **1974**, *27*, 386. Haneishi, T.; Terahara, A.; Arai, M.; Hata, T.; Tamura, C. *Ibid.* **1974**, *27*, 393. For a review up to 1979 see: Terahara, A.; Haneishi, T.; Arai, M. *Heterocycles* **1979**, *13*, 353.

(2) Hornemann, U.; Hopwood, D. A. *Tetrahedron Lett.* **1978**, 2977.

(3) Umezawa, H.; Takeuchi, T.; Nitta, K.; Yamamoto, Y.; Yamaoka, S. *J. Antibiot.* **1953**, *6*, 101.

(4) Scarborough, R. M., Jr.; Toder, B. H.; Smith, A. B., III *J. Am. Chem. Soc.* **1980**, *102*, 3904.

(5) Jernow, J.; Tautz, W.; Rosen, P.; Blount, J. F. *J. Org. Chem.* **1979**, *44*, 4210. Jernow, J.; Tautz, W.; Rosen, P.; Williams, T. H. *Ibid.* **1979**, *44*, 4212. Marx, J. N.; Minaskanian, G. *Tetrahedron Lett.* **1979**, 4175. Boeckman, R. K., Jr.; Naegeley, P. C.; Arther, S. D. *J. Org. Chem.* **1980**, *45*, 752. Reference 4. Koreeda, M.; Chen, Y. P. L. *Tetrahedron Lett.* **1981**, *15*. Boschelli, D.; Scarborough, R. M., Jr.; Smith, A. B., III *Tetrahedron Lett.* **1981**, 19.

(6) Bartlett, P. D.; Fate, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 91. For recent application of this compound see: Jenkitkasemwong, Y.; Thebtaranonth, Y.; Wajirum, N. *Tetrahedron Lett.* **1979**, 1615.

(7) We thank Miss Srisuthtiprut, Mrs. Poochaiwattananon, and Mrs. Udcharchon for spectroscopic, mass spectral, and analytical services.

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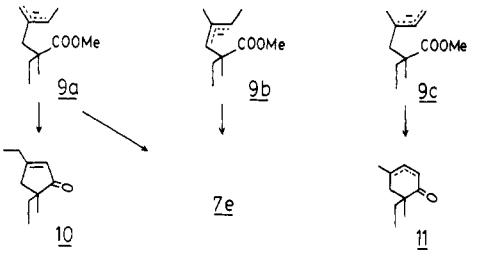
Scheme II

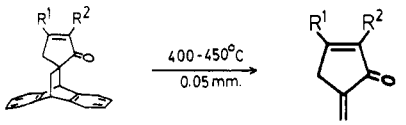


As summarized in Table I, if R^2 = aryl, spirocyclopentenone **7** was isolated as the only product (entries **a–d**). However, if $R^2 \neq$ aryl, the two products **7** and **8** were isolated in almost equal amounts (entries **f** and **g**). These spiro ketones **7** and **8** can be separated by TLC [silica gel plates, with ethyl acetate/hexane (10:1) as the eluent] and are easily distinguished by their spectroscopic data.[10]

The cyclization of **6e** gave only a minor amount of the required **7e** (the precursor of methylenomycin B), while the major product from the reaction was identified as the β-substituted ethylcyclopentenone **10** [mp 84–85 °C (from CCl_4)], obtained in a ratio of 1:6 **7e**/**10** (71%).[11] The formation of these two products is seen as apparently arising from two types of allyl anion intermediates, **9a** and **9b**. The other possibility, the cyclohexanone **11**, which could result from the cyclization of anion **9c**, was not detected (Scheme II).

A modified approach was then used to prepare compound **7e**. Thus when **7f** or **8f** was treated with 1 equiv of LDA in THF/HMPA (10:1) solution followed by addition of methyl iodide, the desired product **7e** was obtained in excellent yield.[12]

Vacuum pyrolysis of spirocyclopentenones **7a–f** and **10** at 400–450 °C (0.05 mm)[13] afforded the corresponding α-methylenecyclopentenones **12** in nearly quantitative



7a-f, 10 12

yields.[10] The liquid methylenecyclopentenones **12e,f,h** (R^1 = Et, R^2 = H) could be further vacuum distilled if needed. However, this was unnecessary since crude pyrolysates from vacuum pyrolyses display quite satisfactory NMR spectra. They can be kept indefinitely under vacuum or argon at −78 °C but polymerize readily at room temperature, especially in solution. The solid samples **12a–d** could be crystallized from methylene chloride/hexane or ether/hexane mixtures. The crystalline products are quite stable and can be stored without any special precaution.

The pyrolysate from the vacuum pyrolysis of **7g** gave, rather interestingly, an NMR spectrum in which could be observed not only the proton resonances assigned to **12g** [the parent compound in this series: NMR (CCl_4) δ 3.21 (2 H), 5.32 (1 H), 5.88 (1 H), 6.21 (1 H), 7.52 (1 H)] but also another set of signals attributed to the isomer **13** [δ

13

2.82 (2 H), 5.18 (1 H), 5.55 (1 H), 6.31 (1 H), 6.61 (1 H)] in a ratio of 4:1, respectively.[14] No attempt was made to separate these two products due to spontaneous polymerization.

In conclusion, we have described a short and novel method for the general synthesis of α-methylenecyclopentenones which looks like a very attractive process. The retro-Diels–Alder reaction works efficiently under the employed conditions for these fairly small molecules. Thus, the method provides a high-yield synthesis of methylenomycin B (**2** or **12e**, 74% overall yield starting from **5**).

Acknowledgment. We thank The National Research Council (Thailand) for the support.

Registry No. **5**, 13294-86-5; **6a**, 79655-54-2; **6b**, 79655-53-1; **6c**, 79655-55-3; **6d**, 79655-56-4; **6e**, 79667-43-9; **6f**, 79667-42-8; **6g**, 79667-41-7; **7a**, 79655-58-6; **7b**, 79655-57-5; **7c**, 79655-59-7; **7d**, 79655-60-0; **7e**, 79655-63-3; **7f**, 79655-62-2; **7g**, 79655-61-1; **8f**, 79655-67-7; **8g**, 79655-68-8; **10**, 79655-64-4; **12a**, 79655-70-2; **12b**, 79655-69-9; **12c**, 79655-71-3; **12d**, 79655-72-4; **12e**, 52775-77-6; **12f**, 79655-74-6; **12g**, 79655-73-5; **12h**, 80160-98-1; **13**, 80160-99-2.

Supplementary Material Available: Experimental procedure for the synthesis of and characterization data for compounds **7**, **8**, **10**, and **12** (12 pages). Ordering information is given on any current masthead page.

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(8) Prempree, P.; Siwapinyoyos, T.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1980**, 1169.
(9) It was found that the solvent ystem THF/TMEDA (4:1) gave different results from those of THF/HMPA (10:1; cf. ref 8). For example, the product **8** was not detected when the latter solvent system was used.
(10) Characterization data on all compounds in this series are available as supplementary material.
(11) This particular cyclization gave, initially, a mixture of several products (TLC; presumably contaminated by nonisomerized spirocyclopentenones, e.g., **8**). This crude mixture was then further treated with LDA in THF/HMPA (10:1) to allow isomerization and, after protonation, yielded **7e** and **10**.
(12) While **8f** gave only **7e** (93%), **7f** yielded **7e** (91%) together with a detectable amount (4%) of **10**. However, the product ratio from this latter reaction is dependent on the reaction conditions and solvent systems employed (for similar observations see the elegant report by: Smith, A. B., III; Levenberg, P. A.; Jerris, P. J.; Scarborough, R. M., Jr.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 1501).
(13) For complete pyrolysis a long heating column (30 in. × 0.5 in. glass column packed with glass chips and wrapped with a heating coil) was used. Numerous reports have appeared on the generation of highly reactive olefins by the retro-Diels–Alder reaction; for the latest review see: Ripoll, J. L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19 (Tetrahedron Report No. 45).
(14) Vacuum pyrolysis of **8g** was also investigated, and it was found that the pyrolysate gave an NMR spectrum very similar to that of **7g**.

On the Reaction of Lithium Diisopropylamide with π-Deficient Heteroaromatics. A Single Electron Transfer Mechanism

Summary: Evidence is presented in support of one-electron transfer as the key step in the reaction of lithium diisopropylamide (LDA) with π-deficient heteroaromatics.

Sir: Since the discovery that pyridine can be coupled with lithium diisopropylamide to afford 2,2′-bipyridine (**1**),[1] this reaction has been utilized in the preparation of various heteroaromatic compounds.[2] Speculation on the mecha-

(1) Clarke, A. J.; McNamara, S.; Meth-Cohn, O. *Tetrahedron Lett.* **1974**, 2373.
(2) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 1.

0022-3263/82/1947-0599$01.25/0