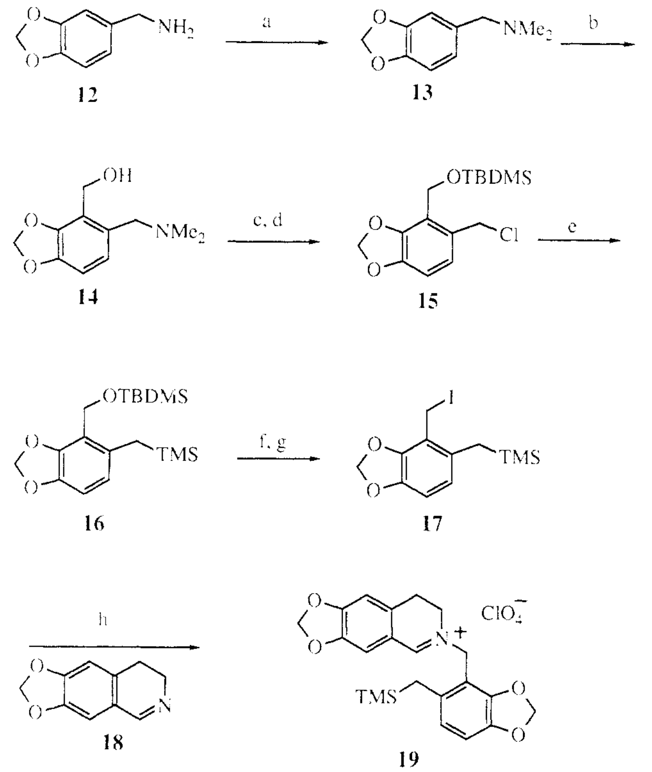
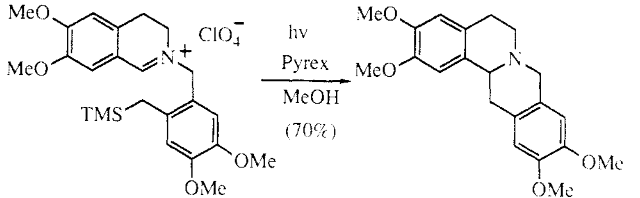
Scheme IV



^{a}(a) HCHO, HCO_2H, 80 °C, 90%; (b) *n*-BuLi, 0 °C, THF/HCHO, −78 °C, 90%; (c) $(i\text{-}Pr)_2EtN$, TBDMSCl, DMF, 98%; (d) $ClCO_2Et$, THF, 25 °C, 99%; (e) Mg, THF, Me_3SiCl, 46%; (f) 1 N H_2SO_4, THF, 25 °C, 93%; (g) I_2, PPh_3, DIPEA, 40%; (h) $AgClO_4$, MeCN, 25 °C, 70%.

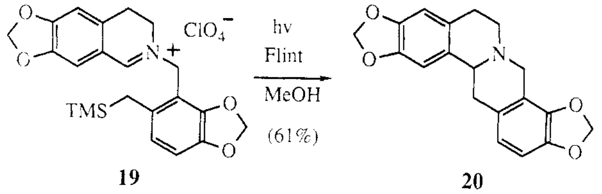
crystalline substance (mp 176–178 °C, MeOH).[13] Irradiation (Pyrex, MeOH) of **10** led to smooth production of (±)-xylopinine (**11**) (mp 154–157 °C, EtOH; lit.[6c] mp 157–158 °C) in a 70% yield. The spectroscopic properties of the synthetic materials matched those previously reported.[6g,14]



10 11

The sequence (Scheme IV) developed for preparation of the benzyl iodide **17** employed in the stylopine synthetic route takes advantage of a procedure described by Rapoport[6g] for C-2 functionalization of (3,4-dialkoxybenzyl)amines. Accordingly, the *N*,*N*-dimethylpiperonylamine **13**, formed by methylation[15] of the commercially available piperonylamine **12**, was converted by *n*-BuLi deprotonation and equilibration to the thermodynamically[16] more stable C-2 anion. Formaldehyde trapping generated the desired C-2 carbinol **14** (mp 89–90 °C, Et_2O). Deamination was then performed subsequent to protection of the hydroxyl function by treatment with $ClCO_2Et$. The benzylic chloride **15** formed in this fashion was converted to the silane **16** via in situ Me_3SiCl trapping of the corresponding Grignard. The alcohol function in **16** was then deprotected and transformed to the benzylic iodide found in the target substrate **17**.

The dihydroisoquinolinium perchlorate **19** needed for the photocyclization process was smoothly formed by silver perchlorate assisted alkylation of the known[11] methylenedioxy-3,4-dihydroisoquinoline **18**. The salt is furnished as a crystalline substance (mp 186–188 °C, $CHCl_3$). Photocyclization occurs upon irradiation of **19** (Flint, MeOH) to produce (±)-stylopine (**20**) (mp 213–215 °C, MeOH, lit.[6a] mp 217–218 °C) which has spectroscopic properties identical with those previously reported.[14]



19 20

The strategy described above for protoberberine alkaloid synthesis appears to rival in overall efficiency those followed in earlier synthetic approaches to this family.[6,7] Our studies focusing on the application of photochemical diradical cyclization methods for natural product synthesis are continuing.

Acknowledgment. Generous support for this research by the NIH (GM-27251) is appreciated. The 400-MHz NMR spectrometer used in this work was purchased with funds provided by the NSF (DMB-84-20175).

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(13) A different sequence employing a Bischler–Napieralski cyclization has been used for synthesis of a salt related to **10**.[6f] We have found that the procedure described here is more efficient.

(14) Shamma, M.; Hindenlang, D. M. *Carbon-13 NMR Shift Assignments of Amines and Alkaloids*; Plenum: New York, 1979.

(15) Pine, S. H.; Sanchez, B. L. *J. Org. Chem.* **1971**, *36*, 829.

(16) Ranade, A. C.; Mall, R. S.; Bhide, S. R.; Metha, S. R. *Synthesis* **1976**, 123.

A Highly Selective Photoinduced Dimerization of Olefins Catalyzed by Alkylcobaloximes

Summary: Olefins having an α-methyl group were dimerized selectively in the presence of alkylcobaloxime as a catalyst under irradiation by a tungsten lamp.

Sir: Considerable attention has been paid to cobaloximes as a model for vitamin B_{12}.[1] The cobalt–carbon bond in alkylcobaloxime is known to cleave homolytically by the irradiation of visible light as in eq 1.[2] To investigate the photoactivated alkylcobaloxime is interesting with respect to the enzymic rearrangement catalyzed by adenosylcobalamin.

$$RCo^{III}(Hdmg)_2B \xrightleftharpoons{h\nu} [R^\bullet + Co^{II}(Hdmg)_2B] \qquad (1)$$

Hdmg, dimethylglyoximato; B, base

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(1) (a) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97. (b) Golding, B. T.; Sell, C. S.; Sellars, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 961. (c) Flohr, H.; Pannhorst, W.; Retey, J. *Helv. Chim. Acta* **1978**, *61*, 1565. (d) Jensen, F. R.; Kiskis, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 5825. (e) Tada, M.; Okabe, M.; Miura, K. *Chem. Lett.* **1978**, 1135.

(2) (a) Jensen, F. R.; Madan, V.; Buchandan, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 5283. (b) Schrauzer, G. N.; Lee, L. P.; Sibelt, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 2997.

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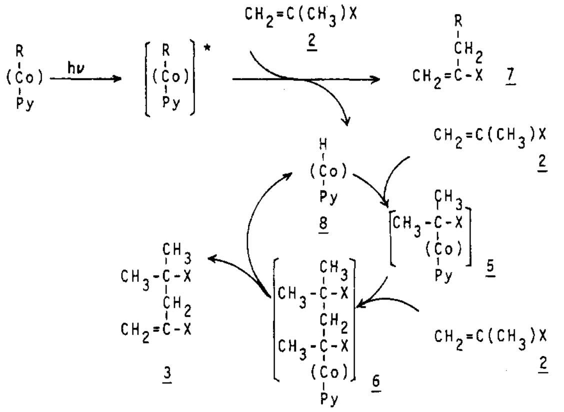
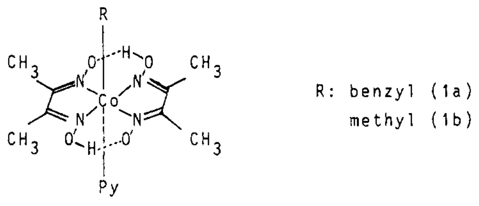
Scheme I. Reaction Pathway of the Dimerization of Olefin Catalyzed by Alkylcobaloxime



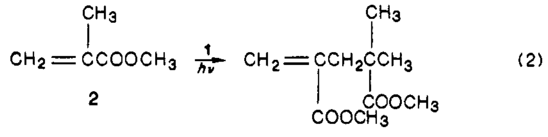
In this paper, we report the first investigation of the reaction between photoactivated alkyl(pyridine)cobaloxime 1, alkylbis(dimethylglyoximato)pyridinecobalt(III), and olefins.



Alkylbis(dimethylglyoximato)
pyridinecobalt(III)

Olefins were irradiated by a tungsten lamp (200 W) in the presence of a catalytic amount of 1 for 48 h at room temperature under an argon atmosphere.

While methyl acrylate gave a polymer, acrylonitrile, styrene, and *n*-butyl vinyl ether were recovered unchanged under the conditions. Methyl methacrylate (2) which has a methyl group α to the carbonyl group dimerized selectively to give dimethyl 2,2-dimethyl-4-methylenepentanedioate (3) (eq 2, Table I). The dimerization did



$$\underset{\mathbf{2}}{CH_2{=}C(CH_3)COOCH_3} \xrightarrow[h\nu]{1} CH_2{=}C(COOCH_3)CH_2C(CH_3)_2COOCH_3 \qquad (2)$$

3

not occur in the dark (run 3), in the absence of an alkylcobaloxime catalyst (run 4), or by the addition of *p*-dinitrobenzene, galvinoxyl, or oxygen (run 5). Thus, the reaction might involve some radical or electron-transfer steps. Further, some olefins which had a methyl group at the α-position such as other methacrylate, methacrylonitrile, and α-methylstyrene dimerized similarly.[3]

Obviously the photoactivated alkylcobaloxime is an active intermediate in the dimerization reaction. The fact that a cobalt hydride complex catalyzes the dimerization of olefins[4] and methacrylonitrile is inserted into the Co–H bond in hydridocobaloxime to give α-cyanoisopropylcobaloxime under neutral conditions[5] suggest the dimerization of α-methyl olefins proceed as in Scheme I.

Table I. Dimerization of Methyl Methacrylate Catalyzed by Alkylcobaloxime under Irradiation[a]

run	catalyst	dimer yield, %	turnover no. of catalyst
1	**1a**	48	4800
2	**1b**	14	1400
3	**1a**[b]	0	0
4	none	0	
5	**1a**[c]	0	0

[a] Conditions: olefin:1 = 100:1, tungsten lamp (200 W), distance from lamp to reaction vessel (15 cm), 48 h, at room temperature, under an argon atmosphere. [b] Dark reaction. [c] Addition of *p*-dinitrobenzene, galvinoxyl, or oxygen.

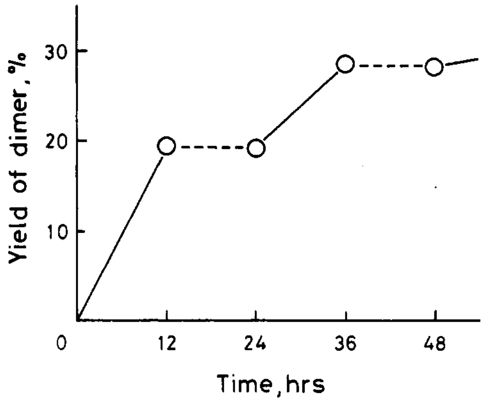


Figure 1. Effect of light on the dimerization of 2 catalyzed by **1a**. Conditions: **1a**:2 = 1:500, 20 ± 1 °C (—) under irradiation with a tungsten lamp (400 W) at a distance of 15 cm; (---) light switch off. Yields were determined by ^{1}H NMR.

At the first stage, the α-methyl olefins are inserted into the cobalt–carbon bond of photoactivated alkylcobaloxime to liberate the olefin 7 and hydridocobaloxime 8 by the β-hydrogen elimination. At the second stage, 2 mol of olefin are inserted successively into the Co–H bond of 8 and the Co–C bond of 5 to generate the complex 6, which liberate the product 3 and hydridocobaloxime, an active catalyst for the reaction, by β-elimination of hydrogen.

In order for the reaction to be proceeded, irradiation must be continuously carried out. That the irradiation is required not only for initiation stage is learned by switching off the light source which stopped the reaction progress as shown in Figure 1. The reaction intermediate 7 was identified by GC–MS. Furthermore, the hydridocobaloxime prepared by the reported method[5] was found to catalyze the dimerization of methyl methacrylate under the same irradiation conditions.[6]

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[3] The yield of the dimers: diethyl 2,2-dimethyl-4-methylenepentanedioate (54%), diallyl 2,2-dimethyl-4-methylenepentanedioate (38%), 2,2-dimethyl-4-methylenepentanedinitrile (15%), 4-methyl-2,4-diphenylpent-1-ene (5%).

[4] Pu, L. S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1968**, *90*, 7170.

[5] Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 1999.

[6] Cobalt acetate and dimethylglyoxime were dissolved in methanol, and the solvent was evaporated after the addition of pyridine. Methyl methacrylate (20 mmol) was added to the complex (0.2 mmol), and the mixture was degassed and replaced with hydrogen. The reaction was carried out by irradiation with a tungsten lamp (200 W) for 24 h to give the corresponding dimer (22%).