4-Spiro[cyclopropanecholestan-3β-ol] (9). A solution of 51 mg (0.12 mmol) of **14** and 25 mg (0.68 mmol) of $NaBH_4$ in 25 mL of methanol was stirred at room temperature for 1 h. Concentration in vacuo and an ether workup afforded 50 mg of white solid. Preparative TLC (2:1 hexane–ether) gave 48 mg (94%) of **9** and recrystallization from methanol gave 39 mg (76%) of pure **9** as silky needles: mp 173–174 °C; IR 3400 cm^{-1}; NMR δ 0.68 (s, 3, H_3C_{18}–), 0.84 (s, 3, H_3C_{19}–), and 3.5–3.9 ppm (bm, $3\alpha H^{25}$); M^+ *m/e* 414.3955 (calcd for $C_{29}H_{50}O$, 414.3861).

Anal. Calcd for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found: C, 84.08; H, 12.10.

Acknowledgment. This research was generously supported by USPHS Research Grant AM 12855. The use of **9** as an enzymic substrate was suggested originally by Dr. D. J. Hupe.

Registry No.—**9**, 62742-97-6; **10**, 601-57-0; **11**, 601-55-8; **12**, 566-91-6; **13**, 62742-98-7; **14**, 62742-99-8; **17** Me_3Si ether, 62743-00-4; **18**, 38367-88-3; **19**, 62743-01-5; **20**, 62743-02-6; **21**, 62743-03-7; **22**, 62743-04-8; **23**, 62743-05-9; **24**, 62743-06-0; ethylene glycol, 107-21-1.

References and Notes

(1) K. B. Sharpless, T. E. Snyder, T. A. Spencer, K. K. Maheshwari, G. Guhn, and R. B. Clayton, *J. Am. Chem. Soc.*, **90**, 6874 (1968).
(2) K. B. Sharpless, T. E. Snyder, T. A. Spencer, K. K. Maheshwari, J. A. Nelson, and R. B. Clayton, *J. Am. Chem. Soc.*, **91**, 3394 (1969).
(3) J. A. Nelson, S. Kahn, T. A. Spencer, K. B. Sharpless, and R. B. Clayton, *Bioorg. Chem.*, **4**, 363 (1975).
(4) R. Rahman, K. B. Sharpless, T. A. Spencer, and R. B. Clayton, *J. Biol. Chem.*, **245**, 2667 (1970).
(5) G. A. Youngdale, U.S. Patent 3 793 308; *Chem. Abstr.*, **80**, 108756s (1974); cf. M. S. Newman, V. DeVries, and R. Darlak, *J. Org. Chem.*, **31**, 2171 (1966).
(6) G. F. H. Green and A. G. Long, *J. Chem. Soc.*, 2532 (1961).
(7) K. Florey and A. R. Restivo, *J. Org. Chem.*, **22**, 406 (1957); cf. J. W. Huffman, *ibid.*, **41**, 3847 (1976).
(8) H.-G. Lehmann, H. Müller, and R. Weichert, *Chem. Ber.*, **98**, 1470 (1965), have prepared steroidal spirocyclopropyl ketones by this method.
(9) G. Stork and J. d'Angelo, *J. Am. Chem. Soc.*, **96**, 7114 (1974).
(10) M. R. Czarny, K. K. Maheshwari, J. A. Nelson, and T. A. Spencer, *J. Org. Chem.*, **40**, 2079 (1975).
(11) D. Caine, *Org. React.*, **23**, 1 (1976), especially pp 18–20 and 192. The stereochemistry shown in **17** was assigned by P. Bladon, J. W. Cornforth, and R. H. Jaeger, *J. Chem. Soc.*, 863 (1958).
(12) Z. G. Hajos and D. R. Parrish, *J. Org. Chem.*, **38**, 3244 (1973); R. A. Micheli, Z. G. Hajos, N. Cohen, D. R. Parrish, L. A. Portland, W. Sciamanna, M. A. Scott, and P. A. Wehrli, *ibid.*, **40**, 675 (1975).
(13) N. A. Nelson and R. N. Schut, *J. Am. Chem. Soc.*, **80**, 6630 (1958).
(14) H. L. Finkbeiner and G. W. Wagner, *J. Org. Chem.*, **28**, 215 (1963).
(15) Hajos et al., ref 12, have utilized the β-keto acids resulting from such carboxylations in an efficient synthesis of α-methylene ketones involving treatment with piperidine hydrochloride and formaldehyde. This method was not tried in the present work because of the possibility of decarboxylation during reduction of the double bond in the β-keto acid formed from **11**.
(16) Cf. P. A. Grieco, M. Nishizawa, S. D. Burke, and N. Marinovic, *J. Am. Chem. Soc.*, **98**, 1612 (1976).
(17) U. Mende, B. Radüchel, W. Skuballa, and H. Vorbruggen, *Tetrahedron Lett.*, 629 (1975).
(18) H. R. Nace and R. N. Iacona, *J. Org. Chem.*, **29**, 3498 (1964).
(19) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field", Holden-Day, San Francisco, Calif., 1964, p 124.
(20) Prepared from EXR-101 according to J. A. Moore and D. E. Reed, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 351.
(21) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
(22) Aldrich Chemical Co., Inc., Milwaukee, Wis.
(23) Prepared by the method of N. W. Atwater, *J. Am. Chem. Soc.*, **82**, 2847 (1960).
(24) Ventron Corp., Danvers, Mass.
(25) The broad multiplet is characteristic of an axial 3αH, as opposed to an equatorial 3βH, which shows a much narrower NMR signal: cf. ref 10; ref 19, p 77; and L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Oxford, 1969, p 228.

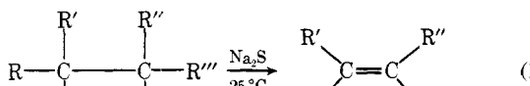
Communications

The Synthesis of Functionalized Tetrasubstituted Olefins. Calcium Amalgam—a Novel Reducing Agent

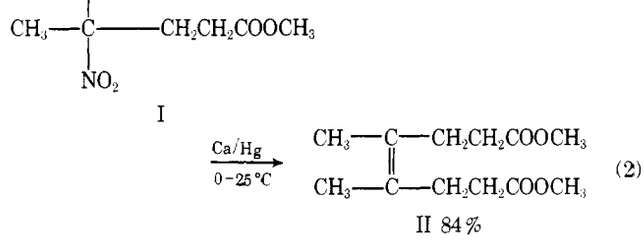
Summary: A general synthesis of symmetrical and unsymmetrical functionalized tetrasubstituted olefins is described.

Sir: In 1971 a synthesis of tetrasubstituted olefins was described which is noteworthy for its simplicity and which gives pure symmetrical and unsymmetrical olefins in high yields.[1] Since then several other very useful procedures for the synthesis of tetrasubstituted olefins have been reported.[2-7] However, except for two methyl ethers, none of the olefins prepared by these procedures contains a functional group. We now describe a simple method for the synthesis of symmetrical and unsymmetrical tetrasubstituted olefins bearing cyano, keto, ester, and ether groups. A further point of interest is the use of a novel reducing agent—calcium amalgam.

In our earlier olefin synthesis[1] vicinal dinitro compounds were treated with sodium sulfide (or sodium thiophenoxide), eq 1. Attempts to extend the reaction of eq 1 to the synthesis of functionalized olefins soon revealed that neither sodium sulfide, nor sodium thiophenoxide, was likely to prove satisfactory.[8] In contrast, amalgamated calcium, which is readily available and inexpensive,[9] is effective in bringing about elimination of vicinal nitro groups without attacking other functions. Equation 2 is illustrative.



(1)

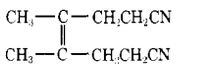
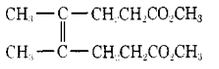
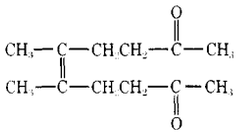
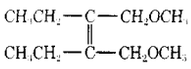
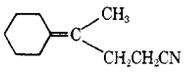
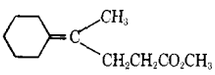
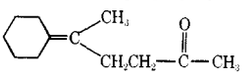
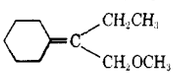
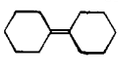


(2)

Table I lists the olefins obtained from vicinal dinitro compounds by the action of calcium amalgam. It should be noted that yields refer to pure, isolated, products which, when the possibility exists, contain both the cis and trans forms. Also, the yields of unsymmetrical olefins are lower than for the symmetrical compounds because the unsymmetrical dinitro compounds employed were not fully purified.

The general procedure is illustrated by the preparation of nitro ester (I) and its conversion to the olefin (II). Lithium methoxide (1.52 g, 40 mmol) in 40 mL of DMF is allowed to

Table I. Olefins Synthesized from Vicinal Dinitro Compounds

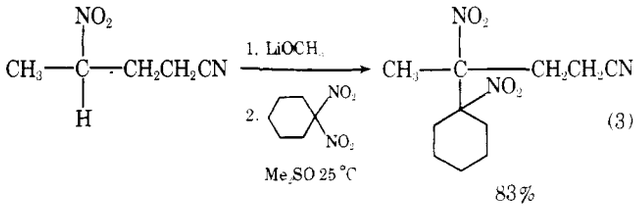
Olefin	% yield
	87
	84
	77
	78
	71
	66
	68
	65
	86

react for 15 min at room temperature with 6.44 g (40 mmol) of methyl 4-nitropentanoate.[10] The resulting solution is cooled to 0 °C, 5.08 g (20 mmol) of I_2 in 30 mL of cold DMF is added in the course of ca. 15 min, and the system is then brought to room temperature and held there for 2 h; stirring and a nitrogen atmosphere are maintained throughout. The reaction product is poured into 600 mL of water and repeatedly extracted with benzene–ether (1:1). The extracts are washed with water and dried, and the solvents removed under reduced pressure. The resulting pale yellow, viscous, residue (6.44 g) crystallizes on standing overnight; mp 51–77 °C. Recrystallization from methanol at −5 °C gives 5.38 g (84% yield) of colorless crystals, mp 71–84 °C. This is analytically pure I;[11] its NMR spectrum, ($CDCl_3$) δ 1.60 and 1.65 (2s, 6 H), 2.0–2.90 (m, 8 H), 3.70 (s, 6 H), is consonant with the view that it consists of roughly equal proportions of the *dl* and meso forms.

A mixture consisting of 0.64 g (16 mmol) of calcium shot[9] and 10 mL of hexamethylphosphoramide (HMPA) is stirred vigorously under argon and then a solution of mercuric chloride (1.35 g, 5 mmol) in 2 mL of DMF and 10 mL of HMPA is added rapidly. The temperature rises to ca. 40–50 °C, but soon drops back and the initially formed grey mixture, after 30 min, becomes black. The reaction flask is cooled in ice for 15 min and then the dinitro compound I (3.20 g, 10 mmol) is added without opening the system. After 1.5 h the ice bath is removed and the reaction is allowed to proceed at room temperature; TLC monitoring reveals that it is complete in 45 h. (With keto compounds the reduction is conducted entirely at 0 °C.)

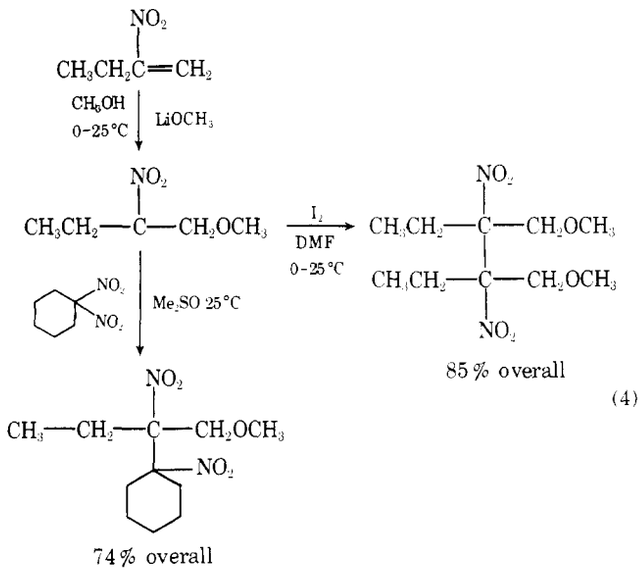
The reaction mixture is poured into ice–water and extracted with ether–benzene (1:1). The extracts are washed with ice–water and dried, and the solvents are removed under reduced pressure. The residue (1.94 g) on short-path distillation [bath 70 °C (0.15 mm)] gave 1.92 g (84% yield) of analytically pure II[11] as a mixture of a colorless oil and white crystals which melt from 48 to 54 °C. That this consists of the cis and trans isomers of dimethyl 4,5-dimethyl-4-octenedioate is clear from the elemental analysis and the NMR and IR spectra.

The requisite unsymmetrical vicinal dinitro compounds are readily obtained by treating a nitroparaffin salt with an α,α-dinitro compound,[1] e.g., as in eq 3.



(3)

The precursors of the ether functionalized olefins were prepared from 2-nitro-1-butene (eq 4).[12]



(4)

This synthesis of functionalized olefins involves the reductive elimination of nitro groups. Its success appears to derive from the fact that of all the common functional groups the nitro group is most readily induced to accept one electron;[13,14] this, coupled with the use of a mild reducing agent, provides the observed selectivity.

Acknowledgment. We thank the Hoffmann-La Roche Co. and the National Science Foundation for generous support. We are also indebted to Drs. Melvin M. Kestner and Harold W. Pinnick for assistance in the preliminary stages of this investigation.

References and Notes

(1) N. Kornblum, S. D. Boyd, H. W. Pinnick, and R. G. Smith, *J. Am. Chem. Soc.*, **93**, 4316 (1971).
(2) M. Julia and J. M. Paris, *Tetrahedron Lett.*, 4833 (1973).
(3) A. P. Krapcho and E. G. E. Jahngen, *J. Org. Chem.*, **39**, 1650 (1974).
(4) G. H. Posner, G. L. Loomis, and H. S. Sawaya, *Tetrahedron Lett.*, 1373 (1975).
(5) S. Hara, H. Taguchi, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 1545 (1975).
(6) J. E. McMurray and L. R. Krepski, *J. Org. Chem.*, **41**, 3929 (1976), and references cited therein.
(7) W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **15**, 161 (1976).
(8) We shall discuss this matter in the full paper.
(9) Calcium shot, 99+%, 6-mesh is obtainable from Research Organic/Inorganic Chemical Corp., 507 Main Street, Bellville, N.J. 07109.
(10) From the Michael condensation of methyl acrylate with nitroethane.
(11) Satisfactory elementary analyses, as well as NMR and IR spectra, were obtained for all new compounds.
(12) A. T. Blomquist and T. H. Shelley, *J. Am. Chem. Soc.*, **70**, 147 (1948).
(13) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963); R. C. Kerber, G. W. Urry and N. Kornblum, *J. Am. Chem. Soc.*, **87**, 4525 (1965), footnote 25.
(14) For a review of electron transfer processes see N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).

Nathan Kornblum,* Leung Cheng
Purdue University, Department of Chemistry
West Lafayette, Indiana 47907

Received May 7, 1977