(6) The dimethylhydrazones of certain epoxy ketones, e.g., **14**, are unstable, and are best prepared at about −35 °C over several hours using only 0.1 equiv of propionic acid.
(7) NMR spectra were taken in carbon tetrachloride.
(8) Small amounts (usually <10%) of the unalkylated enone were also obtained in these reactions. The mechanism of this reduction is not clear; see A. A. Ponaras, Ph.D. Dissertation, Columbia University, New York, N.Y. 1972.
(9) Cf. M. Avaro, J. Levisalles, and H. Rudler, *J. Chem. Soc., Chem. Commun.*, 445 (1969). We were unable to effect hydrolysis of the dimethylhydrazone group using the published reaction conditions. For other possible cleavage methods, see J. R. Maynez, *J. Org. Chem.*, **40**, 3302 (1975); J. E. McMurry, *ibid.*, **40**, 1502 (1975); and, especially, E. J. Corey and D. Enders, *Tetrahedron Lett.*, 3 (1976).
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(11) Identical with an authentic sample prepared by the method of G. Stork and J. Ben Aim, *J. Am. Chem. Soc.*, **93**, 5938 (1971).
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(19) Obtained as a low-melting solid via (1) reduction of *trans*-10-methyl-Δ^3-2-octalone with aluminum hydride to the β-alcohol, (2) epoxidation[20] with 3-chloroperbenzoic acid in chloroform to give a 2:1 mixture of β and α epoxides, (3) Jones oxidation, (4) chromatography.
(20) Cf. H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957); J. W. Bird and D. G. M. Diaper, *Can. J. Chem.*, **47**, 145 (1969).
(21) This method of making β-hydroxy ketones appears to be quite general (A. A. Ponaras, unpublished observations). For another use of oximes of epoxy ketones in an alkylation sequence closely related to our own work, see E. J. Corey, L. S. Melvin, Jr., and M. F. Haslanger, *Tetrahedron Lett.*, 3117 (1975).
(22) The stereochemistry shown in **18** is based on the presence of two separated singlets for the *gem*-dimethyl group at δ 1.00 and 1.11, corresponding to the equatorial and axial methyls of (essentially) a single chair conformation. In contrast, the *gem*-dimethyls of **16** appear as a six-proton singlet at δ 1.05, representing the average of two conformations of very close energy.
(23) For instance, acid-catalyzed opening of certain epoxyhydrazones in protic media is clearly nonconcerted: inter alia, B. Ellis, S. P. Hall, and S. Waddington-Feather, *J. Chem. Soc.*, 4111 (1961).
(24) Introduction of a phenyl substituent on the α carbon of an α,β-unsaturated ketone can also be achieved via reaction of arylcopper reagents with the tosylhydrazones of α,β-epoxy ketones: P. L. Fuchs, *J. Org. Chem.*, preceding paper in this issue.

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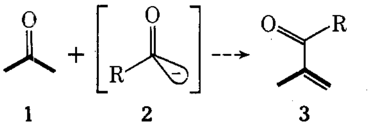
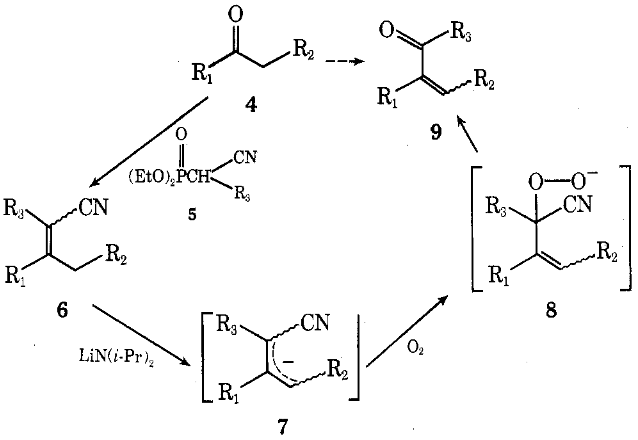
A Synthesis of α,β-Unsaturated Ketones from α,β-Unsaturated Nitriles

Summary: An effective sequence for the synthesis of α,β-unsaturated ketones involves (1) the Horner–Emmons modification of the Wittig reaction to synthesize α,β-unsaturated nitriles, $R_2CH_2(R_1)C{=}C(R_3)CN$, from carbonyl compounds, $R_2CH_2COR_1$, and (2) the oxidative decyanation of the α,β-unsaturated nitriles to afford α,β-unsaturated ketones, $R_2CH{=}C(R_1)COR_3$, by sequential treatment with lithium diisopropylamide, oxygen gas, sodium sulfite, and sodium hydroxide.

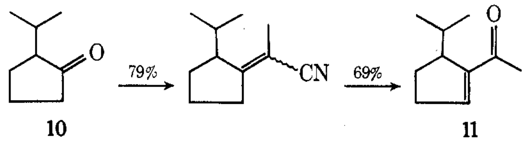
Sir: The condensation–dehydration reaction of a carbonyl compound **1** with an acyl carbanion equivalent **2** would provide an α,β-unsaturated ketone **3** in which the carbonyl carbon of **1** was incorporated as the α carbon of **3**. We required methodology of this type in order to effect the homologation of 17-keto steroids to 20-keto-Δ^{16} steroids.[1] Unfortunately, the classic Rupe rearrangement[2] of 17β-hydroxy-17α-ethynyl steroids derived from 17-keto steroids fails to effect the desired transformation.[3] We now wish to report that the oxidative decyanation[4] of α,β-unsaturated nitriles provides a convenient synthesis of certain α,β-unsaturated ketones including 20-keto-Δ^{16} steroids. In this case, the nitrile group serves as the masked carbonyl group in the acyl carbanion equivalent.[5]



The Horner–Emmons modification of the Wittig reaction[6] of aldehydes **4** (R_1 = H) and ketones **4** with the anions of substituted diethyl phosphonoacetonitriles **5** furnishes α,β-unsaturated nitriles **6** in excellent yield. The reaction of **6** with lithium diisopropylamide in 20% HMPA–THF[7] results in the abstraction of a γ hydrogen from a methylene site to afford the delocalized anion **7**. The introduction of dry oxygen gas results in the regioselective trapping of **7** at the α carbon to produce the hydroperoxide **8**. Reduction of **8** with aqueous sodium sulfite and exposure of the cyanohydrin to sodium hydroxide affords the α,β-unsaturated ketone **9** in good yield (Table I).



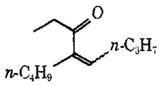
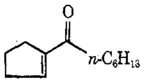
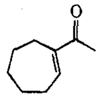
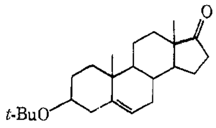
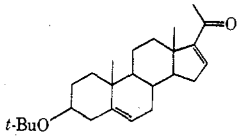
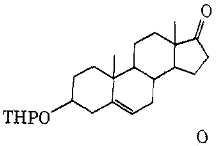
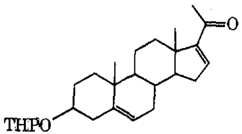
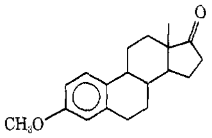
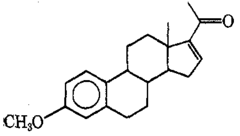
In exploring the scope of this oxidative decyanation procedure, we have found that the reaction is well suited for the synthesis of α,β-unsaturated ketones but not α,β-unsaturated aldehydes. In addition, the reaction is limited to the synthesis of α,β-unsaturated ketones **9** which possess only one nonhydrogen β substituent.[8] This apparent limitation can be turned to some advantage, however, in the synthesis of α,β-unsaturated ketones **9** derived from unsymmetrical ketones **4**. For example, 2-isopropylcyclopentanone (**10**) furnished **11** which



is not otherwise readily accessible. In cases where the yields of **9** were disappointing, we found that a fraction of **6** had been diverted to the production of γ-hydroxy-α,β-unsaturated nitriles. Although the regioselectivity of oxygen trapping at the α or γ sites in **7** varies with structure in a way that is not clearly understood, the oxidative decyanation of α,β-unsaturated nitriles **6** provides a viable solution to the synthesis of an array of α,β-unsaturated ketones **9**.[9]

The following is a typical experimental procedure. To 131 mg (1.3 mmol, 1.3 equiv) of diisopropylamine in 2.0 ml of anhydrous THF under a nitrogen atmosphere at −78 °C was added 0.44 ml of 3.00 M *n*-butyllithium in hexane. To the lithium diisopropylamide solution was added 409 mg (1.0 mmol) of the tetrahydropyranyl ether of 3β-hydroxypregna-5,17(20)-diene-20-carbonitrile in 2.5 ml of 40% HMPA–THF. Oxygen gas was bubbled (250 ml/min) into the solution for 30 min. The reaction was quenched with 2 ml of 1 M sodium sulfite solution, stirred for 1 h at 25 °C, diluted with 25 ml of 20% dichloromethane–ether, washed with 25 ml of 1 M sodium hydroxide solution

Table I. Synthesis of α,β-Unsaturated Ketones 9

Starting material 4	R_3 in phosphonate 5	Isolated yields, % 6	9	Product
$CH_3(CH_2)_5CHO$	n-C_6H_{13}	73	62	(*E*)- and (*Z*)-8-tetradecen-7-one
$(n$-$C_4H_9)_2C{=}O$	CH_2CH_3	81	44	
Cyclopentanone	n-C_6H_{13}	94	57	
Cyclohexanone	H	74	0	1-Cyclohexene-1-carboxaldehyde
	i-C_3H_7	88	45	1-Isobutyryl-1-cyclohexene
Cycloheptanone	CH_3	89	57	
	CH_2CH_3	90	70	
	i-C_3H_7	35	55	
	n-C_6H_{13}	96	72	
Cyclooctanone	CH_3	82	74	(*E*)-1-Acetyl-1-cyclooctene
Cyclododecanone	CH_3	92	81	1:1 (*E*)- and (*Z*)-1-acetyl-1-cyclododecene
	CH_3	74	74	
	CH_3	77	72	
	CH_3	62	78	

and 25 ml of brine, and dried over anhydrous magnesium sulfate. The product was chromatographed on Merck silica gel F254 in 1:1 ether–hexane to afford 301 mg (76%) of the tetrahydropyranyl ether of 3β-hydroxypregna-5,16-dien-20-one having melting point and spectral data in accord with literature values.[10]

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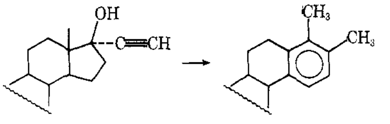

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(5) For an alternative approach to **3** using 1,3-dithianes as the acyl carbanion equivalent, see D. Seebach, M. Kolb, and B.-T. Gröbel, *Tetrahedron Lett.*, 3171 (1974).

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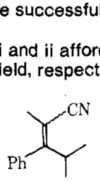
(7) Unlike the oxidative decyanation of secondary nitriles (ref 4), HMPA was required for the successful oxidation decyanation of α,β-unsaturated nitriles.

(8) For example, i and ii afford the corresponding α,β-unsaturated ketones in 0 and 6% yield, respectively.



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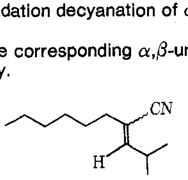

ii

(9) All compounds had ir, NMR, and mass spectral data in accord with assigned structures.

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Reaction of β-Ketosilanes with Alkyllithium. A Stereoselective Synthesis of Trisubstituted Ethylenes

Summary: Reaction of β-ketosilanes with alkyllithium reagents afforded predominantly one diastereoisomer of possible two β-hydroxysilanes, which gave trisubstituted ethylenes stereoselectively by acidic or basic workup.

Sir: Recent progress in organic synthesis via silicon compounds has disclosed novel procedures for the synthesis of 1,2-disubstituted ethylenes with rigorous stereochemistry.[1-7] We describe herein a novel procedure for the stereoselective synthesis of trisubstituted ethylenes via reaction of β-ketosilanes with alkyllithium reagents followed by syn-elimination under basic conditions or by anti-elimination on acid treatment.[8,9]

Treatment of 5-trimethylsilyl-4-decanone (Ia)[10] with methyllithium at −78 °C afforded a reaction mixture containing IIa[11] whose corresponding alcohol was obtained in 80% yield by hydrolytic workup. Treatment of the reaction mixture with potassium *tert*-butoxide afforded (*E*)-4-methyl-4-decene (IIIa)[12] in 74% overall yield (stereoselectivity 91%). When the reaction mixture was treated with glacial acetic acid saturated