Three-dimensional X-ray diffraction data were collected using a Picker automated diffractometer with Mo Kα radiation. The cell has dimensions $a = 12.886$, $b = 16.462$, $c = 13.643$ Å and contains eight molecules. The systematic absence of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd indicates the space group Pbca. The positions of the zinc atoms were determined from a sharpened Patterson synthesis, and the other atoms were found in a series of Fourier syntheses. The structure has been refined by full-matrix least squares to a value of $R = 0.09$. The refinement is being continued and the final results will be published later.

Although the crystals are not isomorphous with the copper compound ($a = 9.158$, $b = 14.000$, $c = 11.285$ Å, $z = 4$, space group $P2_12_12_1$), the compounds are chemically isostructural. The zinc ion is surrounded by five nitrogen atoms from the tren molecule and one thiocyanate ion, in a slightly distorted trigonal bipyramid, with the tertiary nitrogen atom, N(1), and the thiocyanate nitrogen atom, N(5), at the apices, and the three primary nitrogen atoms, N(2), N(3), N(4), in the equatorial positions. Bond lengths and angles in the coordination polyhedron are given in Table I.

Table I. Bond Lengths (Å) and Angles (Degrees)

Zn-N(1)	2.27	N(1)-Zn-N(2)	81
Zn-N(2)	2.07	N(1)-Zn-N(3)	81
Zn-N(3)	2.06	N(1)-Zn-N(4)	81
Zn-N(4)	2.07	N(5)-Zn-N(2)	96
Zn-N(5)	2.03	N(5)-Zn-N(3)	99
		N(5)-Zn-N(4)	102
		N(1)-Zn-N(5)	176
		N(2)-Zn-N(3)	119
		N(2)-Zn-N(4)	118
		N(3)-Zn-N(4)	117

The closest approaches of the second thiocyanate ions to the zinc ion give Zn-N(6) of 3.77 Å and Zn-S(2) of 3.95 Å. Thus the second thiocyanate ion is clearly not coordinated to the zinc ion.

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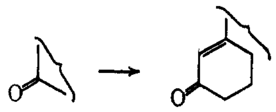
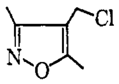
Bis Annelation with 6-Vinyl-2-picoline

Sir:

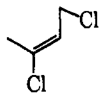
Several methods have been applied to the problem of elaborating a cyclohexenone ring around a carbonyl group and its adjacent carbon atom, as generalized by the transformation I → II. The most commonly used approach involves a four-carbon unit possessing electrophilic character at C_1, an actual or latent ketonic function at C_3, and, thus, nucleophilic capability at C_4. These requirements are, in principle, met by the well-known compound methyl vinyl ketone (MVK). In addition, a series of MVK equivalents,[1] III–VII, has been used to meet various structural challenges.



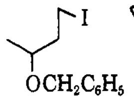
I II



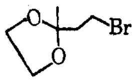
VII



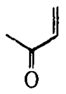
VI



V



IV



III

The problem which stimulated this research is the construction of a 3-ketohexalin ring system about a carbonyl group and its adjacent carbon atom, as illustrated by the transformation I → VIII. If such a transformation could be achieved, with provision for the stereospecific introduction of an angular methyl group and stereospecific saturation of the double bonds, the implements for the total synthesis of naturally occurring nonaromatic steroids would be in hand.[2,3] In the absence of these additional controls, the transformation is of immediate relevance to the synthesis of the physiologically important unsaturated 19-norsteroids.[4]

In principle, the projected transformation I → VIII can be achieved through successive annelations, *i.e.*, I → II followed by II → VIII[5] *via* some combination of the reagents III–VII. We were, however, tempted to explore the feasibility of utilizing the readily available[6] compound, 6-vinyl-2-picoline (IX), as an eight-carbon fragment which would achieve the desired transformation with an economy of synthetic operations. We report here some preliminary findings which augur well for the use of this compound as a bis annelating agent. The process is demonstrated by the conversion of cyclohexanone to the tricyclic dienone XVI.

Reaction of the pyrrolidine enamine of cyclohexanone with IX gave the picolylethylated ketone[7] X (54% yield) which was smoothly converted[8] to the ketal XI. Compound XI was subjected to the following sequence of reactions: (a) $Na-NH_3-EtOH-Et_2O$, (b) $NaOH-H_2O-MeOH$, (c) H^+-H_2O, (d) TsOH-HoAc. At the end of this sequence, the tricyclic dienone XVI was obtained in 40% yield (after molecular distillation). The structure assignment follows from its infrared

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(1) For a critical review on the use of MVK equivalents see G. Stork, *Pure Appl. Chem.*, **9**, 131 (1964). For subsequent publications on some of these reagents see G. Stork, S. Danishefsky, and M. Ohashi, *J. Am. Chem. Soc.*, **89**, 5459 (1967); J. A. Marshall and D. J. Schoeffer, *J. Org. Chem.*, **30**, 3642 (1965).

(2) Recently Stork and McMurry published an extraordinarily elegant bis annelation procedure which did indeed provide for the stereospecific introduction of a 19β-methyl group and 9β-, 10α-, and 14α-hydrogen atoms in converting the Wieland Miescher ketone to *dl*-D-homotestosterone. See G. Stork and J. E. McMurry, *J. Am. Chem. Soc.*, **89**, 5465 (1967).

(3) For comprehensive reviews of steroid total synthesis see I. V. Torgov, *Pure Appl. Chem.*, **6**, 525 (1963); L. Velluz, J. Valls, and G. Nomine, *Angew. Chem. Intern. Ed. Engl.*, **4**, 181 (1965).

(4) For a review of the synthetic approaches to this class of compounds see T. Windholz and M. Windholz, *ibid.*, **3**, 353 (1964).

(5) The transformation II → VIII presumes the presence of at least one γ-hydrogen atom to direct a new alkylation at the α position. In principle our method does not involve this structural condition.

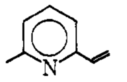
(6) K. S. N. Prasad and R. Raper, *J. Chem. Soc.*, 257 (1957). We wish to thank Dr. Frank Cislak of the Reilly Tar and Chemical Corp. for providing us with generous supplies of this compound.

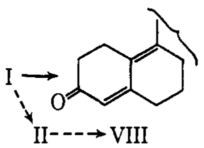
(7) *Cf.* G. Singerman and S. Danishefsky, *Tetrahedron Letters*, 2249 (1964).

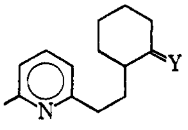
(8) *Cf.* S. Danishefsky and M. Feldman, *ibid.*, 1131 (1965).

[$\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.04, 6.18, and 6.29 (sh) μ], ultraviolet [$\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 304 mμ (ϵ 15,500)], nmr [τ (CCl_4) 4.49 (1 H, singlet), 7.05–8.91 (17, complex)], and mass (parent at *m/e* 202) spectra.[9]

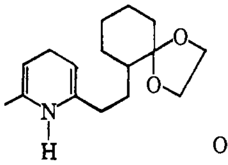
When the sequence was interrupted after step c, the enedione XV was obtained in 42% yield (after silicic acid chromatography). The structural assignment of this compound is consistent with its infrared [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.85, 5.99, and 6.10 μ], ultraviolet [$\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 237 mμ (ϵ 9710), nmr [τ ($CDCl_3$) 4.30 (1 H, singlet), 7.52–8.85 (19 H, complex)], and mass (*m/e* 220) spectra. Treatment of compound XV with 10% TsOH–HoAc at 100° for 15 min gave a near-quantitative yield of XVI.[10] Although the intermediate ketal enone XIV was not isolated or characterized, its presence as the major component upon interruption of the sequence after step b was suggested by analysis of the reaction mixture by combined gas chromatography (5-ft O.V-17 column, 220°, 100 cc/min) and mass spectrometry,[11] wherein the major peak (retention time 4.8 min) had a molecular weight of 264. Similar efforts to identify the presumed progenitors of XIV, the labile 1,4-dihydropyridine XII, and the diketoketal XIII were unrewarding.

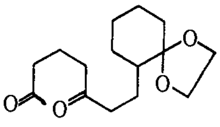

IX

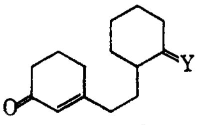



X, Y = O

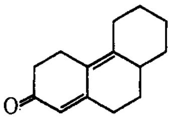
XI, Y =

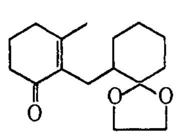

XII


XIII


XIV, Y =

XV, Y = O


XVI


XVII

In a model study, the reduction of 2,6-lutidine was conducted with Na–NH_3–EtOH. Evaporating the ammonia and slurrying the residue with water gave a 72% yield of 2,6-heptanedione,[12] mp 30–33°. Thus the 1,4-dihydropyridine is hydrolyzed with great facility.

The 1,4 reduction of 2,6-dialkylpyridines has been used by Birch[13] as a route to cyclohexenones, albeit in low yield. Our results indicate that Birch's hydrolysis conditions (30% H_2SO_4, 100°, 6 hr) were unduly harsh and that this, rather than the reduction or cyclization steps, was responsible for the low yields obtained.

The predominant cyclization of the presumed intermediate XIII in the desired (in steroidal terms) sense may be due to the avoidance of the serious steric repulsion which arises from cyclization in the alternate sense (*i.e.*, XVII). Studies involving the factors governing the directionality of this type of aldol condensation, as well as the applicability of this bis annelation procedure to more complicated cases, are in progress.

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[9] Although we were unable to crystallize this material, its homogeneity is vouchsafed by its gas chromatographic behavior and by the agreement with theory of the integrated ratio of the lone "vinylic" signal relative to the remaining absorptions in its nmr spectrum. Its ultraviolet spectrum defines the position of the tetrasubstituted double bond.

[10] For previous examples of vinylogous aldol condensations see: A. Eschenmoser, J. Schrieber, and S. A. Julia, *Helv. Chim. Acta*, **36**, 482 (1953); C. Sannie and J. J. Panouse, *Bull. Soc. Chim. France*, 1453 (1956).

[11] This measurement was conducted on a LKB-9000 instrument. We thank Mr. John Nawarol for the mass spectrometric determinations.

[12] C. Harris, *Ber.*, **47**, 784 (1914).

[13] A. J. Birch, *J. Chem. Soc.*, 1270 (1947).

Effect of Water on Photoreduction of Aromatic Ketones by Tertiary Amines[1]

Sir:

We wish to report that photoreduction in aqueous solution of a diaryl ketone by tertiary aliphatic amines proceeds rapidly and cleanly. The reactions lead to high yields of the diarylcarbinol and of the products of oxidative cleavage of the amines, carbonyl compounds and secondary amines (eq 1).

$$\mathrm{Ar,Ar'C{=}O + RCH_2NR'_2 + H_2O \xrightarrow{h\nu} Ar,Ar'CHOH + RCH{=}O + HNR'_2} \quad (1)$$

In the absence of water the photoreduction of benzophenone by primary amines such as 2-butylamine (I) is similar in its high efficiency to that by 2-propanol, and the pinacol and an imine are formed in high yields.[2] Rates of photoreduction by tertiary amines, however, vary with structure of the amine, are increased by dilution with a hydrocarbon, and are generally lower than rates of photoreduction by primary amines.[2] Photoreduction by tertiary amines may not lead to high yields of pinacol and may lead to mixed coupling products.[3,4] A quantitative study of these reactions has been published.[5]

We find that in aqueous solution the primary amine I and the tertiary amine N,N-dimethyl-2-butylamine (II) show high, equal reactivities. Photoreductions, under argon in Pyrex with a high-pressure mercury lamp, of 0.1 *M* 4-benzoylbenzoic acid in 1.5 *M* solutions of I and II in H_2O and in 2.0 *M* solutions of I and II in D_2O all proceeded at the same rate, 1.0×10^{-3} *M* min^{-1}. At the same time photoreduction of benzophenone by neat I, taken as a standard, was twice as fast, 2.0×10^{-3} *M* min^{-1}, and led to benzpinacol. Photoreduction by the aqueous amines led to 4-carboxybenzhydrol in >80% yield. It was identical

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[1] We are pleased to acknowledge generous support of this work by the U. S. Atomic Energy Commission (AT(30-1)2499) and the National Science Foundation (GP-6366).

[2] S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.*, **87**, 2996 (1965); **89**, 3471 (1967).

[3] S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967).

[4] R. S. Davidson, *Chem. Commun.*, 575 (1966).

[5] S. G. Cohen and H. M. Chao, *J. Am. Chem. Soc.*, **90**, 165 (1968).