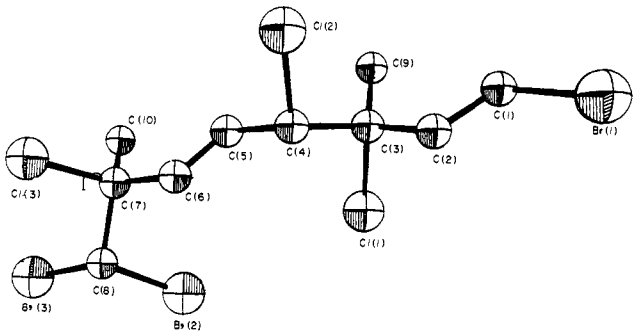

Figure 1. A computer-generated perspective drawing of the title compound.

radiation (0.7107 Å). During the data collection the crystal yellowed and periodically checked standard reflections declined ~10% in intensity. After Lorentz, polarization, and background correction 1091 reflections were judged observed ($F_o \geq 3\sigma(F_o)$). Normalized structure factors were computed in the usual fashion and phase angles were assigned to the 160 E values larger than 1.40 by a multiple solution, weighted tangent formula scheme.[7] The phased three-dimensional E synthesis revealed the six heavy atom positions and the subsequent electron density synthesis revealed the ten remaining carbon atoms. Full-matrix least-squares refinements smoothly converged to an unweighted crystallographic residual of 0.10.[8] At this stage anomalous scattering factor corrections were made for the heavy atoms and refinement continued to weighted residues of 0.081 and 0.077 for the structure and its mirror image, respectively. A computer-generated drawing of the structure with the significantly lower residual is shown in Figure 1.[9] All bond distances and angles agree well with generally accepted values.[10] The molecules are extended with the molecular axis roughly parallel to b. There are no unusually short intermolecular contacts.

As can be seen in the figure the double bonds C-1–C-2 and C-5–C-6 are trans.

The tribromotrichloromonoterpene **1** is the first member of a unique series of monoterpenes containing a vinyl bromide function. A second halogenated monoterpene is currently under investigation. Two sesquiterpenes containing both bromine and chlorine have been isolated from red algae of the genus *Laurencia;*[11] both have subsequently been found in *Aplysia californica* digestive gland extracts. This terpene represents the most highly polyhalogenated naturally occurring substance found to date. It appears that *Aplysia* naturally performs the complex task of concentrating halogen-containing compounds from algae.

(7) (a) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942); (b) J. Karle and H. Hauptmann, *Acta Crystallogr.*, **9**, 635 (1956); (c) P. Main, M. Woolfson, and G. Germain, MULTAN (1972), Department of Physics, University of York, York, England.

(8) W. R, Busing, K. O. Martin, and H. A. Levy, ORFLS, U. S. Atomic Energy Commission Report No. ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(9) (a) C. K. Johnson, ORTEP, U. S. Atomic Energy Commission Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; (b) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(10) O. Kennard and D. G. Watson, "Molecular Structures and Dimensions," Crystallographic Data Centre, Cambridge, England, 1970.

(11) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, **93**, 3774 (1971); *Tetrahedron Lett.*, 195 (1972).

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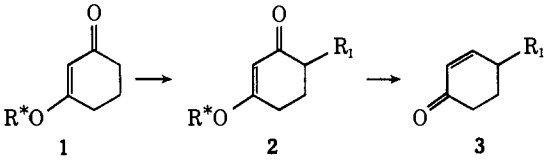
Spiroannelation of Enol Ethers of Cyclic 1,3-Diketones. A Simple Stereospecific Synthesis of β-Vetivone

Sir:

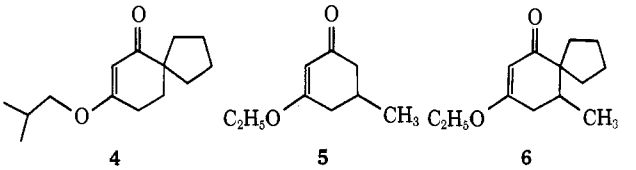
We have reported[1] that enol ethers of 1,3-cyclohexanediones can be alkylated *via* their kinetic enolates (**1** → **2**). The resulting alkylated products can then be



transformed by conventional methods to 4-alkyl-Δ^2-cyclohexenones (**2** → **3**).

We now report on the use of this method for the synthesis of spiroannelated cyclohexenones.

The isobutyl enol ether of 1,3-cyclohexanedione (**1**), R* = isobutyl,[2] was added at ~−60° to a solution of 3 equiv of lithium diisopropylamide in tetrahydrofuran containing 3 equiv of hexamethylphosphoramide. Addition of 2.5 equiv of 1,4-dibromobutane was followed by stirring at room temperature for 48 hr. Work-up then gave after evaporative distillation (90–111° (0.1 mm)) and purification on silica gel (5% ethyl acetate in benzene) the spiroannelated enol ether **4** (*m/e* 222.1589;



nmr δ 5.3 (1 H, s), 3.16 (2 H, d), 1.5–2.0 (11 H), 1.0 ppm (6 H, d)) in about 35% conversion (44% yield).

Similarly, the ethyl enol ether of 5-methyl-1,3-cyclohexanedione (**5**)[3] gave the spiroannelated enol ether **6** (*m/e* 208.1436; ir 6.04, 6.19 μ; nmr δ 0.97 (3 H, d, J = 6 Hz), 5.2 ppm (1 H, s)) in ~36% conversion (50% yield).

The application of this synthesis of 4,4-spiroannelated cyclohexenones to a stereospecific synthesis of β-vetivone[4] (**12**) from **5** demonstrates its usefulness. The

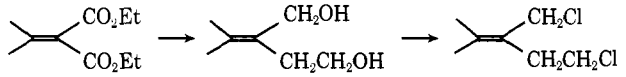
(1) G. Stork and R. L. Danheiser, *J. Org. Chem.*, **38**, 1775 (1973).

(2) J. Panouse and C. Sanie, *Bull. Soc. Chim. Fr.*, 1272 (1956).

(3) J. P. Blanchard and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 5863 (1951).

(4) *Cf.* J. A. Marshall and P. C. Johnson, *J. Org. Chem.*, **35**, 192 (1970), for the structure and first total synthesis of this substance.

alkyl halide **9** required for the spiroannelation of **5** was synthesized from diethylisopropylidene succinate (**7**)[5] by reduction with lithium aluminum ethoxy hydride (~2 mol, ether at room temperature) to the glycol **8** (90% yield, bp 99–107° (0.15–0.2 mm); mp ~35°; *m/e* 130.0973; nmr δ 1.7 (3 H, s), 1.8 (3 H, s, 2.4 (2 H, t), 3.63 (2 H, t), 4.1 (2 H, s), 4.4 ppm (2 H, s)) and conversion of **8** into the corresponding dichloride **9**. This last conversion was, not unexpectedly, difficult (cyclic ether formation). It was finally achieved[6] by slow addition (N_2) of a solution of the dilithium salt of **8** (methyllithium, triphenylmethane indicator, 75:50 ether–hexamethylphosphoramide) into an ether solution (−35–50°) of 2.2 equiv of methanesulfonyl chloride and 7 equiv of lithium chloride. Further addition of hexamethylphosphoramide (final ratio ether–hexamethylphosphoramide 2.2:1), followed by 45 hr at room temperature, gave the required dichloride **9** in 35% yield

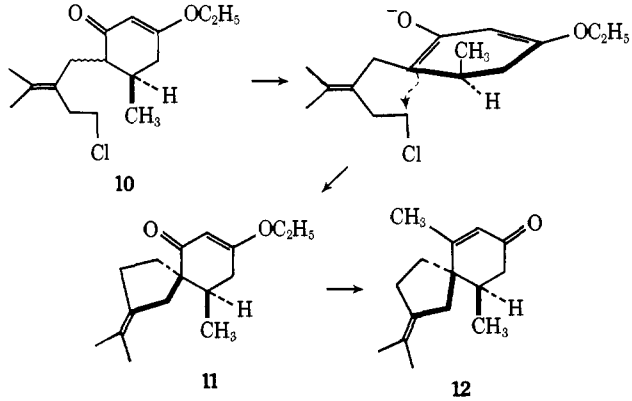


7 8 9

(bp 88–90° (8 mm); nmr δ 4.21 (2 H, s), 3.52 (2 H, t), 2.62 (2 H, t), 1.81 (3 H, s), and 1.76 ppm (3 H, s)).

Spiroannelation of **5** with **9** was carried out by allowing the lithium enolate of **5** (from **5** in tetrahydrofuran containing 1 equiv of hexamethylphosphoramide and 1 equiv of lithium diisopropylamide in tetrahydrofuran at −78°) to react with the dichloride **9** (30% excess) for 13 hr at room temperature. Addition of 2 additional equiv of lithium diisopropylamide, followed by 30 hr at room temperature, gave after chromatography (silica gel, benzene) in ~45% yield the annelated enol ether **11** (one spot on silica gel, 15:85 ethyl acetate–benzene, *m/e* 248.1773; ir 6.01, 6.17 μ; nmr δ 5.25 (1 H, b, $J \sim 2$ Hz), 3.85 (2 H, q), 1.63 (6 H, s (b)), 1.37 (3 H, t), 1.8–2.9 (9 H, m), 0.98 ppm (3 H, d).

The stereochemistry of the spiroannelated enol ether **11** was anticipated to be as shown because the first alkylation would obviously involve the allylic halide to give **10**. The subsequent enolate ion geometry then



forces the ring methyl into an axial conformation[7] and one would expect completion of the ring trans to that methyl. The correctness of this assumption was easily checked by transformation to (±)-β-vetivone (**12**). Addition of methyllithium (1.2 equiv) to **11** in ether at 0°, followed by 12 hr at room temperature and treatment with 1 *N* HCl at room temperature for 3 hr, gave, in ~60% yield after chromatography (silica gel, benzene), (±)-vetivone (**12**), mp 40–44° (lit.[4] mp 43.5–46°), homogeneous on silica gel (15:85 ethyl acetate–benzene). The identity of the substance was established by glc comparison with natural material, by the identity of the infrared, mass, and 220-Hz nmr spectra with those of authentic natural material. In addition, the melting point of the (±)-2,4-dinitrophenylhydrazone of our synthetic material gave no depression with the authentic ± derivative of the same melting point.[8–10]

(5) C. G. Overberger and C. W. Roberts, *J. Amer. Chem. Soc.*, **71**, 3618 (1949).
(6) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Lett.*, 1393 (1969).
(7) F. Johnson and S. K. Malhotra, *J. Amer. Chem. Soc.*, **87**, 5492 (1965).

(8) We wish to thank Professor Marshall for his kindness in providing us with the 2,4-dinitrophenylhydrazone of his synthetic material.
(9) We thank Professor P. M. McCurry, Jr., for making available to us samples of pure natural β-vetivone and for carrying out the glc comparisons of the synthetic and natural materials.
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α-Lactams. IX. Conjugation Effects of the α-Lactam Ring

Sir:

The previously reported ultraviolet absorption maxima of aliphatic α-lactams at 250 nm has been explained by considering a dipolar, delocalized amide type of structure for the excited state.[1] This resonance form of α-lactams is supported by the fact that these compounds have been successfully O-alkylated.[2]

While observing the ultraviolet spectra of C-3 phenyl-substituted α-lactams in pentane solution a new property of this structure was discovered—a bathochromic shift of the primary benzene band which we suggest is due to conjugative interaction of the α-lactam ring with the phenyl ring. 1-*tert*-Butyl-3-phenylaziridinone (**1**)[3] (λ_{max} (pentane) 226 nm (log ε ~4.0)) and 1-*tert*-butyl-3-(*p*-trifluoromethyl)phenylaziridinone (**2**) (λ_{max} (pentane) 237 nm (log ε ~4.0)) exhibit benzene bands considerably shifted from the corresponding absorptions of model ring-opened compounds **3** (λ_{max} (pentane) 207 nm (log ε ~3.9)) and **4** (λ_{max} (pentane) 208 nm (log ε ~3.9)), Figures 1 and 2. This phenomenon is analogous to the well-documented bathochromic shift observed with phenylcyclopropanes where the effect of the ring is intermediate to that of straight chain and olefinic substituents.[4,5] In the present case the absorption of the α-lactam carbonyl at 250 nm could not be distinguished from aromatic absorptions appearing in the same region.

The aziridinones **1** and **2** are prepared using a modification of our general procedure for synthesis of α-

(1) J. C. Sheehan and M. N. Nafissi-V., *J. Amer. Chem. Soc.*, **91**, 1176 (1969).
(2) J. C. Sheehan and M. M. Nafissi-V., *J. Org. Chem.*, **35**, 4246 (1970).
(3) (a) H. E. Baumgarten, R. L. Zey, and U. Krolls, *J. Amer. Chem. Soc.*, **83**, 4469 (1961); (b) H. E. Baumgarten, *et al.*, *ibid.*, **85**, 3303 (1963).
(4) A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964).
(5) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969).