The retention of olefin configuration in the 1,2, 1,3, and 1,4 additions suggests that these reactions are concerted. There is good evidence[3] that 1,3 addition involves the singlet (B_{2u}) state of benzene. It is likely that this state is also involved in 1,2 and 1,4 addition, since the relative (initial) yields of the various adducts remain constant[16] over a wide range of concentrations and proportions of reactants, such that the benzene singlet–triplet ratio would almost certainly vary. From orbital symmetry considerations, however, Bryce-Smith has concluded[6] that concerted 1,2 and 1,4 cycloadditions in which configuration is retained are allowed from excited olefin plus ground-state benzene, or from B_{1u} benzene plus ground-state olefin, but *not* from B_{2u} benzene plus ground-state olefin. If all of these interpretations are correct, an apparently forbidden process does, in fact, occur with at least moderate quantum efficiency.[9] This result can, perhaps, be rationalized by the intervention of an excited complex, formed from $^1B_{2u}$ benzene and ground-state olefin, in which mixing of states[17] results in relaxation of orbital-symmetry restrictions. The formation of such benzene–olefin exciplexes has been previously suggested[18] but not yet proven.

(16) R. Srinivasan (ref 5) has observed similar invariance in the relative yields of 1,3 and 1,4 cycloadducts of benzene and cyclobutene.
(17) M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 6991 (1970).
(18) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 268 (1969).

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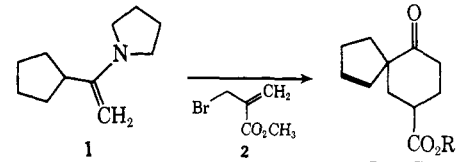
The Synthesis of Spiro Systems by the $\alpha\alpha'$-Annelation Process

Sir:

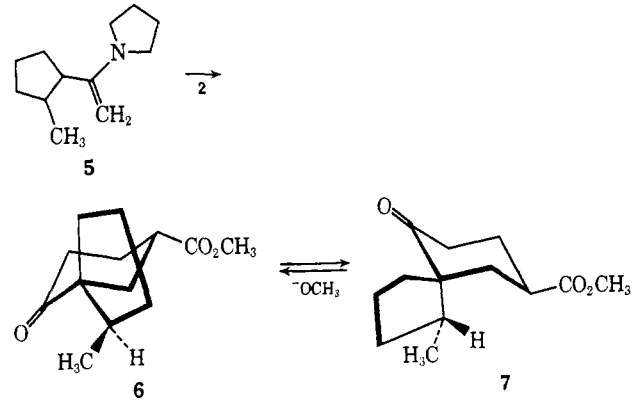
The synthesis of spiro-fused ring systems has usually been accomplished by multistep techniques which often preclude the obtention of structures having diverse functionality.[1] The $\alpha\alpha'$-annelation reaction,[2] which has been used for the synthesis of a variety of bridged bicyclic compounds,[3] may be applied to enamines of certain ketones to afford, in essentially a single step, spiro frameworks having functionality usefully disposed for the conversion to other systems.

Condensation of the pyrrolidine enamine of acetylcyclopentane[4] (**1**) (54% from ketone; bp 76–80° (0.1 mm); ν_{max}^{neat} 2790, 1620, 1385 cm^{-1}) with methyl α-(1-bromomethyl)acrylate[5,6] (**2**) (bp 68–74° (12 mm); $\nu_{max}^{CHCl_3}$ 2940, 1715, 1630, 1175 cm^{-1}) in benzene[7] followed by addition of triethylamine, acetonitrile, and reflux afforded, after aqueous acetic acid hydrolysis, a

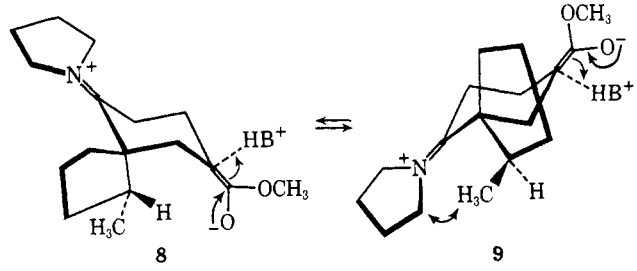


78% yield of methyl spiro[4:5]decan-1-one-4-carboxylate[6] (**3**) (bp 130–135° (0.25 mm); ν^{CHCl_3} 2960, 1730, 1710, 1440, 1175 cm^{-1}; $\tau_{ppm}^{CDCl_3}$ 6.32 (3 H, s), 7.0–8.50 (envelope)). The corresponding acid **4** (mp 102–103°; ν^{CDCl_3} 2960 (b), 1730 cm^{-1}; τ 5.33 (2 H, s), 7.20–8.80 (envelope)) was produced by basic hydrolysis.

In a similar fashion, reaction of **2** with the pyrrolidine enamine of 1-acetyl-2-methylcyclopentane[8] (**5**) produced a 78% yield of a *single isomer* of methyl 6-methylspiro[4:5]decan-1-one-4-carboxylate (bp 110–112° (0.2 mm); ν^{CHCl_3} 1735, 1710 cm^{-1}; $\tau_{ppm}^{CDCl_3}$ 6.30 (3 H, s), 7.00–8.70 (envelope), 9.00 (3 H, bd)) shown to have



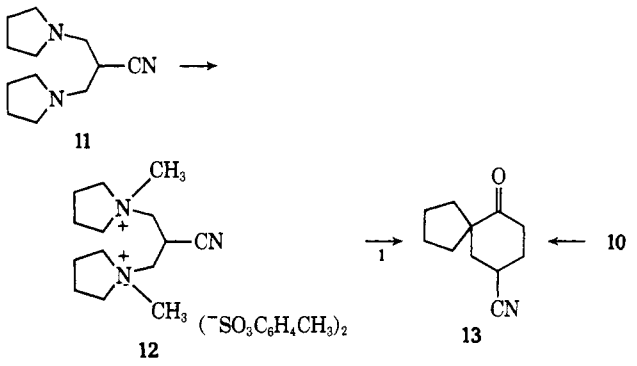
the configuration **6** by its sodium methoxide isomerization to isomer **7** (ν^{CHCl_3} 2960, 1735, 1710, cm^{-1}; τ^{CDCl_3} 6.28 (3 H, s), 7.0–8.70, envelope with strong peaks at 7.65, 7.90, and 8.40, 9.15 (3 H, d, J = 6.5 Hz)) having a *shielded* methyl doublet. Interestingly, at equilibrium the ratio of **7** to **6** is 70:30. The production of **6** as a single isomer in the annelation suggests the intramolecular Michael is occurring from the least-hindered side, opposite the methyl, and that the protonation transition state has a configuration and idealized conformation approaching those of **8**. In the alternate transition state **9**, severe nonbonded interactions develop between the methyl and the α-methylene



(1) R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 756 (1957); M. Mousseron, H. Christol, and F. Pleint, *C. R. Acad. Sci.*, **245**, 1281 (1957); H. deJongh, F. Gerharth, and H. Wynberg, *J. Org. Chem.*, **30**, 1409 (1965); M. Khuda and A. Ray, *J. Indian Chem. Soc.*, **16**, 525 (1939); M. Monsseron, R. Jacquier, and H. Christol, *Bull. Soc. Chim. Fr.*, 346 (1957); E. J. Corey and J. I. Shulman, *J. Amer. Chem. Soc.*, **92**, 5522 (1970).
(2) R. P. Nelson and R. G. Lawton, *ibid.*, **88**, 3884 (1966).
(3) (a) R. P. Nelson, J. M. McEwen, and R. G. Lawton, *J. Org. Chem.*, **34**, 1225 (1969); (b) **35**, 690 (1970).
(4) Prepared by Jones oxidation of 1-cyclopentylethanol, Aldrich Chemical Co.
(5) Prepared most easily by diisopropylethylamine dehydrohalogenation of methyl β,β'-dibromoisobutyrate.[3b] See A. F. Ferris, *J. Org. Chem.*, **20**, 780 (1955), and ref 3. The compound has vesicant properties.
(6) Correct analytical figures have been obtained for all compounds for which physical and spectral data are given.
(7) The intermediate methyl α-(3-keto-3-cyclopentyl-*n*-propyl)acrylate (bp 108–110° (0.2 mm): $\nu_{max}^{CHCl_3}$ 1715, 1630, 1450, 1155, 960 cm^{-1}; $\tau_{ppm}^{CDCl_3}$ 3.92 (1 H, d), 4.48 (1 H, bd), 6.23 (3 H, s), 7.40 (4 H, s), 8.16–8.45 (envelope)) may be isolated.
(8) I. Tabushi, K. Fujita, and R. Oda, *Tetrahedron Lett.*, 4248 (1968).

of the pyrrolidine ring which precludes the formation of the corresponding isomer. After hydrolysis of the iminum salt, the stable conformation of configuration **6** is undoubtedly assumed. Parallel observations of this kind of phenomena are seen in the synthesis of bridged bicyclic compounds.[3b]

The combination of the pyrrolidine enamine of acetylcyclopentane (**1**) and the nitrile corresponding to ester **2**, α-(chloromethyl)acrylonitrile (**10**),[9] also provides the spiro framework **13** but the relative inaccessability of this particular alkylation–Michael reagent encouraged the development of a useful alternative. Cyanoacetic acid, pyrrolidine, and formaldehyde undergo facile bis-Mannich[10] condensation with concomitant decarboxylation to yield 1,3-bis(pyrrolidino)-2-cyanopropane (**11**) (40% yield, bp 120–122° (0.15 mm); $\nu_{max}^{CHCl_3}$ 2980, 2260 cm^{-1}; τ 7.12 (1 H, t), 7.16–7.60 (envelope), 8.03–8.42 (envelope)). Reaction of this diaminonitrile **11** with methyl *p*-toluenesulfonate in refluxing acetonitrile gives the bis quaternary salt **12** (highly hydroscopic) which can be utilized directly



in the annelation reaction. Condensation of **1** and **12** in acetonitrile produces **13** in 30% (mp 84–85°; bp 120–122° (0.25 mm); $\nu_{max}^{CHCl_3}$ 2940, 2245, 1704 cm^{-1}; τ^{CDCl_3} 6.9 (1 H, heptet), 7.3–8.6 (envelope of hydrogens with strong absorptions at 7.60, 7.85, and 8.35)).

The generality of these pathways to spiro compounds was further demonstrated by the conversion of acetylcyclohexane enamine to methyl spiro[5:5]undecan-1-one-4-carboxylate (homolog of **4**) (bp 95–100° (0.1 mm); $\nu_{max}^{CHCl_3}$ 1735, 1710, 1440, 1230 cm^{-1}; τ^{CDCl_3} 6.30 (3 H, s), 7.00–8.90 (envelope with strong peaks at 7.60, 7.80, and 8.50)).

The extensions of this reaction to other systems and the further use of these products in synthesis are continuing. The utilization of such spiro structures in the synthesis and study of angularly substituted decalins is described in the accompanying communication.

(9) R. P. Nelson, Ph.D. Dissertation, University of Michigan, 1967; A. F. Ferris and I. Marks, *J. Org. Chem.*, **19**, 1971 (1954).
(10) C. Mannich and E. Ganz, *Ber.*, **55**, 3486 (1922).
(11) Visiting Professor of Chemistry, 1970–1971; to whom inquiries should be addressed at: University of Wisconsin, Madison, Wis.

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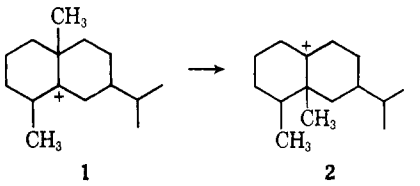
Spiro Intermediates in Sesquiterpene Rearrangements and Synthesis

Sir:

The eremophilane-type sesquiterpenes have long been considered to be derived from species of the eudesmane structure by migration of the angular methyl group (**1** → **2**).[1] Similar migrations have been proposed to occur in a variety of sesquiterpene and steroid systems[2] as well as in a model series.[3a] Nevertheless, Erdtman and Norin[4] have noted that it is surprising that the angular methyl of structures such as nootkatene



and nootkatone which would be expected on the basis of these biosynthetic hypotheses to have the same α orientation as the isopropyl group, in fact, has the wrong, β, orientation. In the course of synthetic studies to sesquiterpenes *via* spiro intermediates, we have made an observation relating to the mechanistic chemistry of these types of structures which suggests an alternative pathway to methyl migration.

A convenient synthetic route to angularly substituted decalins develops from a one-step synthesis of spiro keto ester **3b**.[5] Treatment of the corresponding acid **3a** with methylene triphenylphosphorane in dimethyl sulfoxide[6] produced the spiromethylene acid **4a**[7] (85% yield; mp 40–43°; ν^{CHCl_2} 2980, 1715, 1648 cm^{-1}; τ^{CDCl_3} 0.40 (1 H, s), 5.25 (2 H, broad s), 7.00–8.55 (envelope with sharp peaks at 7.75 and 8.40)). Treatment of **4a** with boron trifluoride in acetic acid[8] at room temperature effected rearrangement (quantitative) to a 1:1 mixture of two γ-lactones **8** (previously prepared;[3a] mp 70.2–70.8°; ν^{CHCl_3} 1780, 1460, 1240 cm^{-1}; τ^{CDCl_3} 8.95 (3 H, s)) and **9** (mp 87–88°; ν^{CHCl_3} 1772, 1300, 1115 cm^{-1}; τ^{CDCl_3} 8.98 (3 H, s)). Rearrangement of the spiro ester **4b** under the same conditions gave only the single configurational isomer **10b** (ν^{CHCH_3} 2950, 1735, 1660 cm^{-1}; τ^{CDCl_3} 4.55 (1 H, 6s), 7.30–8.60 (envelope), 8.92 (3 H, s)) previously prepared by Heathcock[3b] and used as an intermediate

(1) R. Robinson, "The Structural Relations of Natural Products," Clarendon, Oxford, 1955, p 12.
(2) See, for example: (a) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959; (b) P. deMayo, "Molecular Rearrangements," Part II, P. deMayo, Ed., Interscience, New York, N. Y., 1964; and (c) P. deMayo, "The Higher Terpenoids," Interscience, New York, N. Y., 1959.
(3) (a) C. H. Heathcock and T. R. Kelly, *Tetrahedron*, **24**, 3753 (1968); (b) *ibid.*, **24**, 1801 (1968); (c) C. H. Heathcock and Y. Amons, *ibid.*, **24**, 4917 (1968). We thank Dr. Heathcock for his help in providing comparison spectral data.
(4) H. Erdtman and T. Norin, *Fortschr. Chem. Org. Naturst.*, **24**, 245 (1966).
(5) D. J. Dunham and R. G. Lawton, *J. Amer. Chem. Soc.*, **93**, 2073 (1971).
(6) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962); **87**, 1345 (1965).
(7) Correct analytical figures have been obtained for all compounds for which physical and spectral data are given.
(8) See J. W. Rowe, A. Malera, D. Arigoni, O. Jeger, and L. Ruzicka in "Festschrift Prof. Dr. Arthur Stoll," Birkhaeuser, Basel, 1957, p 886, for the introduction of the concept at this route. Also, see *Helv. Chim. Acta*, **40**, 1 (1957).