($\equiv$ log k_c)[8] for the nonparticipating 2-adamantyl tosylate in the same solvents (eq 2). This modified Y treatment with 2-adamantyl as a standard for Y values appropriate to tosylate leaving groups[24] yields nicely linear correlations (correlation coefficient >0.99) with slopes: H, 0.69; m-CH_3, 0.74; p-CH_3, 0.65; m,p-$(CH_3)_2$, 0.74; av 0.71 ± 0.04. The lack of significant variations or trends in these values indicates that the Fk_Δ pathway does not respond selectively to changes in ionizing power.

The 7500-fold variation in the β-phenethyl tosylate/ethyl tosylate rate ratio (Table I, column 4) can be reproduced quantitatively by assuming that only effects 1 and 2a are operative. Equation 2 correlates k_Δ for β-

$$\log (k_\Delta/k_\Delta{}^\circ) = m_\Delta Y \qquad (2)^{26}$$

phenethyl tosylate, while eq 3 is generally applicable to

$$\log (k_s/k_s{}^\circ) = m_s Y + l_s N \qquad (3)$$

k_s processes.[9,27]

Combination of eq 1–3 and insertion of the appropriate m and l values[28] gives eq 4 which allows calcula-

$$\frac{k_t(\beta\text{-PhEtOTs})}{k_t(\text{EtOTs})} = \frac{Fk_\Delta{}^\circ[10^{0.69Y}] + k_s{}^\circ[10^{(0.33Y+0.78N)}]}{k_t{}^\circ[10^{(0.36Y+0.82N)}]} \qquad (4)^{29}$$

tion of the relative ratio (Table I, column 5). The agreement with the experimental ratios is remarkably good.

Our evidence indicates that the β-phenethyl tosylate/ethyl tosylate rate ratios are influenced by both solvent ionizing power and nucleophilicity, but that the latter is generally more important. This follows from the comparably large range of N and Y values (Table I, last two columns) and the fact that the m_s coefficients (0.3–0.4) are smaller than the l_s coefficients (0.75–0.85) in eq 4. An increase in ionizing power does favor k_Δ over k_s since $m_\Delta > m_s$, but we could detect little change in the kinetically significant magnitude of bridging of the neighboring group (effect 2b). Are these conclusions general for all k_Δ systems? The answer to this question is under investigation and will be reported subsequently.

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[24] Dispersion in mY plots because of leaving group effects is well known.[25] Winstein, *et al.*, have proposed p-methoxyneophyl tosylate, a k_Δ substrate, as a standard to measure ionizing power for compounds with sulfonate leaving groups.[25b] 2-Adamantyl and p-methoxyneophyl tosylates are linear (corr coeff 0.999) in the range of solvents where common data are available.

[25] (a) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1608 (1957); (b) S. G. Smith, A. H. Fainberg, and S. Winstein, *ibid.*, **83**, 618 (1961).

[26] Inclusion of the solvent nucleophilicity term, lN, does not significantly improve the simple mY correlation for the k_Δ pathway.

[27] (a) S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, **73**, 2700 (1951); (b) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

[28] m_Δ is the m value for the k_Δ pathway (β-PhEtOTs, 75°).[26] Values of (m_s, l_s) were obtained by the four-parameter Winstein–Grunwald equation[9,27] (eq 3) for the dissected k_s values of β-PhEtOTs and k_t of EtOTs at 75° in the solvents EtOH, 50% aqueous EtOH, AcOH, and HCO_2H.

[29] $k_\Delta{}^\circ$, $k_s{}^\circ$, and $k_t{}^\circ$ are the rates for the appropriate processes in 80% aqueous EtOH calculated from literature data.[6,25b,27a] For F values[11] see ref 6, 15a, c, 17, and 23.

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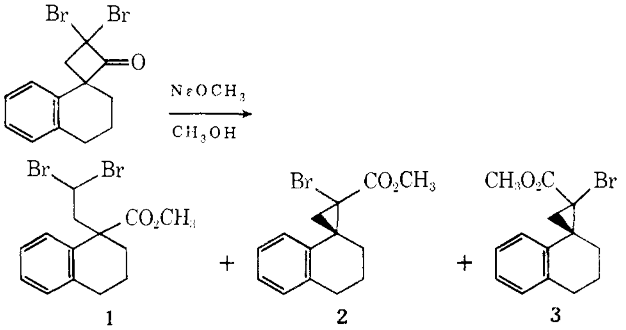
New Synthetic Reactions. New Approach to Geminal Alkylation

Sir:

We reported the stereoselective creation of geminal substitution from a carbonyl group based upon spiroannelation, bromination, and subsequent ring cleavage.[1] Such an approach was clearly limited to the spiroannelated products derived from ketones and to those which did not possess functionality sensitive to molecular bromine. A further limitation arose in extension of the work to the spiroannelated product of 1-tetralone. The desired ring cleaved compound (**1**) constituted only a minor product. The major products **2** and **3** arose from a modified Favorskii reaction (semibenzilic acid rearrangement).[2] In this communication, we report an alternative approach which does not suffer from such limitations and which results in the stereoselective creation of an α-methylcarboxylic acid unit, a common structural feature found in terpenes.



Introduction of a dithiane unit, an anion stabilizing but nonleaving group, required activation of the α-methylene unit of the spiroannelated product. An aminomethylene group, introduced by condensation of the cyclobutanone[3] (*e.g.*, **4**) with *tert*-butoxybis(dimethylamino)methane,[4] has such an activating function. The vinylogous amides are characterized by two carbonyl infrared bands at 1608–1620 (s) and 1680–1710 (m) cm^{-1} and nmr absorptions at δ 2.95–3.05 (N-

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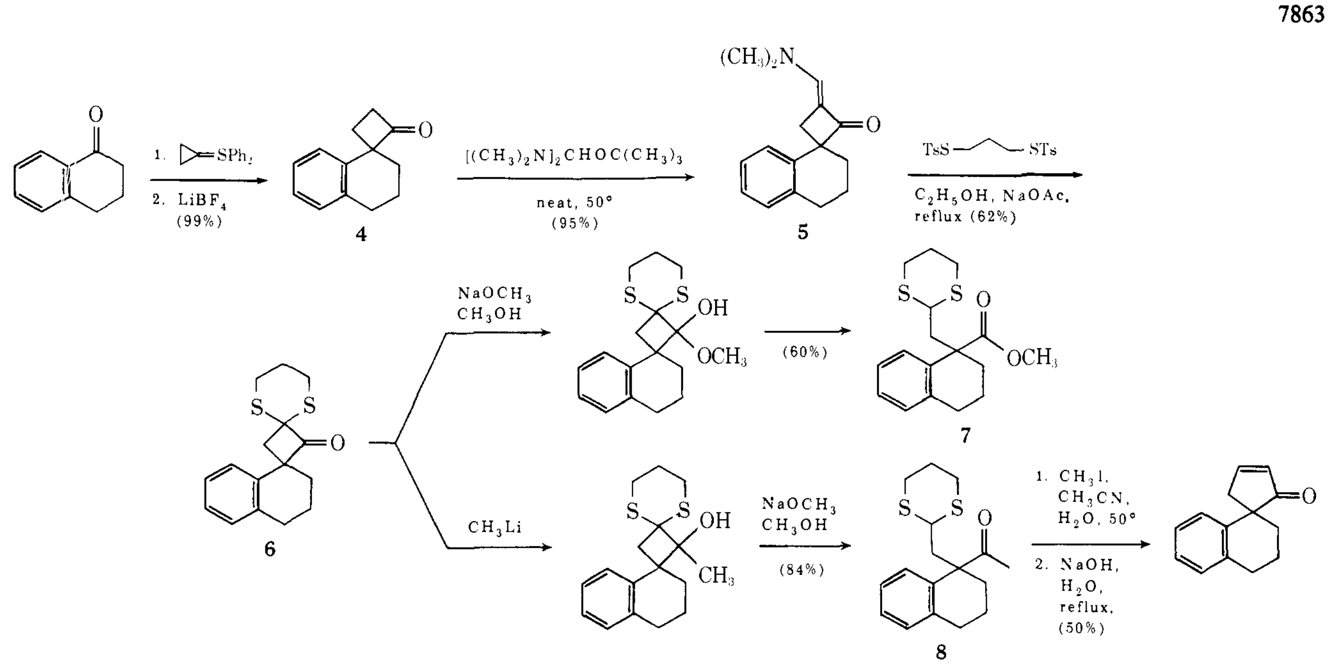
[1] B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 2038 (1973). For some recent alternative approaches to geminal alkylation, see G. H. Posner and D. J. Brunelle, *Tetrahedron Lett.*, 935 (1973); D. Seebach, M. Kolb, and B.-T. Gröbel, *Angew. Chem., Int. Ed. Engl.*, **12**, 69 (1973); D. Seebach, B.-T. Gröbel, A. K. Beck, M. Braun, and K. H. Geiss, *ibid.*, 11, 443 (1972); F. E. Ziegler and P. A. Wender, *J. Amer. Chem. Soc.*, **93**, 4318 (1971); E. J. Corey and J. I. Shulman, *ibid.*, **92**, 5522 (1970); E. Wenkert, R. A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi, *ibid.*, **92**, 7428 (1970).

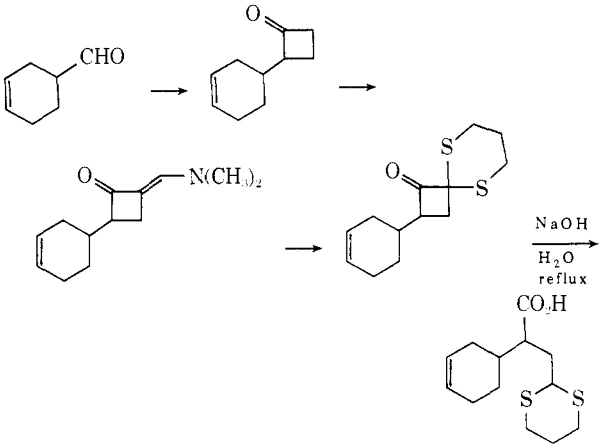
[2] For a review of related reactions in cyclobutanes see J. M. Conia and J. R. Salaun, *Accounts Chem. Res.*, **5**, 33 (1972).

[3] Lithium fluoroborate appears to be superior to lithium perchlorate for the rearrangement of the oxospiropentanes. For preparation of this salt see I. Shapiro and H. G. Weiss, *J. Amer. Chem. Soc.*, **75**, 1753 (1953).

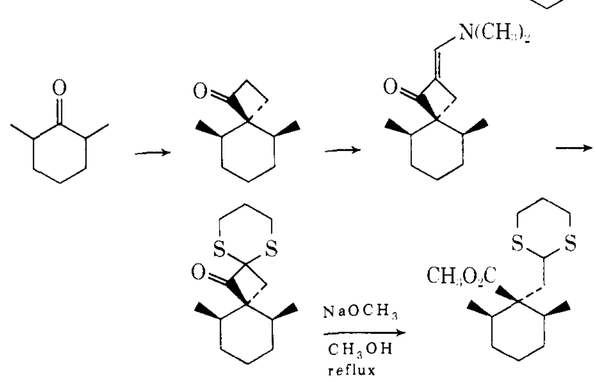
[4] J. Gutzwiller, G. Pizzolato, and M. Uskokovic, *ibid.*, **93**, 5907 (1971); H. Bredereck, F. Effenberger, and G. Simchen, *Chem. Ber.*, 101, 41 (1968), and references therein.



methyl) and δ 6.8–7.2 (vinyl).[5] Reaction of the derived vinylogous amide (*e.g.*, **5**) with 1,3-trimethylenedithiotosylate smoothly replaced the dimethylaminomethylidene unit with the trimethylenedithio unit.[6] Normal cyclobutanone infrared carbonyl absorptions at 1757–1765 cm^{-1} and the appearance of multiplets for two of the hydrogens of the methylene groups α to sulfur at δ 3.2–3.8 in the nmr spectra provide structural confirmation. The resultant dithiane, **6**, cleaved in good yield to **7** upon refluxing in methanolic sodium methoxide. The facility of this cleavage compared to that of larger ring ketones (which fail under such conditions[7]) presumably arises from the release of 27 kcal/mol of strain energy. In principle, the addition of any nucleophile could initiate cleavage. For example, treatment of **6** with methyllithium in ether at room temperature followed by refluxing methanolic sodium methoxide provided the methyl ketone **8** which, after dithiane hydrolysis, undergoes intramolecular aldol condensation. Since we have previously shown the creation of the cyclobutanone is highly stereoselective, the net transformation constitutes a stereoselective cyclopentenone spiroannelation. Equations 1 and 2 further exemplify the process. The conversion to the α-dithianyl ketones is identical with that described above. These examples also demonstrate the regiospecificity, stereospecificity, and lack of interference of a double bond.[8]



(1)



(2)

The synthesis of methyl desoxypodocarpate (and consequently podocarpic acid[9]) offers an opportunity to demonstrate the stereoselectivity of the process. Previous attempts to utilize the tricyclic ketone **9**, available in three steps by the method of Stork and Burgstahler,[10] in stereoselective diterpene resin acid synthesis failed.[10,11] Spiroannelation gave a homogeneous cyclobutanone, **10** (see Scheme I), tentatively assigned the stereochemistry depicted on the basis of spectroscopic data.[1] Condensation with the amide aminal and subsequently with the dithiotosylate gave a sharp melting crystalline α-ketodithiane, **11**, mp 163.0–163.5°. Sur-

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(5) All compounds had nmr, ir, mass spectral, and elemental composition data consistent with the assigned structures.

(6) J. C. A. Chivers and S. Smiles, *J. Chem. Soc.*, 697 (1928); R. B. Woodward, I. J. Pachter, and M. L. Scheinbaum, *J. Org. Chem.*, **36**, 1137 (1971).

(7) J. A. Marshall and H. Roebke, *Tetrahedron Lett.*, 1555 (1970); J. A. Marshall, C. T. Buse, and D. E. Seitz, *Syn. Commun.*, **3**, 85 (1973).

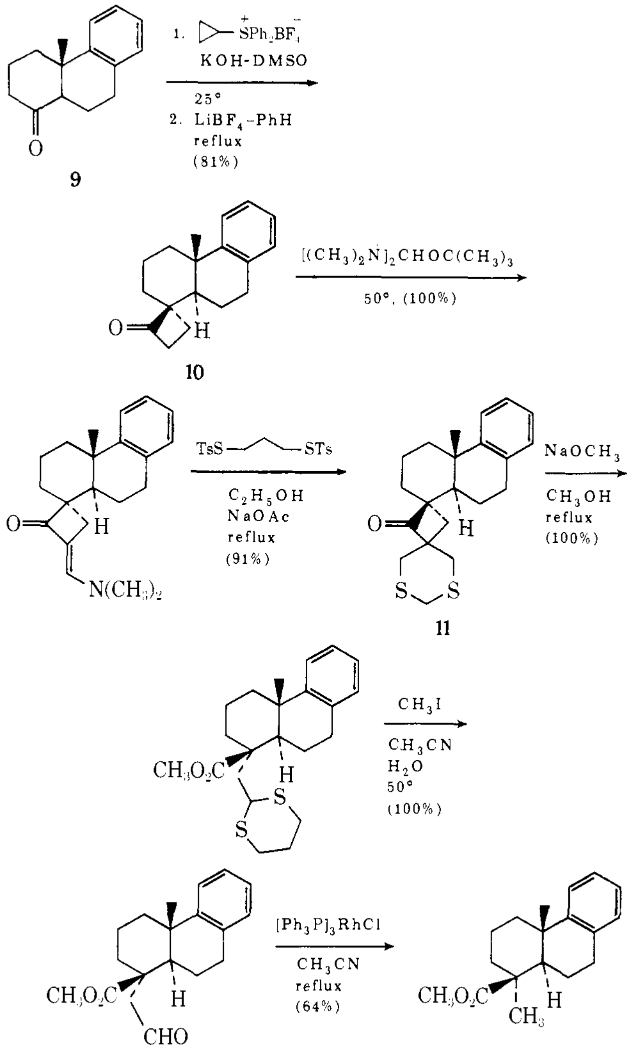
(8) The carboxylic acid product of eq 1 had spectral, tlc, and physical (mp 89.0–89.5°) properties consistent with a single diastereomer although no stereochemical assignment could be made.

(9) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 217 (1958). For related work in this area, see W. L. Meyer and K. K. Maheshwari, *Tetrahedron Lett.*, 2175 (1964); K. Mori and M. Matsui, *ibid.*, 175 (1966); F. Giarrusso and R. E. Ireland, *J. Org. Chem.*, **33**, 3560 (1968); M. E. Kuehne and J. A. Nelson, *ibid.*, **35**, 161 (1970); T. A. Spencer, T. D. Weaver, R. M. Villarica, R. J. Friary, J. Posler, and M. A. Schwartz, *ibid.*, **33**, 712 (1968); S. W. Pelletier, R. L. Chappell, and S. Prabhakar, *J. Amer. Chem. Soc.*, **90**, 2889 (1968); S. C. Welch and C. P. Hagan, *Syn. Commun.*, **2**, 221 (1972); **3**, 29 (1973).

(10) G. Stork and A. Burgstahler, *J. Amer. Chem. Soc.*, **73**, 3544 (1951).

(11) G. Stork and J. W. Schulenberg, *ibid.*, **84**, 284 (1962). See, however, M. Sharma, U. R. Ghatak, and P. C. Dutta, *Tetrahedron*, **19**, 985 (1963); J. A. Barltrop and A. C. Day, *Chem. Ind.* (*London*), 1450 (1959).

Scheme I. Stereoselectivity of Modified Geminal Alkylation, Synthesis of Methyl Desoxypodocarpate



prisingly, even with such a hindered carbonyl system, cleavage to **12** (mp 135.0–135.5°) occurred smoothly with methanolic sodium methoxide at reflux. Following a sequence patterned after the recently reported work of Wenkert, *et al.*,[12] would lead into the stereochemistry of the abietic acid series from **11**. Alternatively dithiane hydrolysis and decarbonylation utilizing Wilkinson's catalyst completes the sequence in the podocarpate series. Comparison of ir, nmr, and tlc properties with an authentic sample confirmed the identity of the compound and consequently the stereochemistry of **10**.

The development of this alternative approach to geminal alkylation should ensure the generality of the approach for a wide range of structural types.

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[12] J. P. Tresca, J. L. Fourrey, J. Polonsky, and E. Wenkert, *Tetrahedron Lett.*, 895 (1973).

[13] Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

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Ligand and Geometry Effects in the Quenching of the Tris(2,2′-dipyridyl)ruthenium(II) Phosphorescence by Some Chromium(III) Complexes

Sir:

The quenching of the excited states has extensively been studied in the field of organic chemistry.[1] When energy and spin requirements are satisfied, these processes are generally diffusion controlled in fluid solution at room temperature.[1,2] This "rule," however, does not apply when coordination compounds are involved.[3–13] It has been reported that the quenching efficiency in the collision encounter is strongly affected by the charge[7,10,11,13] and the geometry[12] of the complex and by the nature of the ligands.[4–6,10] However, systematic studies are needed in order to establish what is the actual role played by these and other factors in determining the quenching efficiency. We wish to report here the results of an investigation which was carried out using Ru(dipy)$_3{}^{2+}$ as a donor and several Cr(III) complexes as quenchers.

The experiments were carried out in aqueous solutions at 22°. The ionic strength was adjusted by adding KCl. The quenching of the Ru(dipy)$_3{}^{2+}$ phosphorescence intensity was measured with a Perkin-Elmer MPF3 spectrofluorimeter. In some cases, the quenching of the phosphorescence lifetime was measured with the equipment previously described.[14] The τ^0/τ values were practically equal to the corresponding I^0/I values, showing that no static quenching occurred.[15] In the case of *trans*-Cr(en)$_2$(NCS)$_2{}^+$, the quenching of the Ru(dipy)$_3{}^{2+}$ phosphorescence was accompanied by the sensitized emission of the quencher.[16]

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(6) T. Ohno and S. Kato, *Bull. Chem. Soc. Jap.*, **42**, 3385 (1969).

(7) H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta*, **20**, 186 (1971).

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(9) J. Eisinger and A. A. Lamola, *Biochim. Biophys. Acta*, **240**, 299 (1971).

(10) A. Pfeil, *J. Amer. Chem. Soc.*, **93**, 5395 (1971).

(11) N. J. Demas and A. W. Adamson, *J. Amer. Chem. Soc.*, **93**, 1800 (1971); N. J. Demas, Proceedings of the XIVth International Conference on Coordination Chemistry, Toronto, June 1972, p 166.

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(13) I. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 115 (1972).

(14) F. Bolletta, M. Maestri, and L. Moggi, *J. Phys. Chem.*, **77**, 861 (1973).

(15) W. R. Ware, "Creation and Detection of the Excited State," Vol. 1, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, Part A, p 213.