lowing spectral characteristics: IR 2985 (s), 2955 (s), 1735 (s) cm^{-1}; NMR (60 MHz) δ 0.92–2.62, 1.67 (m, s, 19 H), 3.58 (s, 3 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.24; H, 10.60.

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the national Institutes of Health through Grant No. GM-24680, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation. In addition, we thank S. T. Bella of the Rockefeller University for the microanalyses and the Middle Atlantic Regional NMR Facility (NIH No. RR 542) at the University of Pennsylvania where the 220- and 360-MHz spectra were recorded.

Registry No. 8a, 54445-53-3; **8a** (acid), 16642-54-9; **8a** (acid chloride), 71647-57-9; **8b**, 54495-73-7; **8b** (acid), 18294-87-6; **8b** (acid chloride), 84189-13-9; **8c**, 54445-52-2; **8c** (acid), 16642-55-0; **8c** (acid chloride), 90173-13-0; **8d**, 56268-19-0; **8d** (acid), 16642-56-1; **8d** (acid chloride), 90173-12-9; **9a**, 38142-79-9; **9b**, 54445-57-7; **9c**, 54445-59-9; **9d**, 90172-84-2; **10a**, 54445-56-6; **10b**, 54445-54-4; **10c**, 54445-55-5; **10d**, 90172-85-3; **11**, 5261-30-3; **11** (acid), 21622-08-2; **20**, 90172-76-2; **20** (acid), 2243-53-0; **21a**, 90172-86-4; **21b**, 90172-87-5; **21c**, 90172-88-6; **22**, 57690-97-8; **22** (acid), 10276-09-2; **22** (ethyl ester), 58544-20-0; **23**, 90172-77-3; **23** (acid), 1577-18-0; **24**, 76803-37-7; **24** (acid), 14472-55-0; **25**, 90172-89-7; **26**, 90172-90-0; **27a**, 90172-91-1; **27b**, 90172-92-2; **27c**, 90172-93-3; **28a**, 90172-94-4; **28b**, 90172-95-5; **29**, 76803-43-5; **29** (acid), 68317-77-1; **30**, 62861-92-1; **31**, 90172-78-4; **32**, 52358-09-5; **33**, 76803-53-7; **34**, 90172-96-6; **35**, 90172-97-7; **36**, 90172-79-5; **36** (acid), 90173-18-5; **36** (ethyl ester), 90173-19-6; **37**, 90172-80-9; **37** (acid), 90173-20-9; **37** (methyl ester), 66052-38-8; **38**, 90172-81-9; **38** (acid), 90173-21-0; **38** (ethyl ester), 64861-91-2; **39**, 76803-44-6; **39** (acid), 90173-22-1; **40**, 90172-82-0; **40** (acid), 90173-23-2; **41** (isomer 1), 90172-98-8; **41** (isomer 2), 90173-24-3; (*E*)-**42**, 90172-99-9; (*Z*)-**42**, 90173-25-4; **43** (isomer 1), 90173-00-5; **43** (isomer 2), 90243-13-3; (*E*)-**44**, 90173-01-6; (*Z*)-**44**, 90173-26-5; **45** (isomer 1), 90173-02-7; **45** (isomer 2), 90243-14-4; (*E*)-**46**, 90173-03-8; (*Z*)-**46**, 90173-27-6; **47** (isomer 1), 90173-04-9; **47** (isomer 2), 90173-28-7; (*E*)-**48**, 90173-05-0; (*Z*)-**48**, 90173-29-8; **49**, 61346-63-2; **49** (acid), 90173-16-3; **49** (ethyl ester), 54281-01-5; $\Delta^{\alpha,1}$-**49** (ethyl ester), 13733-50-1; **50**, 90172-83-1; **50** (acid), 90173-14-1; **50** (ethyl ester), 25289-62-7; **50** (alcohol), 90173-15-2; **51**, 61346-64-3; **51** (acid), 2205-24-5; **52**, 61140-39-4; **53**, 67463-12-1; **54**, 67463-13-2; **55a**, 90173-06-1; **55b**, 90173-07-2; **56a**, 90173-08-3; **56b**, 90173-09-4; **57**, 90173-10-7; **58**, 90173-11-8; **59**, 61140-29-2; **60**, 61140-28-1; **64**, 23786-13-2; **65**, 68682-48-4; **65** (acid), 20430-18-6; **66**, 90173-17-4; **67a**, 4934-95-6; **67b**, 13672-64-5; **67c**, 75032-18-7; MeOH, 67-56-1; BnOH, 100-51-6; *t*-BuOH, 75-65-0; $CuSO_4$, 7758-98-7; $Cu(AcAc)_2$, 13395-16-9; $Cu(OTf)_2$, 34946-82-2; Ag_2O, 20667-12-3; ethyl tiglate, 5837-78-5; ethyl β-methylcinnamate, 945-93-7; allyl bromide, 106-95-6; methyl tiglate, 6622-76-0; 1-chloro-2-methyl-2-propene, 563-47-3; ethyl 2,3-dimethyl-3-butenoate, 14387-99-6; 2-carboethoxycyclopentanone, 611-10-9; ethyl bromoacetate, 105-36-2; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 1-(1-cyclohexen-1-yl)pyrrolidine, 1125-99-1; 1-(1-cyclohepten-1-yl)pyrrolidine, 14092-11-6.

Supplementary Material Available: All spectral characterization data, elemental composition data, and experimental procedures for the diazo ketones, their precursor acids, and the derived vinylogous Wolff and other products listed in Tables III–VI are available as supplementary material (14 pages). Ordering information is given on any current masthead page.

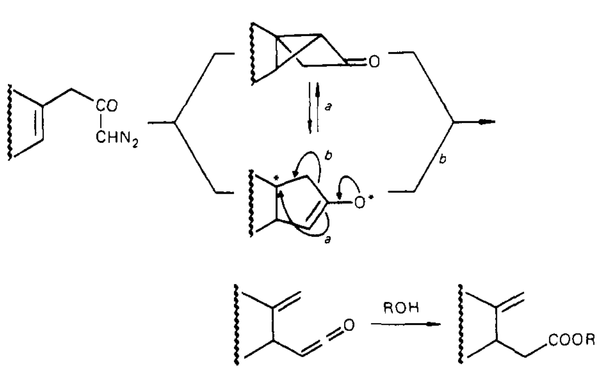
Vinylogous Wolff Rearrangement. 5. Mechanistic Studies

Amos B. Smith, III,*[1] Bruce H. Toder, Ruth E. Richmond, and Stephen J. Branca

Contribution from the Department of Chemistry, The Laboratory for Research on the Structure of Matter, and the Monell Chemical Senses Center, The University of Pennsylvania, Philadelphia, Pennsylvania 19104. *Received October 11, 1983*

Abstract: A detailed study of the vinylogous Wolff rearrangement (VWR), a general transformation involving skeletal rearrangement of β,γ-unsaturated diazo ketones, is described. Evidence is presented which suggests that the skeletal rearrangement involves initial insertion of the diazo carbon into the β,γ-olefinic bond. The resultant bicyclo[2.1.0]pentan-2-one then undergoes fragmentation to a β,γ-unsaturated ketene which in turn is captured by available nucleophiles (e.g., alcohol) to afford the observed γ,δ-unsaturated ester.

In the preceding paper[2] of this issue we demonstrated that β,γ-unsaturated diazo ketones, through agency of either silver(I) or copper(II) salt–alcohol couples, undergo a novel transformation termed the vinylogous Wolff rearrangement (VWR) to afford γ,δ-unsaturated esters (eq 1). To account for this transformation we postulated[3] initial silver or copper ion induced insertion of the diazo carbon into the β,γ-olefinic bond to yield a bicyclo[2.1.0]pentanone and/or zwitterionic species. Subsequent thermal or metal ion induced fragmentation followed by capture of the resultant β,γ-unsaturated ketene by alcohol would then afford the observed vinylogous Wolff ester (eq 1). Refinement of this scheme allows the insertion and/or fragmentation to proceed in either a concerted or stepwise fashion. In no case employing silver ion to promote the decomposition did the yield of vinylogous Wolff ester exceed that of the normal Wolff product.[2] Copper(II) salts, on the other hand, in general afforded only the vinylogous Wolff esters.[2]



(1)

Vinylogous Wolff Rearrangement

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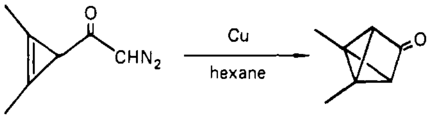
[1] Camille and Henry Dreyfus Teacher–Scholar, 1978–1983; Recipient of a National Institutes of Health (National Cancer Institute) Career Development Award, 1980–1985.

[2] Smith, A. B., III; Toder, B. H.; Branca, S. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

[3] Smith, A. B., III; Toder, B. H.; Branca, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 7456.

0002-7863/84/1506-4001$01.50/0

Initial support for participation of a bicyclo[2.1.0]pentanone in the vinylogous Wolff rearrangement derived from the observations of Stork,[4] Gutsche,[5] Deslongchamps,[6] and McCurry[7] concerning the intramolecular insertion of diazo ketone carbons into olefinic bonds situated γ,δ or further removed from the carbonyl functionality. In such cases the resultant bicyclic systems proved stable. At the outset of our work, however, only one report existed concerning the copper-induced decomposition of a β,γ-unsaturated diazo ketone (see eq 2).[8] The yield of the derived insertion product, however, was extremely poor (ca. 1%). Furthermore no information concerning the thermolysis of this proposed bicyclopentanone system was available.[9]

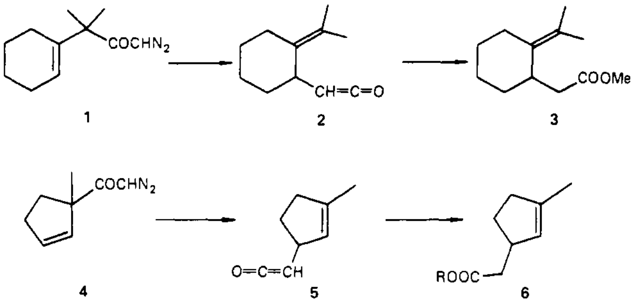


(2)

In this, the second of two full accounts on the vinylogous Wolff rearrangement, we describe our study of the mechanism of this rearrangement. We note in advance that we have (a) established the existence of a β,γ-unsaturated ketene on the vinylogous Wolff reaction coordinate, (b) demonstrated the viability of the postulated thermal fragmentation process (i.e. bicyclo[2.1.0] pentanone to β,γ-unsaturated ketene), and (c) obtained evidence in at least one case suggestive of a zwitterionic intermediate. Taken together these results provide strong support for the proposed mechanism of the vinylogous Wolff rearrangement.

Results

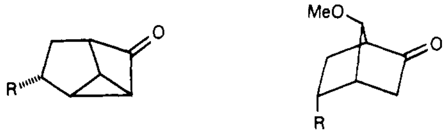
(i) Observation of the Ketene Intermediate. At the outset of our mechanistic study we sought evidence for involvement of a β,γ-unsaturated ketene. Two diazo ketones (**1** and **4**) known to undergo the vinylogous Wolff rearrangement were selected for study.[2] Both were subjected to $Cu(AcAc)_2$ induced decomposition at high dilution in cyclohexane (ca. 1 mg/mL) in the absence of alcohol. In both cases an intense absorption at 2110 cm^{-1} in the infrared spectra characteristic of the ketene functionality[10] (i.e., **2** and **5**) was observed. Subsequent addition of methanol to the reaction mixture led to the replacement of the 2110-cm^{-1} absorption with an intense band at 1735 cm^{-1} diagnostic of an ester carbonyl.[10] Finally, vinylogous esters **3** and **6a** were isolated in 67 and 56% yield, respectively.[11]



(a) R = Me
(b) R = Bn

(ii) Bicyclo[2.1.0]pentanones and the Fragmentation Process. Having demonstrated formation of an unsaturated ketene as the penultimate intermediate on the vinylogous Wolff reaction coordinate, we turned to the acquisition of chemical evidence for the intermediacy of the postulated initial insertion product (i.e., bicyclopentanone). We were, however, faced with the fact that isolation of such systems under conditions of the vinylogous Wolff rearrangement (i.e., cyclohexane at reflux) would be difficult due to the presumed instability of the bicyclo[2.1.0]pentanone system. This being the case, our strategy was to prepare the proposed bicyclo[2.1.0]pentanone system via an alternative method and then to explore the proposed fragmentation process under the conditions of the vinylogous Wolff reaction.

The parent bicyclo[2.1.0]pentan-2-one as well as closely related simple derivatives were not readily accessible.[12] Fortunately for our purposes, S. M. Roberts[13] in connection with his elegant work in the prostaglandin area reported the preparation of several tricyclic ketones (e.g., **7a–d**) which incorporate the bicyclo[2.1.0]pentanone skeleton. An X-ray structure has even been accomplished for bromo derivative **7c**.[14]



7 **8**

(a) R = OMe
(b) R = $OSiMe_3$
(c) R = Br
(d) R = OTHP

Two observations of Roberts were of particular interest to our work. First, such tricyclic ketones were found to be unstable. For example, it was not possible to distill these systems without complete decomposition.[13] Second, treatment with methanol at reflux led in high yield to bicyclic ketone **8**.[13] No information however was provided concerning the thermal behavior of these systems in the absence of nucleophiles. Given our working hypothesis for the mechanism of the vinylogous Wolff rearrangement, we conjectured that a fragmentation process not unlike that proposed for the bicyclo[2.1.0]pentanone in the vinylogous Wolff rearrangement was in fact the mode of thermal decomposition. Under the distillation conditions the resultant ketene would, of

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(4) Stork, G.; Ficini, J. *J. Am. Chem. Soc.* **1961**, *83*, 4678.

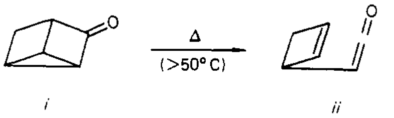
(5) Fawzi, M. M.; Gutsche, C. D. *J. Org. Chem.* **1966**, *31*, 1390.

(6) Mongrain, M.; Lafontaine, J.; Belanger, A.; Deslongchamps, P. *Can. J. Chem.* **1970**, *48*, 3273.

(7) McCurry, P. M., Jr. *Tetrahedron Lett.* **1971**, 1845.

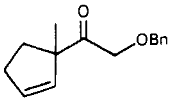
(8) von E. Doering, W.; Pomerantz, M. *Tetrahedron Lett.* **1964**, 961.

(9) Simultaneous with our initial disclosure of the vinylogous Wolff rearrangement [Smith, A. B., III *J. Chem. Soc. Commun.* **1974**, 695] Bond demonstrated that tricyclo[2.2.0.$0^{2,6}$]hexan-3-one (i) undergoes facile fragmentation to ketene ii above 50 °C; see : Ho, C.-Y.; Bond, F. T. *J. Am. Chem. Soc.* **1974**, *96*, 7355. Bond, F. T.; Ho, C.-Y. *J. Org. Chem.* **1976**, **41**, 1421



(10) Nakanishi, K.; Solomon, P. H. "Infrared Absorption Spectroscopy", 2nd end; Holden-Day: San Francisco, 1977; Chapter 2.

(11) The $Cu(AcAc)_2$-promoted decomposition of diazo ketone **4** also produced benzyl ether i (ca. 39%). Presumably i arrives via copper(II)-promoted insertion of the diazo carbon into the O–H bond of benzyl alcohol. Such a process is well-known where saturated alkyl diazo ketones are subjected to copper(II)-induced decomposition, see: Yates, P. *J. Am. Chem. Soc.* **1952**, *74*, 5376.

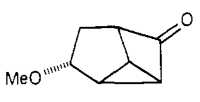


(12) (a) For the parent bicyclo[2.1.0]pentan-3-one see: M. Hanack *Suom. Kemistil.* **1966**, *39*, 93. (b) A CAS ONLINE search for compounds possessing the bicyclo[2.1.0]pentan-2-one part structure revealed 41 examples since 1967. From the preparative point of view, those of Roberts[13] were clearly the more accessible.

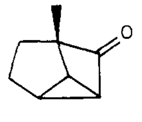
(13) (a) Grudzinski, Z.; Roberts, S. M. *J. Chem. Soc.* **1975**, 1767. (b) Lee, T. V.; Roberts, S. M.; Dinsdale, M. J.; Newton, R. F.; Rainey, D. K.; Webb, C. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1176. (c) Lee, T. V.; Roberts, S. M; Newton, R. F. *Ibid.* **1978**, *1179*. (d) Davies, J.; Roberts, S. M.; Reynolds, D. P.; Newton, R. F. *Ibid.* **1981**, 1317. (e) Finch, M. A. W.; Roberts, S. M.; Woolley, G. T.; Newton, R. F. *Ibid.* **1981**, 1725. (f) Newton, R. F.; Reynolds, D. P.; Webb, C. F.; Roberts, S. M. *Ibid.* **1981**, 2055 and references cited therein.

(14) Gilbert, J. C.; Luo, T.; Davis, R. E. *Tetrahedron Lett.* **1975**, 2545.

course, undergo further reactions (i.e., polymerization) and thereby not be observed.[9]



7a



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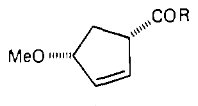

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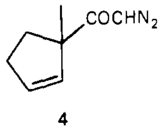
(a) R = CHN_2
(b) R = OH
(c) R = OMe



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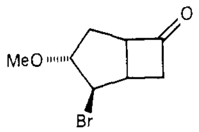

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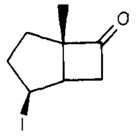


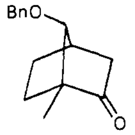
12

With this as background two tricyclic systems **7a** and **9** incorporating the bicyclo[2.1.0]pentanone skeleton were prepared. It should be recognized that tricyclic ketones **7a** and **9** chosen for study were the precise intermediates that would arise respectively from diazo ketones **10a** and **4**, if we assume the proposed vinylogous Wolff reaction coordinate. Indeed, we had demonstrated that diazo ketone **4** affords the vinylogous Wolff ester in 56% yield.[2] Diazo ketone **10a**, on the other hand, due to the relative inaccessability of the requisite acid **10b**, had not been studied. Our intention was to prepare diazo ketone **10a** after demonstrating the feasibility of the fragmentation process in both **7a** and **9**. For our purposes here it is important to note that both ketones **7a** and **9** were prepared via the Roberts 1,3-dehydrohalogenation strategy employing the corresponding bromo or iodo ketones **11** and **12**. Synthesis of the latter will be presented in detail with the preparative experiments. Interestingly, tricyclic ketone **9** proved to be considerably less stable than **7a**. In fact, unlike **7a**, ketone **9** could not be isolated in the neat state without major decomposition. It was therefore prepared, characterized, and handled in dilute solution.

With tricyclic ketones **7a** and **9** in hand, each was subjected to thermolysis in cyclohexane at reflux both with and without 1.2 equiv of benzyl alcohol, the alcohol shown to participate best in the vinylogous Wolff rearrangement.[2] The results are illustrated in Scheme I.

In both examples, if the thermolysis was carried out for a period of 10–15 min at a concentration of 1 mg/mL the infrared spectrum of an aliquot displayed a strong absorption at 2110 cm^{-1} characteristic of a ketene carbonyl.[10] Addition of benzyl alcohol (1.2 equiv) again led to replacement of the ketene absorption with a band at 1735 cm^{-1} indicative of an ester. Normal workup afforded **13** and **6b** respectively in 96 and 59% yield. Since tricyclic ketone **9** is unstable, the yield of benzyl ester **6** was based on iodo ketone **12**. The structure and stereochemistry of benzyl ester **13** was established rigorously by chemical conversion to the known lactone (**15**),[15] an authentic sample of which was kindly provided by Dr. John Partridge.[16]

Having demonstrated that the bicyclo[2.1.0]pentanone incorporated in **7a** and **9** can in fact undergo the postulated thermal fragmentation process, we next subjected both systems to the conditions of the vinylogous Wolff rearrangement, that is, to thermolysis in the presence of copper(II) salt–alcohol couples. Initially our results were quite straightforward. That is, when $Cu(AcAc)_2$ was employed with benzyl alcohol, vinylogous Wolff esters **13** and **6b** were again obtained, in this case the yields were 71 and 45%, respectively. Thermolysis of **7a** and **9** in the presence of the copper triflate–benzyl alcohol couple, however, gave mixed results. In the case of **9**, vinylogous ester **6b** was again obtained, albeit in only 6% yield, the major product identified being bicycloheptanone **16**.[17] Tricyclic ketone **7a** on the other hand afforded only the bicycloheptanone **17** in 91% yield. Structural assignments for **16** and **17** were based on their elemental composition data in conjuction with comparison of their spectroscopic properties (IR, NMR) with that of methyl ether **8a** reported by Roberts.[13]



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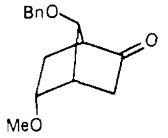

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Several comments concerning these results are in order. First, taken alone the $Cu(AcAc)_2$ result would constitute strong support for the proposed intermediacy of a bicyclo[2.1.0]pentanone or like intermediates. That is, under the reaction conditions such intermediates, prepared and characterized by alternative means, afford the vinylogous Wolff rearrangement product. In both studies, however, we are assuming that by placing the proposed tricyclic systems in contact with Cu(II) salt–alcohol couples, we in fact reproduce the precise conditions of the vinylogous Wolff rearrangement. At present however, no information concerning the fate of the copper(II) salt after the initial decomposition process exists. A possible explanation for the observed dichotomy between $Cu(AcAc)_2$ and $Cu(OTf)_2$ is that the $Cu(OTf)_2$–benzyl alcohol couple acts as a Lewis acid to induce formation of bicyclic ketones **16** and **17**. Possibly during the diazo ketone decomposition process the acidic nature of $Cu(OTf)_2$ is in some way reduced to a level such that the thermal fragmentation process of the vinylogous Wolff reaction can effectively compete.

(iii) The Vinylogous Wolff Rearrangement Revisited. At this point in our investigation, we had demonstrated the intermediacy of an unsaturated ketene and the fact that tricyclic ketones such as **7a** and **9**, which embody the bicyclo[2.1.0]pentanone system undergo efficient fragmentation to unsaturated ketenes. The missing link in the chain of evidence was direct observation of the postulated bicyclo[2.1.0]pentanone. To secure such evidence we reexamined the $Cu(AcAc)_2$-induced decomposition of diazo ketone **4** by employing infrared spectroscopy. We were by this time quite familiar with the infrared spectrum of tricyclic ketone **9** (prepared from **12**) as well as unsaturated ketene **5** and diazo ketone **4**. Each displayed quite characteristic carbonyl frequencies (ca. 1755 cm^{-1} for tricyclic ketone **9**, 2110 cm^{-1} for ketene **5**, and 2100 and 1650 cm^{-1} for diazo ketone **4**). In the event, decomposition of **4** led to the initial formation of a band at 1755 cm^{-1}, which we attribute to tricyclic ketone **9** and which appeared at the expense of the diazo ketone absorptions. As the reaction progressed, the absorption band at 1755 cm^{-1} was completely replaced by an absorption at 2110 cm^{-1}, identical with that of ketene **5**. Furthermore, we were able to follow the vinylogous Wolff reaction of **4** by TLC, observing in turn the disappearance of the diazo ketone **4** and the buildup of an intermediate having the same TLC retention index as tricyclic ketone **9**. The tricyclic ketone **9** was then replaced by a new TLC band, identical in retention index with the unsaturated ketene produced independently from thermolysis of tricyclic ketone **9**.

Having observed the formation and fragmentation of the presumed bicyclo[2.1.0]pentanone intermediate in one example, we immediately undertook preparation of diazo ketone **10a** with the intent to reproduce the above infrared and TLC observations with a second system. Unfortunately, diazo ketone **10a** failed to

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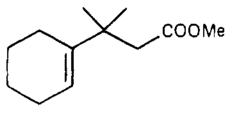
[15] Corey, E. J.; Arnold, Z.; Hutton, J. *Tetrahedron Lett.* **1970**, 307. Also see: Partridge, J. J.; Chadha, N. K.; Uskokovic, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 7171.

[16] We are grateful to Dr. John J. Partridge of Hoffman La Roche, Nutley, NJ, for the generous sample of lactone **15**.

[17] A third, as yet unidentified, product was also observed.

undergo the vinylogous Wolff rearrangement in acceptable yield (ca. 10%) for such studies.[18]

(iv) Zwitterionic Intermediates and the Vinylogous Wolff Rearrangement. One final observation concerning the mechanism of the vinylogous Wolff rearrangement deserves comment. Of the numerous systems explored, only one provided any evidence suggestive of a zwitterionic intermediate. The specific case was that of the *silver oxide* induced decomposition of diazo ketone **1**. In addition to the normal and vinylogous Wolff esters (**18** and **3**) formed respectively in 50 and 5% yield, methoxyindanone **19** was produced in 30% yield. Structural assignment for **19** will be discussed with the preparative experiments.



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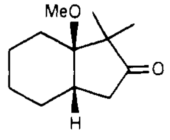
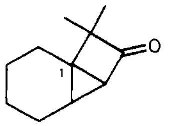
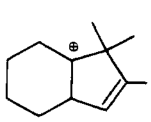


19

Two explanations are available for formation of **19**. Either the intermediate bicyclo[2.1.0]pentanone 20 undergoes addition of methanol at C(1) or zwitterionic intermediate **21** suffers capture by methanol. The basic nature of the silver oxide–methanol reaction conditions would, however, tend to preclude the latter explanation. No information concerning the genesis of the postulated zwitterionic species (i.e., directly from diazo ketone **1** or from bicyclo[2.1.0]pentanone **20**) is currently available. Finally, the generality of this observation will have to await further study of the silver oxide induced decomposition of β,γ-unsaturated diazo ketones.



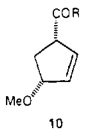
20



21

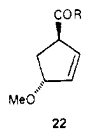
Preparative Experiments

The unsaturated diazo ketones employed in this study were prepared from the respective acid as described in the preceding article.[2] The previously unknown acid **10b** was prepared from known acid **23a**[19] in the following manner. Addition of phenylselenophtalimide[20] in the presence of methanol to methyl ester **23b** afforded a 1:1 diastereomeric mixture of methoxy selenides **24** in 92% yield. Oxidative-elimination via the Reich–Sharpless protocol[21] produced a 1:1 mixture (94%) of β,γ-unsaturated esters **10c** and **22c**, which were easily separated by preparative vapor-phase chromatography.

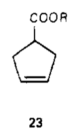


10

(a) R = CHN_2
(b) R = OH
(c) R = OMe

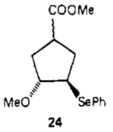


22



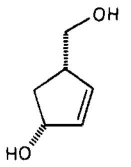
23

(a) R = OH
(b) R = OMe

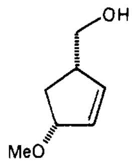


24

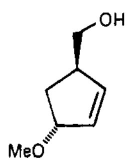
The structures of **10c** and **22c** were tentatively assigned based on consistent elemental composition data in conjunction with spectral properties. Confirmation of both the structure and stereochemistry of **10c** was obtained by chemical correlation with **25** previously prepared by Sutherland.[22] Toward this end, individual reduction of **10c** and **22c** with $LiAlH_4$ afforded unsaturated alcohols **26** and **27** respectively in 91 and 89% yield. Demethylation of **26** was then effected by treatment with excess BBr_3 in CH_2Cl_2 to yield cis-diol **25**, the NMR spectrum of which was identical with that previously reported by Sutherland. Finally, Jones oxidation of **26** gave the requisite acid (**10b**).



25

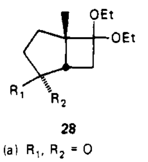


26



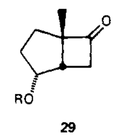
27

Preparation of Tricyclic Ketone 9. The synthesis of tricyclic ketone **9** was based in large part on the efficient dehydrohalogenation strategy developed by Roberts[12] for similar systems (i.e., **7a–d**); we, of course, utilized this protocol for preparation of **7a**. The bicyclic skeleton required for **9** was readily assembled via [2+2]-photocycloaddition of 1,1-diethoxyethylene to 3-methylcyclopenten-2-one.[23] This cycloaddition was most conveniently carried out on a 5–10-g scale employing the standard Hanovia medium-pressure Hg arc fitted with a Pyrex filter. The yield of **28a** was reproducibly in the 75–80% range. Reduction with $NaBH_4$ in the presence of 0.4 M $CeCl_3$ to assure attack of the carbonyl functionality from the less hindered convex face of the bicyclic system[24] led to endo alcohol **28b** in 89% yield as the sole product. Subsequent hydrolysis of the acetal functionality, followed by treatment with mesyl chloride and pyridine, afforded endo mesylate **29b**; the yield for the two steps was 65%. Treatment of the latter with sodium iodide in 2-butanone at reflux led to a mixture of exo and endo iodides. The ratio of exo to endo iodides was observed to depend upon conversion. The higher the conversion, the higher the yield of endo iodide **30**. Presumably, endo iodide **30** arises via a Finkelstein reaction[25] on the initially formed exo iodide. Fortunately, for our purposes, the exo iodide **12**, which proved to be a crystalline solid (mp 56–58 °C), could be readily separated from the endo isomer via flash chromatography. The exo iodide (**12**) could also be prepared directly from endo alcohol **29a** via treatment with P_2I_4 at 0 °C in carbon disulfide.[26] While the desired exo iodide was the sole product, the yield was only 20%.



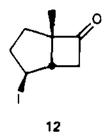
28

(a) R_1, R_2 = O
(b) R_1 = H; R_2 = OH

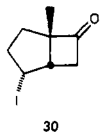


29

(a) R = H
(b) R = Ms



12



30

Stereochemical assignments for iodides **12** and **30** derive from the method of preparation in conjunction with the observation that treatment of **12** with 1.1 equiv of potassium *tert*-butoxide in anhydrous ether at −78 °C for 0.5 h led to tricyclic ketone **9**. Similar treatment of the endo iodide led only to recovery of starting material. We emphasize again that tricyclic ketone **9** could not

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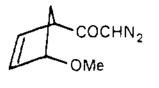
(18) A possible reason for the poor performance of diazo ketone **10a** in the vinylogous Wolff rearrangement is the close proximity of the ether oxygen to the diazo carbon, which could have a deleterious effect on the copper-promoted insertion into the β,γ-olefinic bond.



For a review on the reaction of carbenes and carbenoids with neighboring groups such as ether groups, see: Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751.

(19) Schmid, G. H.; Wolkoff, A. W. *J. Org. Chem.* **1967**, *32*, 254.

(20) Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704.

(21) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1973**, *95*, 5813. Sharpless, K. B.; Lauer, R. F. *Ibid.* **1973**, *95*, 7395.

(22) Bajorek, J. S.; Battaglia, R.; Pratt, G.; Sutherland, J. K. *J. Chem. Soc.* **1974**, 1243.

(23) For a review on the synthetic aspects of [2+2]-photochemical cycloaddition reaction, see: Baldwin, S. W. In "Organic Photochemistry"; Padwa A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 123.

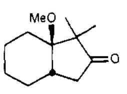
(24) Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2226. For an example exploiting the considerable steric bulk of the $NaBH_4$–Ce^{+3} reagent, see: Wencker, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 6340. Also see: Smith, A. B., III; Richmond, R. E. *J. Org. Chem.* **1981**, *46*, 4814.

(25) Finkelstein, H. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1528.

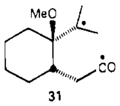
(26) Lauwers, M.; Regnier, B.; Van Eenoo, M.; Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1979**, 1801.

be isolated in the neat state without extensive decomposition. Consequently, the structural assignment for tricyclic ketone **9** is based on the solution IR and NMR spectral data. In particular, a strong carbonyl stretching frequency was observed at 1755 cm^{-1}.

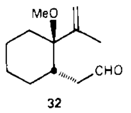
Structure Assignment of Indanone 19. In view of the potential importance of indanone **19** a chemical correlation was undertaken to establish both the structure and stereochemistry of this unknown compound. Two alternatives were available. The chemical transformation employed either must proceed in a stereospecific manner at the ring junctions of **19** or must not involve these centers. We chose the latter approach.



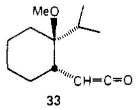
19



31

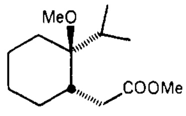


32

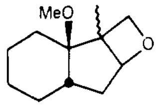


33

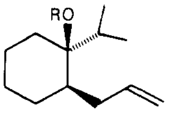
Consider for the moment the outcome of ultraviolet irradiation of indanone **19** in methanol.[27] Initial carbon–carbon bond cleavage α to the more highly substituted side of the carbonyl functionality (i.e., Norrish type I process) would lead to biradical **31**. Disproportionation via hydrogen atom transfer would then lead to aldehyde **32** and/or ketene **33**. Capture of the latter with methanol would produce methyl ester **34**. Significant from the view of structure proof, the relative configuration at the ring junction would be unaffected via such a transformation.



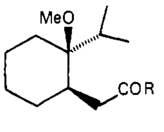
34



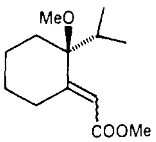
35



36
(a) R = H
(b) R = Me



37
(a) R = H
(b) R = OMe



38

In the event, irradiation of **19** in methanol led as anticipated to methyl ester **34**; the yield was 62%. Also obtained as a minor product was oxetane **35**. Presumably the latter derives from aldehyde **32** via a secondary intramolecular [2+2]-photocycloaddition.

Having tentatively assigned the structure of methoxy ester **34** on the basis of the spectroscopic properties, it was now incumbent upon us to prepare **34** with appropriate stereochemistry via an alternative method. To this end addition of isopropylmagnesium chloride to 2-allylcyclohexanone[28] afforded alcohol **36a** in 52% yield as well as the reduced starting material, 2-allylcyclohexanol. The stereochemical assignment of **36a** is based on the classical observations of Nazarov,[29] namely that the major mode of addition of alkyl Grignards to 2-substituted cyclohexanones occurs from the equatorial direction. Methylation of **36a** with sodium hydride and methyl iodide afforded **36b** in 76% yield, which in turn was subjected to ozonolysis followed by reductive workup (dimethyl sulfide). Oxidation of the resultant aldehyde **37a** with Jones reagent[30] and esterification with diazomethane afforded a single methoxy methyl ester **37b** in 92% overall yield from **36b**. While **37b** possessed quite similar spectroscopic properties, the two compounds (**37b** and **34**) were clearly different. The simplest explication was that the two compounds were diastereomeric.

To obtain the alternative diastereomer (i.e., **34**), we subjected **37b** to the Reich–Sharpless oxidative-elimination protocol.[21] A single unsaturated ester (**38**) was obtained in 77% yield. The configuration about the double bond was not determined.

It was now expected (hoped) that hydrogenation of **38** would provide both diastereomers (**34** and **37b**). In the event, however, a single product in 95% yield was obtained. Fortunately, the spectral properties proved to be identical in all respects with those of the product derived via photolysis of indanone **19**. Thus, having prepared both possible diastereomers (one via a stereocontrolled process) and having demonstrated that one possessed identical spectroscopic properties with the product derived from **19**, a rigorous structural proof was in hand. As anticipated the stereochemistry at the ring juncture was cis.

Summary

In this and the preceding paper[2] we have demonstrated that the vinylogous Wolff rearrangement is a general reaction of β,γ-unsaturated diazo ketones. Furthermore, we have provided evidence that the rearrangement involves initial copper-promoted insertion of the diazo carbon into the β,γ-olefinic bond. The resultant bicyclo[2.1.0]pentan-2-one then undergoes a thermal fragmentation to a β,γ-unsaturated ketene, which in turn is captured by available nucleophiles (i.e., alcohols) to afford the observed γ,δ-unsaturated esters. Given the ready availability of β,γ-unsaturated diazo ketones, we anticipate that the vinylogous Wolff rearrangement holds considerable promise in the area of natural product synthesis.

Experimental Section[31]

Preparation of Tricyclic Ketone 7a. Following the procedure of Roberts,[13] a solution of 1.1 equiv of potassium *tert*-butoxide (71.6 mg, 0.638 mmol) in 1 mL of ether was cooled to −78 °C under argon. Cyclobutanone **11** (127.1 mg, 0.587 mmol) in 2 mL of ether was added dropwise, and the reaction mixture stirred for 1 h at −78 °C. The mixture was filtered through Celite and evaporated to dryness in vacuo at room temperature to afford 70.9 mg of tricyclic ketone **7a** (88%). Tricyclic ketone **7a** was identical with that previously prepared by Roberts.[13]

Thermolysis of Tricyclic Ketone 7a in the Presence of Benzyl Alcohol. Tricyclic ketone **7a**[13] (108 mg, 0.78 mmol) was dissolved in 75 mL of cyclohexane. Benzyl alcohol (101 mg, 1.23 equiv) was added, and the solution was heated at reflux under a nitrogen atmosphere for 1.5 h. Upon cooling, the reaction mixture was concentrated in vacuo to provide 201 mg of an oil. Product analysis on column E indicated the presence of only one component. An analytical sample obtained by preparative VPC was determined to be *c*-5-methoxy-2-cyclopentene-*r*-1-acetic acid benzyl ester (**13**) (96% yield), which possessed the following spectral characteristics: IR 3070 (w), 3030 (w), 3010 (w), 2935 (m), 2835 (m), 1725 (s), 690 (s) cm^{-1}; NMR (360 MHz) δ 1.30–1.43 (m, 3 H), 1.63 (dd, J = 18 Hz, J' = 5 Hz, 1 H), 3.13–3.23, 3.21 (m, s, 4 H), 3.95–4.02 (m, 1 H), 5.12 (AB q, J = 9 Hz, J' = 12.6 Hz, 2 H), 5.61–5.72 (m, 2 H),

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(27) For a review on the Norrish Type I Reaction in Cycloalkanes, see: Weiss, D. S. In ref 23, p 347.

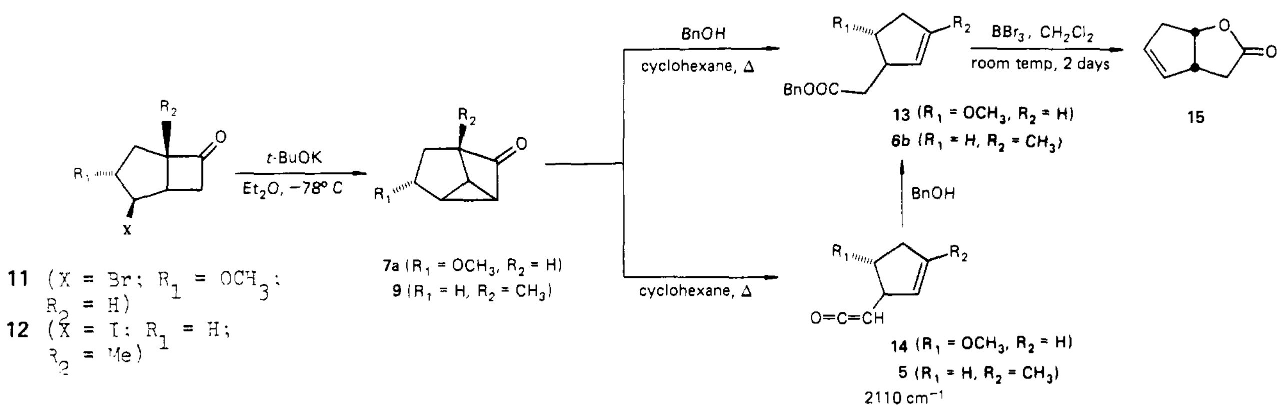
(28) Conia, J.-M.; Leyendecker, F. *Bull. Soc. Chim. Fr.* **1967**, 830.

(29) Nazarov, I. N.; Akhrem, A. A.; Kamernitzky, A. V. *Izv. Akad. Nauk SSSR Otd. Khim, Nauk* **1958**, 631.

(30) Bowers, A.; Halsall, T. C.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548. Djerassi, C.; Engle R. R.; Bowers, A. *J. Org. Chem.* **1956**, *21*, 1547.

(31) **Materials and Methods.** Separations were accomplished on a Varian Aerograph Model 920 employing one of the following columns: A, 25% Carbowax 20 M, 10 ft × 0.375 in.; B, 6% Carbowax 20 M, 50 ft × 0.25 in.; C, 6% SE-30, 10 ft × 0.375 in.; D, 25% DEGS, 10 ft × 0.375 in.; E, 6% Carboxax 20 M, 10 ft × 0.375 in.; the column oven was operated at 150–190 °C and the helium carrier gas flow rate was 100–120 mL/min. Compounds purified by the VPC were obtained as colorless liquids. All yields were determined by VPC calibration methods unless otherwise noted. Melting points were taken on a Thomas Hoover capillary melting point apparatus and were corrected; boiling points were uncorrected. Solutions were dried over MgSO$_4$. IR spectra were obtained for CCl$_4$ solutions on a Perkin-Elmer Model 337 spectrometer. NMR spectra were obtained on a Varian A-60 (60 MHz, CCl$_4$), T-60 (60 MHz, CCl$_4$), HR-220 (220 MHz, CCl$_4$), Bruker WM-250 (250 MHz, CDCl$_3$), and WH-360 (360 MZ, CDCl$_3$) spectrometers. Carbon-13 spectra were obtained in CDCl$_3$ on a JEOL PS-100 spectrometer. The internal standard for both ^{1}H and ^{13}C NMR spectroscopy was Me$_4$Si. Photochemical experiments were carried out with a Hanovia Model L mercury lamp (No. 679A-360) in a quartz immersion well with use of a Pyrex 7740 as a filter. All liquids, reagents, and solvents were distilled prior to use. The following drying agents were employed: CaH$_2$ for cyclohexane and hexamethylphosphoramide (HMPA) and sodium-benzophenone for THF and Et$_2$O. Copper(II) acetylacetonate was obtained from Alfa.

Scheme I



7.24–7.38 (m, 5 H); electron impact mass spectrum *m/e* 246.1235 (calcd M^+ for $C_{15}H_{18}O_3$, 246.1255).

Preparation of *cis*-3,3a,6,6a-Tetrahydro-2*H*-cyclopenta[*b*]furan-2-one (15). Ester **13** (21.4 mg, 0.092 mmol) was dissolved in 5 mL of CH_2Cl_2. Upon cooling to −78 °C under a nitrogen atmosphere, BBr_3 (87 μL, 10 equiv) was added. The reaction mixture, having stirred for 1 h at −78 °C and 2 days at room temperature, was washed with 5 mL of H_2O and dried. Removal of the solvent in vacuo afforded 25.0 mg of an oil. Product analysis on column C indicated the presence of two components. A sample of each was obtained by preparative VPC. The first fraction was benzyl alcohol; the second, lactone **15** (93% yield), had identical IR and NMR spectra to that of an authentic sample of **15** provided to us by Dr. J. Partridge of Hoffman-La Roche.[16]

Thermolysis of Tricyclic Ketone 7a in the Absence of Benzyl Alcohol. Tricyclic ketone **7a** prepared as described above was dissolved in 1 mL CCl_4 and heated slowly to reflux. A sample was removed and ketene formation followed by the appearance of an infrared band of 2110 cm^{-1} and the disappearance of the carbonyl band at 1750 cm^{-1}. The remainder of the reaction mixture was dissolved in 20 mL of tetrahydrofuran containing 50 μL of benzyl alcohol and heating was continued. Isolation in the usual manner confirmed the formation of benzyl ester **13**.

Thermolysis of Tricyclic Ketone 7a in the Presence of $Cu(OTf)_2$ and Benzyl Alcohol. Ketone **7a**[13] (71.0 mg, 0.521 mmol) was dissolved in a solution consisting of cyclohexane (75 mL), benzyl alcohol (85.0 mg, 1.2 equiv), and $Cu(OTf)_2$ (10 mol %). The resultant mixture was heated at reflux under a nitrogen atmosphere for 1.5 h. Upon cooling the contents were washed with 25 mL of 10% aqueous HCl and dried. Removal of the solvent in vacuo afforded 190 mg of an oil. Product analysis on column E indicated the presence of a single compound. An analytical sample of ketone **17** (91% yield), obtained by preparative VPC possessed the following spectral characteristics: IR 3085 (w), 3060 (w), 3030 (m), 3025 (m), 2975 (m), 2930 (s), 2895 (s), 2815 (m), 1745 (s), 1220 (s), 1150 (s), 1110 (s), 1085 (s), 1030 (m), 980 (m), 935 (w), 905 (m), 690 (s) cm^{-1}; NMR (360 MHz) δ 1.38–1.47 (m, 2 H), 1.92 (dd, $J = 18$ Hz, $J' = 4$ Hz, 1 H), 2.43–2.62 (m, 2 H), 2.68 (d, $J = 4$ Hz, 1 H), 2.83–2.90 (m, 1 H), 3.30 (s, 3 H), 4.01 (d, $J = 1$ Hz, 1 H), 4.20–4.29 (m, 1 H), 4.50 (s, 2 H), 7.28–7.38 (m, 5 H); electron impact mass spectrum *m/e* 246.1251 (calcd M^+ for $C_{15}H_{18}O_3$, 246.1255).

Tricyclic Ketone 9: Preparation of Ketal 28a. A solution of 3-methyl-2-cyclopentenone (5.72 g, 0.059 mol) and 1,1-diethoxyethylene (12.3 g, 0.106 mol) in 750 mL of anhydrous benzene was degassed with argon for 20 min and then irradiated through Pyrex for 48 h. The reaction was monitored by thin-layer chromatography [(50:50) ether/hexane (v/v)]. The solvent was then removed in vacuo and excess 1,1-diethoxyethylene was removed via distillation through a short vigreux column. Flash chromatography[32] (silica gel, 20% ether–hexane (v/v)) afforded ketal **28a** as a colorless oil (9.67 g, 77%); IR 2850–3000 (s), 1740 (s), 1445 (m), 1380 (m), 1250 (m), 1150 (m), 1040 (s), 1110 (w), 970 (w), 925 (w), 835 (w) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.12 (t, $J = 6.3$ Hz, 3 H), 1.10 (t, $J = 6.3$ Hz, 3 H), 1.22 (s, 3 H), 1.56–1.77 (m, 1 H), 2.08 (m, 2 H), 2.25–2.66 (m, 4 H), 3.22–3.55 (m, 4 H); electron impact mass spectrum *m/e* 212.1415 (M^+, calcd for $C_{12}H_{20}O_3$, 212.1418).

Preparation of Alcohol 28b. Ketone **28a** (301 mg, 1.42 mmol) was dissolved in a solution of cerium chloride (3.55 mL, 0.4 M $CeCl_3$) in methanol. The reaction mixture was cooled to 0 °C, and sodium borohydride (53.9 mg, 1.42 mmol) was added slowly with stirring. The mixture was allowed to stir for 10 min, followed by the addition of water to destroy excess sodium borohydride. The solution was then extracted with ether, washed with brine, and dried. Removal of solvent in vacuo afforded 273 mg (89%) of **28b** as a pale yellow oil: IR 3640 (w, sh), 3160–3575 (m, br), 2800–3040 (s), 1450 (m), 1395 (m), 1345 (w), 1260 (s), 1120 (m), 1045 (s), 990 (w), 925 (m), 845 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.08–1.30 (m, 9 H), 1.58–2.06 (m, 7 H), 3.14 (d, $J = 12$ Hz, 1 H), 3.22–3.40 (m, 4 H), 4.22 (m, 1 H); electron impact mass spectrum *m/e* 214.1573 (M^+, calcd for $C_{12}H_{22}O_3$, 214.1569).

Preparation of Cyclobutanone 29a. A mixture of ketal **28b** (273 mg, 1.28 mmol), 3 mL of acetic acid, 2 mL of water, and 2 mL of tetrahydrofuran was stirred under nitrogen for 1.5 h. The reaction mixture was poured into ether, washed with water and brine, and dried over potassium carbonate. After concentration under reduced pressure, residual acetic acid was removed in vacuo via an ether–heptane azeotrope. Purification via flash chromatography[32] on silica gel (50:50 ether:hexane) afforded **29a** [138 mg (78%)] as a colorless oil: IR 3635 (w, sh), 3100–3600 (m, br), 2800–3000 (s), 1770 (s), 1445 (m), 1390 (m), 1250 (w), 1110 (m), 1080 (s), 1050 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.20 (s, 3 H), 1.24–1.68 (m, 1 H), 1.60–1.68 (m, 2 H), 1.89–2.14 (m, 2 H), 2.52 (m, 1 H), 2.98–3.14 (ABX m, $J_{ab} = 17$ Hz, $J_{ax} = 8$ Hz, $J_{bx} = 6$ Hz, 2 H), 4.44–4.60 (m, 1 H); electron impact mass spectrum *m/e* 140.0833 (M^+, calcd for $C_8H_{12}O_2$, 140.0837).

Preparation of Mesylate 29b. To a solution of alcohol **28b** (242 mg, 1.73 mmol) in 5 mL of methylene chloride cooled to 0 °C was added 1.5 equiv (362 μL, 2.60 mmol) of triethylamine. Methanesulfonyl chloride (161 μL, 2.07 mmol) was then slowly added to the reaction mixture, and the resultant mixture was allowed to stand at 0 °C for 2 h. The solution was then poured onto ice and extracted into ether, washed with cold 10% hydrochloric acid, sodium bicarbonate, and brine, and dried. The solvent was evaporated in vacuo to afford 313 mg (83%) of mesylate **29b** as a colorless oil: IR ($CHCl_3$) 2805–3150 (m), 1760 (s), 1450 (m), 1350 (s), 1180 (s), 1080 (m), 995 (m), 965 (s), 930 (m), 890 (s), 830 (m), 720 (m) cm^{-1}; NMR (60 MHz, CCl_4) δ 1.20 (s, 3 H), 1.4–2.35 (comp m, 4 H), 2.65–2.95 (m, 1 H), 3.0 (s, 3 H), 3.0–3.2 (m, 2 H), 4.95–5.25 (m, 1 H).

Preparation of Iodides 12 and 30. Mesylate **29b** (1.36 g, 6.30 mmol) was heated at reflux under argon in 40 mL of dry 2-butanone with 1.2 equiv of sodium iodide (1.12 g, 7.64 mmol) for 24 h. The reaction mixture was filtered through a plug of glass wool and then evaporated in vacuo. Separation and purification of the resultant mixture by silica gel flash chromatography[32] (20:80 ether/hexane) afforded iodides **12** and **30** (51 and 31%, respectively).

The higher R_f material, iodide **12** (810 mg, 51%), was a white crystalline solid (mp 56–57.5 °C), which displayed the following spectral properties: IR ($CHCl_3$) 2825–3050 (s), 1755 (s), 1450 (s), 1380 (s), 1320 (m), 1290 (m), 1275 (m), 1230 (m), 1160 (m), 1065 (s), 990 (m), 970 (m), 890 (m), 865 (m), 830 (m), 710 (m), 640 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.40 (s, 3 H), 1.94–2.32 (m, 4 H), 2.42 (dd, $J = 10.0$, 25.0 Hz, 1 H), 2.96–3.18 (m, 2 H), 4.48 (br d, $J = 4.5$ Hz, 1 H); chemical ionization mass spectrum *m/e* 250.9935 (MH^+, calcd for $C_8H_{12}IO$, 250.9933).

The lower R_f isomer, iodide **30** (493 mg, 31%), was a colorless oil, which displayed the following spectral properties: IR ($CHCl_3$) 2825–3050 (s), 1760 (s), 1450 (m), 1370 (m), 1290 (m), 1220 (m, br), 1180 (m), 1160 (m), 1135 (m), 1085 (s), 990 (w), 970 (w), 890 (w), 870 (m), 830 (w), 720 (m, br), 660 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.28 (s, 3 H), 1.42 (ddd, $J = 6.0$, 10.0, 20.0 Hz, 1 H), 1.90 (dd, $J = 6.0$, 14.0 Hz, 1 H), 2.02–2.24 (m, 1 H), 2.26–2.44 (m, 1 H), 2.64–2.78 (m, 1 H), 2.88 (dd, $J = 5.0$, 20 Hz, 1 H), 3.16 (dd, $J = 10.0$, 20.0 Hz, 1 H), 4.42 (dt, $J = 8.0$, 5.0, 5.0 Hz, 1 H); chemical ionization mass spectrum *m/e* 250.9993 (MH^+, calcd for $C_8H_{12}IO$, 250.9993).

Preparation and Thermolysis of Tricyclic Ketone 9 in the Presence of Benzyl Alcohol. A solution of 1.1 equiv of potassium *tert*-butoxide (39.7 mg, 0.354 mmol) in 1 mL of ether was cooled to −78 °C under an argon atmosphere. Cyclobutanone **12** (80.5 mg, 0.322 mmol) was added in 1 mL of ether, and the reaction was stirred for 1 h at −78 °C. The reaction mixture was then filtered through Celite and evaporated almost to dryness. It is important that the solution was never allowed to evaporate completely to dryness due to the instability of tricyclic ketone **9** (i.e., fragmentation to the ketene). The infrared spectrum of **9** displayed a strong absorption at 1755 cm^{-1}, and the high-field (250 MHz) ^{1}H NMR spectrum was δ 1.22 (s, 3 H), 1.50–1.88 (m, 4 H), 1.98–2.46 (m, 2 H), 2.78 (ddd, J = 12, 8, 5 Hz, 1 H).

The reaction mixture was dissolved in 35 mL of tetrahydrofuran. Benzyl alcohol (47 μL, 1.5 equiv) was added and the solution was heated at reflux under argon for 1.5 h. After cooling the reaction mixture was flash chromatographed[32] [2% ether/hexane (v/v)] and benzyl ester **6b**[2] (41.1 mg) was obtained as a colorless oil in 59% yield from iodide **12**.

Thermolysis of Tricyclic Ketone 9 in the Absence of Benzyl Alcohol. Tricyclic ketone **9**, prepared from iodide **12** (31.3 mg) as described above, was dissolved in 1 mL of carbon tetrachloride and slowly heated to reflux. A small sample was removed and ketene formation was followed by formation of an infrared band at 2110 cm^{-1} and disappearance of the ester carbonyl absorption at 1755 cm^{-1}. The remainder of the reaction mixture was dissolved in 20 mL of tetrahydrofuran containing 50 μL of benzyl alcohol, and the mixture heated at reflux. Isolation in the usual manner confirmed the formation of benzyl ester **6b**.

Thermolysis of Tricyclic Ketone 9 in the Presence of Cu(AcAc)$_2$ and Benzyl Alcohol. To tricyclic ketone **9** (prepared from 35.0 mg of iodide **12** as described above) in 20 mL of tetrahydrofuran were added 4 mg of Cu(AcAc)$_2$ and 22 μL (1.5 equiv) of benzyl alcohol. The reaction mixture was heated at reflux for 2 h. Upon cooling, the mixture was extracted with ether, washed with 10% aqueous HCl, dried over $MgSO_4$, and concentrated in vacuo. After flash chromatography[32] (2% ether/hexane (v/v)), benzyl ester **6b** (13.1 mg) was isolated in 45% yield. TLC analysis of the reaction mixture prior to purification showed no trace of the bicycloheptanone **16**.

Thermolysis of Tricyclic Ketone 9 in the Presence of Cu(OTf)$_2$ and Benzyl Alcohol. Tricyclic ketone **9**, prepared from iodide **12** (47.8 mg) as described previously, was dissolved in 30 mL of tetrahydrofuran. Benzyl alcohol (30 μL, 1.5 equiv) and Cu(OTf)$_2$ (5 mg, 10 mol %) were added, and the reaction was heated at reflux for 2 h. Upon cooling, the mixture was extracted with ether. The latter was washed with 10% aqueous HCl, dried, and concentrated in vacuo. After flash chromatography[32] [2% ether/hexane (v/v)] benzyl ester **6b** (5.0 mg, 6%) and bicycloheptanone **16** (20.1 mg, 22%) were isolated.

Bicycloheptanone **16** displayed the following spectroscopic properties: IR (CCl_4) 2800–3100 (m), 1755 (s), 1400 (m), 1350 (m), 1300 (w), 1160 (m), 1145 (m), 1110 (s), 1060 (m), 695 (m) cm^{-1}; NMR (250 MHz, $CDCl_3$) δ 1.12 (s, 3 H), 1.28–1.54 (m, 2 H), 1.96–2.22 (m, 4 H), 2.62 (bs, 1 H), 3.48 (s, 1 H), 4.60 (AB q, J_{AB} = 11 Hz, 2 H), 7.24–7.46 (m, 5 H); electron impact mass spectrum m/e 230.1307 (M$^+$, calcd for $C_{15}H_{18}O_2$, 230.1307).

Preparation of *cis*- and *trans*-4-Methoxy-2-cyclopentene-1-carboxylic Acid Methyl Ester (10c and 22c). Into 100 mL of dry methylene chloride were dissolved 3-cyclopentene-1-carboxylic acid methyl ester (**23b**)[19] (1.26 g, 10.0 mmol), phenylselenophthalimide[20] (3.18 g, 1.05 equiv), camphorsulfonic acid (46.4 mg, 2 mol %), and methanol (1.28 g, 4 equiv). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 24 h. Phthalimide, which formed as a byproduct, precipitated out of solution. The contents were filtered, concentrated in vacuo, and the desired seleno ester was purified by flash column chromatography[32] (10% ether:methylene chloride) to afford 2.89 g (92% yield) of a 1:1 diastereomeric mixture of *r*-3-methoxy-*t*-4-phenylselenocyclopentanecarboxylic acid methyl ester (**24**): IR 3075 (w), 3030 (w), 2965 (m), 2950 (m), 2925 (m), 1735 (s), 700 (s) cm^{-1}; NMR (60 MHz) δ 1.67–3.13 (m, 5 H), 3.19, 3.21 (s, s, total of 3 H), 3.55–3.95, 3.66 (m, s, 5 H), 7.19–7.78 (m, 5 H); electron impact mass spectrum m/e 314.0428 (calcd M$^+$, for $C_{14}H_{18}O_3Se$, 314.0421).

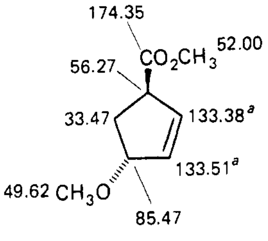
Seleno ester **24** (1.44 g, 4.59 mmol) was dissolved in 50 mL of THF. At 0 °C under a nitrogen atmosphere, 30% aqueous H_2O_2 (4.60 mL) was added dropwise. Stirring was continued at room temperature for 2 h. The reaction mixture was washed with saturated aqueous sodium bicarbonate and extracted with 3 × 50 mL of ether. The combined organic extracts were washed with brine and dried. Removal of the solvent in vacuo followed by distillation (85–87 °C/2.5 mmHg) afforded 673.1 mg (94% yield) of a 1:1 mixture of *cis*- and *trans*-4-methoxy-2-cyclopentene-1-carboxylic acid methyl ester (**10c** and **22c**, respectively). An analytical sample of each isomer was obtained by preparative VPC.

The first component was *trans*-4-methoxy-2-cyclopentene-1-carboxylic acid methyl ester (**22c**): IR 3010 (w), 2985 (s), 2955 (w), 1735 (s) cm^{-1}; NMR (360 MHz) δ 2.05 (ddd, J = 13.2 Hz, J' = 7.7 Hz, J'' = 2.5 Hz, 1 H), 2.44 (ddd, J = 13.7 Hz, J' = 7.7 Hz, J'' = 4.9 Hz, 1 H), 3.34 (s, 3 H), 3.69 (s, 3 H), 3.72–3.80 (m, 1 H), 4.55–4.62 (m, 1 H), 5.98–6.06 (m, 2 H); ^{13}C NMR (25 MHz) δ 33.47 (t), 49.62 (q), 52.00 (q), 56.27 (d), 85.47 (d), 133.38 (d), 133.51 (d), 174.35 (s).

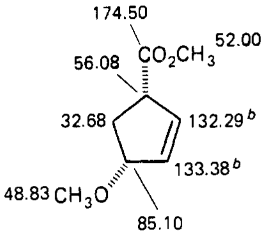
Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.40; H, 7.68.

The second component was *cis*-4-methoxy-2-cyclopentene-1-carboxylic acid methyl ester (**10c**): IR 3010 (m), 2975 (s), 2965 (w), 2945 (m), 1735 (s) cm^{-1}; NMR (360 MHz) δ 2.05 (ddd, J = 14.8 Hz, J' = 7.2 Hz, J'' = 4.6 Hz, 1 H), 2.51 (ddd, J = 14.4 Hz, J' = 10.15 Hz, J'' = 7. Hz, 1 H), 3.35 (s, 3 H), 3.43–3.52 (m, 1 H), 3.71 (s, 3 H), 4.43–4.51 (m, 1 H), 5.94–6.02 (m, 2 H); ^{13}C NMR (25 MHz) δ 32.68 (t), 48.83 (q), 52.00 (q), 56.08 (d), 85.10 (d), 132.29 (d), 133.38 (d), 174.50 (s).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.22; H, 7.73.



22c



10c

a, b; interchangeable

Preparation of *cis*- and *trans*-4-Methoxy-2-cyclopentene-1-methanol (26 and 27). To a stirred suspension of lithium aluminum hydride (103 mg, 2.72 mmol) in 25 mL of ether cooled to 0 °C under a N_2 atmosphere was added dropwise trans ester **22c** (213 mg, 1.36 mmol) dissolved in 10 mL of ether. The reaction mixture was then stirred at room temperature for 4 h followed by cooling to 0 °C. Cautiously 3 mL each of H_2O and 5% aqueous sodium hydroxide were added. The contents were poured into 25 mL of H_2O and extracted with ether. The combined organic extracts were washed with brine and dried. Removal of the solvent in vacuo followed by distillation (92–94 °C/2.5 mmHg) afforded *trans*-4-methoxy-2-cyclopentene-1-methanol (**27**) (154.9 mg, 89% yield). An analytical sample was obtained by preparative VPC and had the following spectral properties: IR 3640 (w), 3575–3120 (broad, s), 3115 (w), 2940 (s), 2885 (s), 2825 (s) cm^{-1}; NMR (60 MHz) δ 1.53–1.82 (m, 2 H), 2.67–3.62, 3.27 (m, s, 7 H), 4.28–4.57 (m, 1 H), 5.95 (s, 2 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.87; H, 9.27.

In a similar manner, ester **10c** (286 mg, 1.83 mmol) was reduced to *cis*-4-methoxy-2-cyclopentene-1-methanol (**26**) (213.2 mg, 91% yield). An analytical sample obtained by preparative VPC possessed the following spectral characteristics: IR 3640 (w), 3570–3125 (broad, s), 3115 (w), 2940 (s), 2875 (s), 2830 (s) cm^{-1}; NMR (60 MHz) δ 1.13–1.68 (m, 1 H), 1.93–2.97 (m, 2 H), 3.28 (s, 3 H), 3.33–3.55 (m, 2 H), 3.33–3.55 (m, 2 H), 4.27 (dd, J = 7 Hz, J' = 3 Hz, 1 H), 5.90 (s, 1 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.85; H, 9.33.

Preparation of *cis*- and *trans*-4-Methoxy-2-cyclopentene-1-carboxylic Acid (10b and 22b). Hydroxy ether **26** (119 mg, 0.93 mmol) was dissolved in 25 mL of reagent grade acetone. At 0 °C under a nitrogen atmosphere, Jones reagent[30] (1.33 mL, 1.4 M, 2 equiv) was slowly added. After stirring for 1 h at room temperature, 2-propanol (~0.5 mL) was added to quench any unreacted Jones reagent. The contents were poured into 25 mL of H_2O and extracted with ether. The combined organic material was washed with brine and dried. Removal of the solvent in vacuo followed by distillation (102–105 °C/2 mmHg) afforded cis acid **10b** (106 mg, 80% yield), which had the following spectral properties: IR 3500–2400 (broad, s), 1700 (s) cm^{-1}; NMR (60 MHz) δ 1.98–2.73 (m, 2 H), 3.20–3.60, 3.32 (m, s, 4 H), 4.22–4.56 (m, 1 H), 5.95 (s, 2 H), 10.25 (m, 1 H).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.33; H, 7.15.

In a similar manner, trans hydroxy ether **27** (115 mg, 0.90 mmol) was oxidized to trans carboxylic acid **22b** (105 mg, 82% yield) with Jones reagent. This acid had the following spectral properties: IR 3550–2400 (broad, s), 1705 (s) cm^{-1}; NMR (60 MHz) δ 1.73–2.78 (m, 2 H), 3.26 (s, 3 H), 3.40–3.85 (m, 1 H), 4.23–4.71 (m, 1 H), 5.97 (broad, 2 H), 11.07 (m, 1 H).

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09 Found: C, 59.34; H, 7.08.

Cu(II)-Catalyzed Decomposition of *c*-1-(1′-Diazo-2′-oxoeth-2′-yl)-*r*-4-methoxycyclopentene (10a). Diazo ketone **10a** (55.6 mg, 0.33 mmol), prepared in 91% from acid **10b** as described in general procedure C, in

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(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

the preceding paper, was decomposed with $Cu(OTf)_2$ and benzyl alcohol as described in general procedure D to afford 51.4 mg. Interestingly diazo ketone **10a** was only slightly soluble in cyclohexane. Product analysis on column E indicated the presence of two components. An analytical sample of each was obtained by preparative VPC. The first fraction was determined to be benzyl alcohol. The second fraction was determined to be ester **13** (10% yield), which had identical IR and NMR spectra with the ester obtained by the reaction of tricyclic ketone **7a** with benzyl alcohol.

Preparation of *c*-4-Hydroxymethyl-2-cyclopentene-*r*-1-ol (25). Hydroxy ether **26c** (22.1 mg, 0.17 mmol) was dissolved in 10 mL of CH_2Cl_2. Upon cooling to −78 °C under a nitrogen atmosphere BBr_3 (160 μL, 10 equiv) was added. The reaction mixture was stirred for 1 h at −78 °C and for 2 days at room temperature, washed with 5 mL of H_2O, and dried. Removal of the solvent in vacuo followed by distillation (138–142 °C/1 mmHg) afforded 3.8 mg of diol **25**, which had an identical NMR spectrum with that previously reported by Sutherland.[22]

Ag(I)-Induced Decomposition of 1-(1′-Diazo-3′,3′-dimethyl-2-oxoprop-3′-yl)cyclohexene (1). Diazo ketone **1** (1.45 g, 7.57 mmol), prepared in 92% yield from α,α-dimethyl-1-cyclohexene-1-acetic acid[33] was dissolved in 50 mL of anhydrous MeOH. Silver(I) oxide (182 mg, 10 mol %) was added and the contents heated at reflux under a nitrogen atmosphere for 4 h. A silver mirror formed on the walls of the glass. The reaction mixture was poured into 50 mL of 10% aqueous HCl and extracted with ether. The combined organic material was washed with brine and dried. Removal of the solvent in vacuo afforded 1.38 g of an oil. Product analysis on column A indicated the presence of three components. An analytical sample of each was obtained by preparative VPC.

The first fraction was β,β-dimethyl-1-cyclohexene-1-propionic acid methyl ester (**18**)[2] (50%): IR 2975 (s), 2965 (s), 2935 (s), 1735 (s) cm^{-1}; NMR (220 MHz) δ 1.10 (s, 6 H), 1.46–1.74 (m, 4 H), 2.94–2.06 (m, 4 H), 2.25 (s, 2 H), 3.56 (s, 3 H), 5.40 (broad s, 1 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.34; H, 10.15.

The second fraction was 2-(1′-methylethylidene)-1-cyclohexaneacetic acid methyl ester (**3**)[2] (5%).

The third fraction was 3a-methoxy-3,3-dimethyl-*cis*-indan-2-one (**19**) (30%): IR 2980 (s), 2965 (s), 2935 (s), 1740 (s) cm^{-1}; NMR (220 MHz) δ 0.78–1.65, 0.98, 1.03 (m, s, s, 12 H), 1.72–2.48 (m, 5 H), 3.25 (s, 3 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.17.

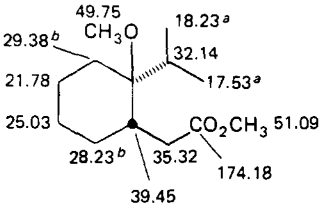
Ketone **19** was purified on a preparative scale as follows: 2.59 g of the material obtained above was added to 20 mL each of 5% aqueous NaOH and methanol and heated at reflux under a nitrogen atmosphere overnight. The reaction mixture was extracted with ether and dried. Removal of the solvent in vacuo followed by distillation afforded 889.5 mg of ketone **19**.

Photolysis of 3a-Methoxy-3,3-dimethyl-*cis*-indan-2-one (19). Ketone **19** (504 mg, 2.57 mmol) dissolved in 65 mL of anhydrous methanol was placed in a Pyrex collar, degassed, and irradiated for 24 h. Removal of the solvent in vacuo afforded 578 mg of an oil. Product analysis on column A indicated the presence of two components. An analytical sample of each was obtained by preparative VPC.

The first fraction was 2b-methoxy-2a-methyl-*cis*-2*H*-oxeto[2′,3′:4,5]indane (**35**) (29% yield): IR 2990 (s), 2975 (s), 2935 (s) cm^{-1}; NMR (220 MHz) δ 1.03–2.18, 1.17 (m, s, 14 H), 3.04 (s, 3 H), 4.19 (d, J = 7 Hz, 1 H), 4.35 (d, J = 7 Hz, 1 H), 4.72 (t, J = 5 Hz, 1 H).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.31; H, 10.30.

The second component was *t*-2-methoxy-2-(1-methylethyl)-*r*-1-cyclohexaneacetic acid methyl ester (**34**) (62% yield): IR 2980 (s), 2960 (s), 1735 (s) cm^{-1}; NMR (60 MHz) δ 0.87–2.42, 0.95 (m, t, J = 7 Hz, 18 H), 3.22 (s, 3 H), 3.63 (s, 3 H); ^{13}C NMR (25 MHz) δ 17.53 (q), 18.23 (q), 21.78 (t), 25.03 (t), 28.23 (t), 29.38 (t), 32.14 (d), 35.32 (t), 39.45 (d), 49.75 (q), 51.09 (q), 174.18 (s).



a, b; interchangeable

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.50; H, 10.44.

Preparation of 1-(1′-Methylethyl)-*c*-2-(3′-propenyl)cyclohexan-*r*-1-ol (36a). Allyl bromide (47.8 g, 1.5 equiv) was added over a period of 1 h to a solution of 1-*N*-pyrrolidino-1-cyclohexene (40.2 g, 0.266 mmol) in 200 mL of absolute methanol held at reflux. Heating was maintained for 3 h, and then 20 mL of water was added and heating continued for 4 h. Upon cooling the methanol was removed in vacuo and the residue was distilled (75–77 °C/6 mmHg) to afford 31.9 g (87% yield) of 2-(3′-propenyl)cyclohexanone, which had spectral properties in agreement with literature values:[28] IR 3080 (w), 2925 (s), 2855 (s), 1705 (s), 1645 (w), 905 (s) cm^{-1}; NMR (60 MHz) δ 1.00–2.83 (m, 11 H), 4.82–5.13 (m, 2 H), 5.46 (m, 1 H).

To a stirred solution of isopropylmagnesium chloride (ether, 2.3 M, 47 mL, 2.5 equiv) in 80 mL of ether chilled to −78 °C under a nitrogen atmosphere was added dropwise the above ketone (10.0 g, 72.5 mmol). The resulting mixture was allowed to stir for 2 h at −78 °C and then at 0 °C for 3 h, at which time 20 mL of H_2O was added dropwise. The mixture was then stirred for 12 h, washed with 50 mL of 20% HCl and brine, and dried. Removal of the solvent in vacuo followed by distillation afforded 10.4 g of an oil whose IR spectrum possessed a sharp hydroxyl band at 3550 cm^{-1} as well as a carbonyl band at 1705 cm^{-1}, which indicated the presence of starting material. Product analysis on column A indicated the presence of three components, two of which had IR bands in the 3500-cm^{-1} region.

Preparative purification of alcohol **36a** was performed as follows: to a stirred solution of the distilled reaction mixture in 100 mL of acetone at 0 °C was slowly added Jones reagent[30] (2.67 M, 1.2 equiv based on starting ketone. After 30 min, 2-propanol (3 mL) was added, followed by concentrating the solution in vacuo. The residue was washed with H_2O and extracted with ether. The combined organic material was washed with brine and dried. Removal of the solvent in vacuo followed by distillation afforded 9.40 g of a colorless mobile oil. Gas chromatographic analysis indicated two components, where the second fraction from the Grignard reaction was now absent with a proportional increase in the area of the first fraction now being present.

This oil was added to a stirring saturated aqueous sodium bisulfite solution (50 mL). After 2 h the solution was extracted with Et_2O. The combined organic material was washed with brine and dried. The aqueous phase contained the bisulfite adduct of unreacted 2-(3′-propenyl)cyclohexanone. Removal of the solvent in vacuo followed by distillation (114–117 °C/15 mmHg) afforded 6.84 g (52% yield) of alcohol **36a** which was 98% pure by VPC analysis and possessed the following spectral data: 3625 (w), 3560 (w), 3070 (w), 2925 (s), 2845 (s), 2630 (w), 990 (m), 970 (m), 940 (m), 905 (s) cm^{-1}; NMR (60 MHz) δ 0.78–2.55 (m, 19 H), 4.53–5.22 (m, 2 H), 5.43–6.22 (m, 1 H).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.84; H, 12.14.

Preparation of 1-(1′-Methylethyl)-*c*-2-(3′-propenyl)cyclohexan-*r*-1-ol Methyl Ether (36b). To a solution of alcohol **36a** (1.53 g, 8.5 mmol) dissolved in 50 mL of THF were added MeI (6.75 g, 8 equiv) followed by NaH (408.0 mg, 2 equiv, 50% dispersion). The mixture was allowed to stir at ambient temperature under a nitrogen atmosphere for 24 h followed by the slow addition of 5 mL of water. The reaction mixture was poured into 25 mL of 10% aqueous HCl and extracted with ether. The combined organic material was washed with brine and dried. Removal of the solvent in vacuo followed by distillation (103–106 °C/15 mmHg) afforded 1.25 g (76% yield) of ether **36b**. An analytical sample obtained by preparative VPC had the following spectral characteristics: IR 3080 (w), 2985 (s), 2940 (s) cm^{-1}; NMR (250 MHz) δ 0.85–1.70, 9.93 (m, d, J = 7 Hz, 15 H), 1.72–1.73 (m, 1 H), 2.12 (sept, J = 7 Hz, 1 H), 2.27–2.42 (m, 1 H), 3.18 (s, 3 H), 4.82–5.01 (m, 2 H), 5.45–5.74 (m, 1 H).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.52. Found: C, 79.39; H, 12.32.

Preparation of *c*-2-Methoxy-2-(1′-methylethyl)-*r*-1-cyclohexaneacetic Acid Methyl Ester (37b). Ether **36b** (239 mg, 1.22 mmol) dissolved in 25 mL of anhydrous methanol was cooled to −78 °C. Ozone was bubbled into the solution until the reaction mixture turned blue in color. Oxygen was then bubbled in until the reaction mixture was clear. Dimethyl sulfide (3 mL) was added and the mixture was allowed to stir overnight at room temperature. The solution was concentrated in vacuo to afford 245.4 mg of an oil whose IR possessed an intense band at 1715 cm^{-1}, indicative of an aldehyde carbonyl.[10] Without purification, the oil was dissolved in 5 mL of acetone and cooled to 0 °C. Jones reagent (2.67 M, 0.91 mL, 2 equiv) was added dropwise. After 2 h 2-propanol (1 mL) was added to quench any unreacted Jones reagent.[30] Acetone and excess 2-propanol were removed in vacuo. The residue was washed with H_2O and extracted with ether, washed with brine, and dried. Removal of the

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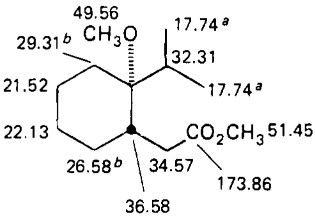
(33) House, H. O. ; Respess, W. L.; Whitesides, G. *J. Org. Chem.* **1966**, *31*, 3128.

solvent in vacuo afforded 260 mg of **37a**, as an oil. The IR possessed a broad band between 3600–2400 cm^{-1} and an intense band at 1705 cm^{-1}, both of which are indicative of a carboxylic acid moiety.[10]

Without purification, **37a** was dissolved in 10 mL of ether and added dropwise to a stirring solution of freshly prepared ethereal diazomethane. After 2 h the solvent was removed in vacuo and the residue distilled (70–72 °C/2 mmHg) to afford 264.4 mg of ester **37b**. An analytical sample obtained by preparative VPC had the following spectral characteristics: IR 2935 (s), 1730 (s) cm^{-1}; NMR (60 MHz) δ 0.96 (d, J = 6 Hz, 6 H), 1.00–1.73 (m, 8 H), 1.85–2.14 (m, 3 H), 2.51 (d, J = 14 Hz, 2 H), 3.16 (s, 3 H), 3.59 (s, 3 H); ^{13}C NMR (125 MHz) δ 17.74 (2, q), 21.52 (t), 22.13 (t), 26.58 (t), 29.31 (t), 32.31 (d), 34.57 (t), 36.58 (d), 49.56 (q), 51.45 (q), 173.86 (s).

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.50; H, 10.44.



a, b; interchangeable

Preparation of *t*-2-Methoxy-2-(1′-methylethyl)cyclohexane-*r*-1-acetic Acid Methyl Ester (34). Ester **37b** (51.0 mg, 0.22 mmol) was alkylated with phenylselenyl chloride via the method of Reich and Sharpless[21] to afford 105.4 mg of a viscous oil, which without further purification was added to 10 mL of THF. Upon cooling to 0 °C, 1 mL of 30% H_2O_2 was added. The reaction mixture was allowed to warm to room temperature. After 2 h the contents were poured into 25 mL of saturated aqueous sodium bicarbonate, extracted with Et_2O, washed with brine, and dried. Removal of the solvent in vacuo afforded 59.4 mg of an oil. Product analysis on column A indicated the presence of only one component. An analytical sample obtained by preparative VPC was determined to be ester **38** (77% yield), which possessed the following spectral characteristics: IR 2940 (s), 1725 (s), 1650 (m) cm^{-1}; NMR (60 MHz) δ 0.85 (d, J = 6 Hz, 6 H), 1.05–2.40 (m, 9 H), 3.06 (s, 3 H), 3.57 (s, 3 H), 5.47 (broad s, 1 H).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.86; H, 10.02.

Ester **38** (48.2 mg, 0.21 mmol) was dissoved in 25 mL of freshly distilled ethyl acetate and 5 mL of glacial acetic acid. Platinum(II) oxide (5.0 mg) was added and the contents were allowed to stir under a hydrogen atmosphere for 24 h at room temperature. The contents of the flask were filtered, washed with 100 mL of saturated aqueous sodium bicarbonate, and dried. Product analysis on column A indicated the presence of only one component. An analytical sample obtained by preparative VPC was identical in all respects (IR, NMR, VPC retention time) with ester **34**.

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Registry No. 1, 54445-52-2; **3**, 90107-30-5; **6b**, 76803-53-7; **7a**, 68974-41-4; **7a** ketene, 90107-31-6; **9**, 90107-32-7; **10a**, 90107-33-8; **10b**, 90107-34-9; **10c**, 90107-35-0; **11**, 56011-37-1; **12**, 90107-36-1; **13**, 90107-37-2; **15**, 26054-46-6; **16**, 90107-38-3; **17**, 90107-39-4; **18**, 54445-58-8; **19**, 90107-40-7; **22b**, 90107-41-8; **22c**, 90107-42-9; **23b**, 58101-60-3; **24** (isomer 1), 90107-43-0; **24** (isomer 2), 90191-43-8; **25**, 53837-32-4; **26**, 90107-44-1; **27**, 90107-45-2; **28a**, 90107-46-3; **28b**, 90107-47-4; **29a**, 90107-48-5; **29b**, 90107-49-6; **30**, 90191-44-9; **34**, 90107-50-9; **35**, 90107-51-0; **36a**, 90107-52-1; **36b**, 90107-53-2; **37a**, 90107-54-3; **37b**, 90107-55-4; **38**, 90107-56-5; Cu(OTf)$_2$, 34946-82-2; Cu(AcAc)$_2$, 13395-16-9; $PhCH_2OH$, 100-51-6; *i*-PrCl, 75-29-6; allyl bromide, 106-95-6; 1,1-diethoxyethylene, 2678-54-8; camphorsulfonic acid, 3144-16-9; 3-methyl-2-cyclopentenone, 2758-18-1; phenylselenophthalimide, 71098-88-9; 1-pyrrolidinocyclohexene, 1125-99-1; α,α-dimethyl-1-cyclohexene-1-acetic acid, 16642-55-0; 2-(3-propenyl)cyclohexanone, 94-66-6.