a catalytic amount of $H_2SO_4$, and the solution was heated at 90 °C under nitrogen for 45 min. The reaction mixture was diluted with ethyl acetate (100 mL), and the solution was washed with dilute $NaHCO_3$ and then water. The ethyl acetate was dried and then removed in vacuo. The crude product was purified by preparative plate chromatography (hexane–EtOAc (1:1)) to give 12 mg of the nidurufin epimer as an orange solid (71%): mp 190–192d °C (recrystallized from chloroform–methanol); $^1H$ NMR (acetone-$d_6$) 1.52 (s, 3 H, $COCH_3$), 4.20 (m, 1 H, C*H*(OH)O), 5.33 (d, 1 H, $J$ = 4.08 Hz, benzylic proton), 6.66 (d, 1 H, $J$ = 2.2 Hz, Ar H), 7.14 (s, 1 H, Ar H), 7.26 (d, 1 H, $J$ = 2.2 Hz, Ar H); MS(CI), $m/e$ (relative intensity) 385 (M + H, 1), 313 (0.9), 299 (0.9), 219 (7.5), 99 (52.8), 71 (95). Anal. Calcd (CI high resolution mass spectrum) for $C_{20}H_{16}O_8$ (M + H) 385.0923, found 385.0933.

**Acknowledgment.** This work was supported by a grant from the National Institutes of Health, Grant NIH ES 03431-01.

# Reductive Carbon–Carbon Cleavage in Caged Systems. A New General Synthesis of Linearly Fused *cis-syn-cis*-Triquinanes

Goverdhan Mehta* and Kotha Sambasiva Rao†

*School of Chemistry, University of Hyderabad, Hyderabad 500134, India*

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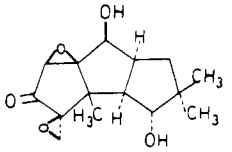
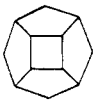
A concise and flexible approach to *cis-syn-cis*-tricyclo[6.3.0.$0^{2,6}$]undecane-4,10-dione derivatives bearing the linearly fused tricyclopentanoid framework has been established. The key concept in this synthetic theme is sequential, reductive carbon–carbon bond cleavage in readily and abundantly available pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (Cookson's dione **7**). Reaction of **7** with zinc dust in acetic acid under sonic irradiation resulted in the formation of tetracyclic dione **8** in excellent yield through $C_1$–$C_7$ bond reduction. The second C–C bond reduction ($C_9$–$C_{10}$ in pentacyclic dione **7**) was achieved by treating the tetracyclic dione **8** with an excess of Na–K alloy in the presence of trimethylchlorosilane to give *cis-syn-cis*-tricyclo[6.3.0.$0^{2,6}$]-undecane-4,10-dione (**6**). Several interesting transformations of the readily available *cis-syn-cis*-triquinane dione **6** are described. In an analogous manner, methyl-substituted derivatives **21** and **22** of the Cookson's caged dione are transformed to tricyclopentanoids **24** and **26**, respectively, in moderate yields. The three hexacyclic diones **29**, **34**, and **35** sharing common structural features with **7** also undergo sequential C–C bond reductions to furnish novel polyquinanes **31**, **36**, and **37**, respectively. These examples support the generality and preparative utility of the approach delineated here.

The high level of contemporary interest in the synthetic design of linearly fused tricyclopentanoids (triquinanes) stems from their wide occurrence in nature with a promising biological profile [e.g., coriolin (**1**)] and their likely role as the building blocks for the syntheses of "exotic" all carbon polyhedra, e.g., [4]peristylane (**2**) and dodecahedrane.[1] Consequently, a variety of novel approaches to

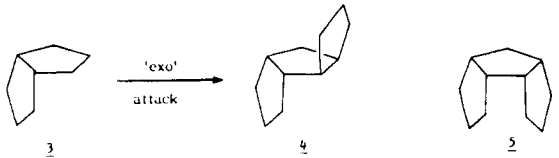


**1**



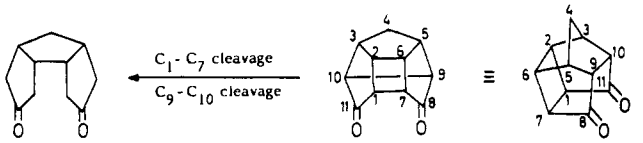
**2**

this ring system have been delineated in the recent past. The most direct and commonly employed approach to linearly fused tricyclopentanoids is the 5,5 → 5,5,5 ring route in which a cyclopentane ring is annulated to a preformed *cis*-bicyclo[3.3.0]octane framework. This approach is eminently suited for generating the cis-anti-cis stereochemical pattern **4** of natural products as the incoming cyclopentane ring is preferentially appended on the convex face of the folded *cis*-bicyclo[3.3.0]octane moiety **3**. Indeed, most synthesis of triquinane natural products have followed this common strategy.[1b] On the other hand, the




**3** **4** **5**

**Scheme I**




**6** **7**

sterically more hindered *cis-syn-cis*-triquinane system, e.g., **5**, has proved difficult to negotiate, and only two methods reported by us[2] and Eaton[3] provide reliable and direct access to this ring system. In pursuit of our work[4] on convex polyquinanes related to dodecahedrane and **2**, we identified the symmetrically functionalized *cis-syn-cis*-triquinanedione **6** as a key building block.[5] It was clear at the outset that neither the existing methodologies[1-3] nor the 5,5 → 5,5,5 route was suited for access to **6** and the desirability of evolving a de novo approach was indicated.

† Abstracted from the Ph.D. thesis of K. Sambasiva Rao, University of Hyderabad, 1984.

(1) (a) Mehta, G. *J. Sci. Ind. Res.* **1978**, *37*, 256. (b) Paquette, L. A. *Top. Curr. Chem.* **1979**, 79, 43; **1984**; *119*, 1. (c) Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

(2) (a) Mehta, G.; Reddy, A. V.; Srikrishna, A. *Tetrahedron Lett.* **1979**, 4863. (b) Mehta, G.; Srikrishna, A.; Reddy, A. V.; Nair, M. S. *Tetrahedron* **1981**, *37*, 4543.

(3) (a) Eaton, P. E.; Giordano, C.; Schloemer, G.; Vogel, U. *J. Org. Chem.* **1976**, *41*, 2238. (b) Eaton, P. E.; Sidhu, R. S., Langford, G. E.; Cullison, D. A.; Pietruszewski, C. L. *Tetrahedron* **1981**, *37*, 4479.

(4) Mehta, G.; Nair, M. S. *J. Chem. Soc., Chem. Commun.* **1983**, 439; **1985**, 629.

(5) It may be recalled that the bicyclic analogue of **6** has already proved to be a versatile intermediate for elaboration into polyquinanes. For some recent examples, see: Carceller, E.; Moyano, A.; Serratosa, F. *Tetrahedron Lett.* **1984**, *25*, 2031. Caille, J. C.; Bellarmy, F.; Guilard, R. *Ibid.* **1984**, *25*, 2345. Belletire, J. L.; Adams, K. G. *Ibid.* **1983**, *24*, 5575. Kubiak, G.; Cook, J. M. *J. Org. Chem.* **1984**, *49*, 561. Venkatachalam, M.; Jawdosiuk, M.; Deshpande, M.; Cook, J. M. *Tetrahedron Lett.* **1985**, *26*, 2275.

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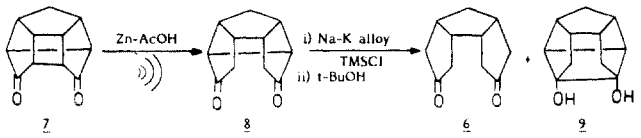
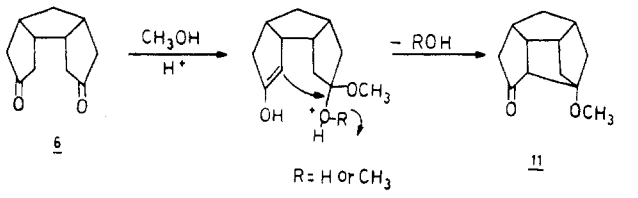
**Scheme II**



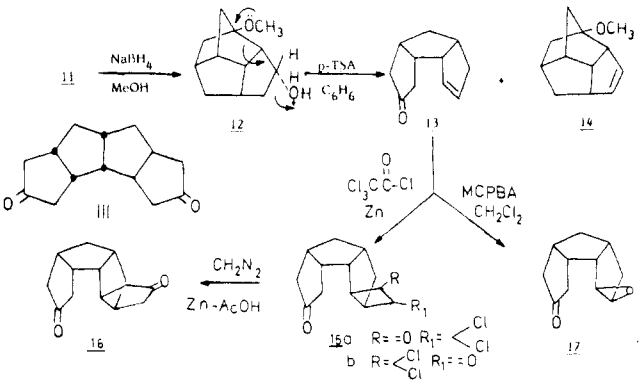

We considered the possibility that a readily available, suitably constituted and symmetrically functionalized caged system could deliver the folded cis-syn-cis geometry and functionality of **6**. The reasoning that prompted this thought was that caged systems are conveniently derived through intramolecular $\pi_s^2 + \pi_s^2$ photocycloadditions that generally follow the rule of five,[6] and thus a five-membered ring(s) is always cogenerated with the cyclobutane ring in such compounds. If a suitable strategy could be developed to extract these five-membered rings from the cage, through specifically designed carbon–carbon cleavage reactions, then a new and versatile synthesis of all-cis quinanes would emerge. Application of this logic in the context of **6** directed our attention to the Cookson's caged dione **7**,[7] which has always appealed to us as a readily accessible source of fused five-membered rings. Two strategic bond disconnections at $C_1$–$C_7$ and $C_9$–$C_{10}$ in **7** reduce it to the desired all-cis triquinanedione **6**. In practice, therefore, the synthesis of **6** required subjecting Cookson's caged dione **7** to two regioselective, reductive C–C bond cleavage reactions within the 1,4-dicarbonyl system present, either sequentially or simultaneously (Scheme I). Herein we describe the realization of this objective and demonstrate the generality of our approach for *cis*-triquinane synthesis.[8,14] A few examples, extending this methodology to all-cis tetraquinanes as well as other related multicyclic systems are also provided.

Reaction of **7** with inexpensive zinc dust in acetic acid under sonic irradiation[9] resulted in the formation of the known tetracyclic dione **8** in excellent yield through $C_1$–$C_7$ bond reduction.[10] Further reaction of **8** with excess of Na–K alloy in presence of trimethylchlorosilane ($Me_3SiCl$)[11] and quenching with *tert*-butyl alcohol furnished a product mixture readily separable by column chromatography, containing two polar compounds and some nonpolar impurities. The minor product (5%) was quickly recognized as the known[10] pentacyclic pinacol **9**. The major product (40%) was unambiguously characterized as the desired cis-syn-cis dione **6** on the basis of its mass spectrum ($M^+$ 178), which indicated an increase in mass by two units over its precursor and the six-line $^{13}C$ NMR spectrum. The signals at $\delta$ 218.9 (s), 44.6 (t), 43.1 (d), 41.2 (d), 40.4 (t), and 40.0 (t) in a ratio of 2:2:2:2:1:1:2 provided unequivocal evidence that not only the symmetry had been maintained during the reduction but the two new $CH_2$ groups had emerged at the expense of two CH units.

**Scheme III**

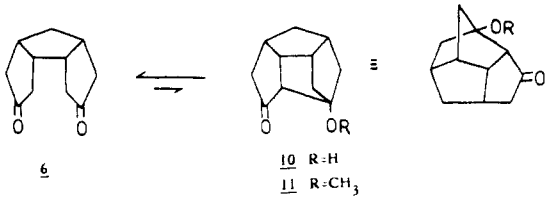



**Scheme IV**




A preparatively useful synthesis of **6** was thus achieved in a fairly straightforward manner (Scheme II).

During the purification of **6**, we noticed the nagging presence of a minor contaminant which showed a clear spot on TLC and seemed to increase on storage, even in the most highly purified sample. In the samples recovered from the NMR tube (traces of acid in $CDCl_3$) the contaminant assumed meancing proportions (~30–40%), and was eventually isolated in the pure form through preparative TLC. Its IR spectrum exhibited both hydroxyl and carbonyl absorptions, and the $^{13}C$ NMR had 11 discrete resonances with $\delta$ 82.6 signal being diagnostic of the COH moiety. The structure of the contaminant was thus revealed as the trans-skeletal aldol cyclization product **10**.




It was readily established that **6** and **10** equilibrated on exposure to acidic medium, and in fact **6** could be converted to the tetracyclic methyl ether **11** on treatment with methanol and traces of *p*-TSA, Scheme III. The same methyl ether **11** could be obtained directly and much more conveniently from **8** on treatment with Na–K alloy/$Me_3SiCl$ followed by quenching with methanol in 50% yield.

As this high propensity of **6** toward trans-skeletal cyclization proved to be a complicating factor in its use in synthesis, it became necessary to transform **6** into a less symmetrical product with well-differentiated functionalities. In this connection, the superficially undesired, albeit interesting, transannular product **11** proved to be quite useful. Reduction of **11** with sodium borohydride furnished exclusively the endo-hydroxy compound **12** in quantitative yield. On exposure to *p*-TSA in refluxing benzene, **12** furnished the tricyclic keto olefin **13** (57%) along with **14** (20%) (Scheme IV). The utility of **13** is demonstrated through two reactions in which we were particularly interested. Dichloroketene addition to **13** proceeded stereoselectively from the convex face but not regioselectively to furnish nearly equal amounts of 1:1

(6) (a) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. (b) Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936. (c) Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1980**, *45*, 3139 and references cited therein.

(7) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3062.

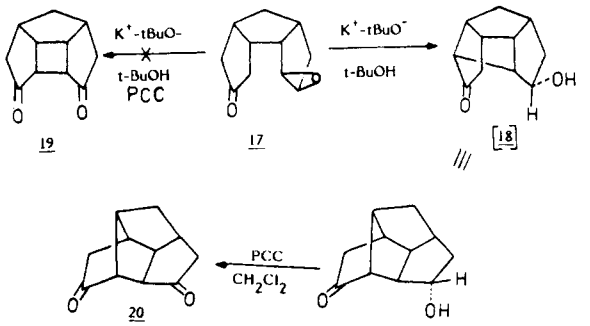
(8) For a preliminary communication of this work, see: Mehta, G.; Sambasiva Rao, K. *Tetrahedron Lett.* **1983**, *24*, 809. One of the examples mentioned in this paper has been described in ref 14.

(9) We were tempted to attempt this reaction under these conditions in view of the recent reports that heterogeneous organic reactions involving organometallic intermediates are significantly accelerated by ultrasound. For some recent examples, see: (a) Luche, J. L.; Petrier, C.; Lansard, J. P.; Greene, A. E. *J. Org. Chem.* **1983**, *48*, 3837. (b) Mehta, G.; Rao, H. S. P., *Synth. Commun.* **1985**, *15*, 991. (c) Han. B. H.; Boudjouk, P. *Tetrahedron Lett.* **1981**, *22*, 2757.

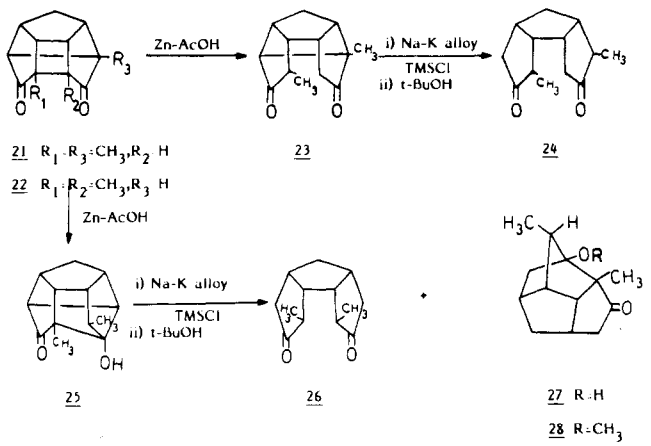
(10) Wenkert, E.; Yoder, J. E. *J. Org. Chem.* **1970**, *35*, 2986.

(11) Bloomfield, J. J.; Martin, R. A.; Nelke, J. M. *J. Chem. Soc. Chem. Commun.* **1972**, 96.

**Scheme V**




**Scheme VI**



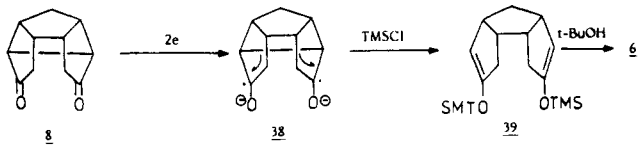

adducts **15a** and **15b**. Diazomethane ring expansion and dechlorination according to the method of Greene[12] furnished the *cis-syn-cis-anti*-tetraquinanedione **16**. Epoxidation of **13** yielded the exo-epoxide **17**. However, base-catalyzed intramolecular opening of **17** gave exclusively **18** and not the desired and expected tetracyclic precursor **19** of [4]peristylane. The structure of **18** followed from its transformation to the diketone **20** and incisive analysis of its $^1H$ and $^{13}C$ NMR data Scheme V.

Having established a concise approach to *cis-syn-cis*-triquinanedione **6**, attention was turned toward generalizing the new synthetic sequence. Four more examples are described here in this connection. Two examples are of methyl-substituted derivatives of **7** while the other two are of interesting annulated systems related to **7**. Reaction of readily available[2b] dimethyl pentacyclic dione **21** with zinc in acetic acid furnished the tetracyclic compound **23**, which exhibited a quaternary methyl [$\delta$ 1.14 (3 H, s)] and tertiary methyl [$\delta$ 1.1 (3 H, d, $J$ = 7 Hz)] in the $^1H$ NMR spectrum in 50% yield. On treatment with Na–K alloy in excess $Me_3SiCl$ and followed by quenching with *tert*-butyl alcohol, **23** furnished the expected tricyclic dione **24** (30%) as a distereoisomeric mixture (Scheme VI). The structure of **24** rests on its mass spectrum ($M^+$ 206) and doubled set of carbon resonances in $^{13}C$ NMR spectrum (vide Experimental Section).

The symmetrical dimethyl pentacyclic dione[2b] **22** on reduction with zinc dust in acetic acid furnished a crystalline product in 54% yield. However, the product exhibited both carbonyl (1750 cm$^{-1}$) and hydroxyl (3400 cm$^{-1}$) absorptions in the IR spectrum and had methyl resonances at $\delta$ 1.08 (d, 3 H, $J$ = 7 Hz) and $\delta$ 1.1 (s, 3 H) in the $^1H$ NMR spectrum. It was assigned the internal aldol formulation **25**. The formation of aldol product **25** in preference to the tetracyclic dione structure (with endo-methyl groups) can be attributed to the relief of steric congestion

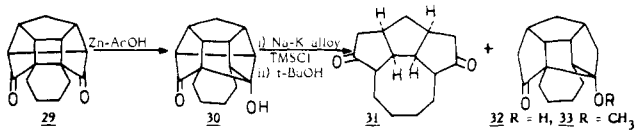
(12) Greene A. E. *Tetrahedron Lett.* **1980**, *21*, 3059.

**Scheme VII**



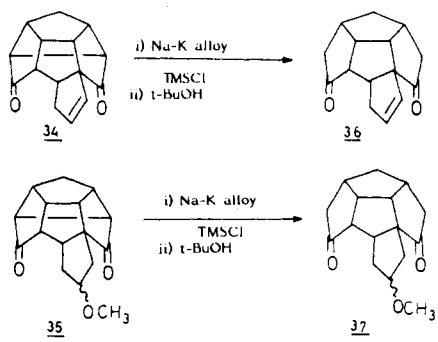

in the former. Although the product **25** was a pentacyclic hydroxy ketone and not the required tetracyclic dione, it was surmised that under the reaction conditions employed there will be sufficient equilibrium concentration of the dione to ensure the success of the reductive C–C bond cleavage reaction. Consequently, **25** was treated with Na–K alloy/$Me_3SiCl$ medium, and the two products **26** and **27** were isolated in 40% and 14% yield, respectively (Scheme VI). The symmetry element present in **26** as exhibited by its seven-line $^{13}C$ NMR spectrum secured its formulation. The minor product **27** was characterized as the trans-skeletal aldol condensation product of **26**. Indeed, **26** could be quantitatively transformed to tetracyclic methyl ether **28** on brief exposure to methanol in presence of *p*-TSA.

Next we turned our attention to the hexacyclic propellane dione **29**, an annulated derivative of Cookson's caged dione and readily available from 1,3-cyclopentadiene and 1,4-naphthoquinone.[13] Reduction of **29** with zinc in acetic acid furnished the hexacyclic internal aldol **30** in 80% yield. The structure was evident from the two quaternary carbon signals at $\delta$ 85.3 and 56.4 in the $^{13}C$ NMR spectrum besides other consonant spectral data. Further



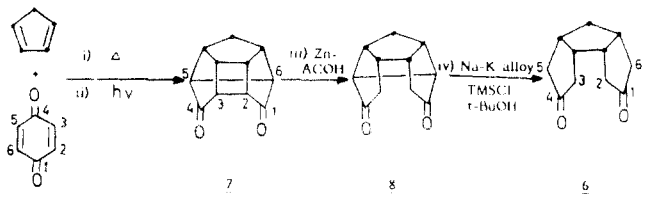

reduction of **30** with Na–K alloy/$Me_3SiCl$ receipe gave the two crystalline products **31** and **32** in 38% and 8% yield respectively. The major product **31**, which bore the novel eight- and five-ring system, had its highest mass peak at 232 and the maintenance of $C_2$ symmetry was readily apparent by the simplified $^{13}C$ NMR spectrum, which contained only eight lines. The minor product was formulated as the internal aldol product **32**. As in the earlier examples, **31** could be quantitatively transformed to **33** with acidic methanol.

Our last example is of hexacyclic diones **34** and **35**.[14] When **34** was subjected to the Na–K alloy reaction, pentaquinane derivative **36**, $M^+$ 228, was obtained in 50% yield. Structure of **36** followed from its $^1H$ and $^{13}C$ NMR data and further secured through single-crystal X-ray diffraction studies.[15] In an analogous manner, **35** un-




(13) Kushner, A. S. *Tetrahedron Lett.* **1971**, 3275.
(14) Mehta, G.; Sambasiva Rao, K.; Bhadbhade, M. M.; Venkatesan, K. *J. Chem. Soc., Chem. Commun.* **1981**, 755.

**Scheme VIII**



derwent the expected uncaging to give **38** in 65% yield. The C–C bond reductions in **34** and **35** thus offer entry into pentaquinane systems bearing both linearly as well as angularly fused tricyclopentanoid moieties.

Now, a word about the mechanism. The reductive carbon–carbon bond cleavage with Na–K alloy described here has not been subjected to any incisive mechanistic scrutiny, but they appear to fall within the precedented category of the reduction of 1,4-dicarbonyl systems.[10] The plausible mechanism represented here in Scheme VII involves transfer of an electron to each of the carbonyl groups of **8** from the metal to give bis-radical–anion of the type **38**, which on C–C bond cleavage is trapped by $Me_3SiCl$ to give **39**. The bis($Me_3Si$) enol ether **39** on protonation gives **6**.

In summary, the new and general synthetic route to *cis-syn-cis*-triquinanes reported here constitutes a four-step bis(cyclopentane)annulation of 1,3-cyclopentadiene involving a formal dissection of *p*-benzoquinone moiety (Scheme VIII). Consequently, the requisite triquinane can be simply designed, by building the complementary substitution pattern into 1,3-cyclopentadiene and *p*-benzoquinone.

## Experimental Section

Melting points were recorded on a Büchi SMP-20 apparatus and are uncorrected. Boiling points refer to bath temperatures. UV, IR, $^1H$ NMR (100 MHz), and $^{13}C$ NMR (25.0 MHz) spectra were recorded on a Shimadzu 200S spectrophotometer, a Perkin-Elmer 297 spectrophotometer, a Jeol MH-100 spectrometer, and a Jeol FX-100 spectrometer, respectively. $^1H$ NMR and $^{13}C$ NMR chemical shifts are given in $\delta$ scale with $Me_4Si$ as the internal standard. In the $^{13}C$ NMR chemical shifts are given in $\delta$ scale with $Me_4Si$ as the internal standard. In the $^{13}C$ NMR spectra, off-resonance multiplicities, when recorded, are given in parentheses. The standard abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Elemental analyses were carried out on a Hewlett-Packard 185-B CHN analyzer. High-resolution mass measurements were carried out on AEI MS-5076 mass spectrometer. Relative abundance of the ions formed compared to the base peak, designated 100%. All hydrogenations were carried out on a Parr hydrogenation apparatus in 250-mL pressure bottles.

Analytical thin-layer chromatographies (TLC) were performed on (10 × 5 cm) glass plates coated (250 $\mu$m) with Acme's silica gel G (containing 13% calcium sulfate as binder). Thick-layer chromatography was performed on (20 × 20 cm) glass plates coated with Acme's silica gel G. Visualization of the spots on TLC plates was achieved either by exposure to iodine vapor or by spraying sulfuric acid and heating the plates at 120 °C. Moisture-sensitive reactions were carried out by using standard syringe-septum techniques.

Pet ether refers to the fraction boiling between 60 and 80 °C. Dichloromethane was distilled over $P_2O_5$. Toluene was distilled over sodium and stored over pressed sodium wire. All solvent extracts were washed with brine, dried over anhydrous $Na_2SO_4$, and concentrated on a Büchi-EL rotary evaporator.

**Tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione (8).** A mixture of the pentacyclic diketone **7** (2 g, 11.4 mmol) and zinc (4 g, 60 mmol) in glacial acetic acid (25 mL) was kept under sonication (10 h) conditions.[9] At the conclusion of the reaction, the insoluble material was removed by suction filtration. The filtrate was concentrated and diluted with ice–water (20 mL) and extracted with dichloromethane (15 mL × 3). The organic layer was washed with saturated $NaHCO_3$ solution and after usual workup gave tetracyclic dione **8**, 1.8 g (90%), as a white solid residue. Recrystallization from toluene furnished colorless, sugarlike crystals: mp 255 °C (lit. mp 255 °C);[10] IR (KBr) $\nu_{max}$ 1750 cm$^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.8–2.0 (m, 2 H), 2.1–2.3 (br s, 4 H), 2.6–2.8 (br s, 4 H), 2.7–2.9 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 217.8, 58.4, 47.8, 40.1, 38.7, 34.6.

**Na–K Alloy Reduction of Tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione (8) and *tert*-Butyl Alcohol Quenching.** In a flame-dried 250-mL three-necked flask, equipped with a condenser, freshly cut sodium (0.4 g, 0.017 g-atom) and potassium (2 g, 0.051 mol) in dry toluene (125 mL) were heated with vigorous stirring until a fine dispersion was formed. After cooling to ambient temperature, a solution of diketone **8** (2.4 g, 13,8 mmol) in dry toluene (25 mL) and trimethylchlorosilane (20 mL) was sequentially injected under nitrogen blanket. The reaction mixture was refluxed under stirring for 3 h and cooled. Filtration through a Celite pad under nitrogen into *tert*-butyl alcohol (15 mL) and concentration under vacuo gave a viscous oily residue, which was charged on a silica gel (80 g) column. Elution with benzene removed minor less polar impurities. Further elution of the column with 2% acetone–benzene gave diketone **6** (0.95 g, 40%), as a colorless oil and was bulb-to-bulb distilled at 170 °C (1 torr): IR ($CCl_4$) $\nu_{max}$ 1750 cm$^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.12 (m, 1 H), 1.8–3.2 (m, 13 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 218.9 (s), 44.6 (t), 43.1 (d), 41.2 (d), 40.4 (t), 40.0 (t); mass spectrum, (70 eV) *m/e* (relative intensity) 178 (molecular ion, 96), 150 (24), 135 (28), 108 (36), 96 (32), 95 (100), 94 (44), 93 (32), 82 (56), 67 (44), 54 (92). Analysis for $C_{11}H_{14}O_2$ Calcd: C, 74.13; H, 7.92; Found: C, 74.25; H, 7.88.

Further elution of the column with 10% acetone–benzene yielded diol **9** (120 mg, 5%) and was recrystallized from dichloromethane–pet ether: mp 201 °C (lit. mp 202 °C);[10] IR (KBr) $\nu_{max}$ 3400 cm$^{-1}$ (hydroxyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.15–1.4 (m, 4 H), 2.2 (s, 2 H), 2.4 (s, 4 H), 3.6 (s, 2 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 81.1, 48.3, 45.6, 39.9, 36.1, 33.4.

**Na–K Alloy Reduction of Tetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione (8) and Methanol Quenching.** Diketone **8** (1.2 g, 6.9 mmol) in 15 mL of dry toluene and trimethylchlorosilane (12 mL) were sequentially injected into a 250-mL flask containing 1.2 g of Na–K alloy (prepared from 0.2 g, 0.0086 mol, of sodium, 1.0 g, 0.025 mol, of potassium as described earlier) in dry toluene (80 mL). The reaction mixture was refluxed for 3 h and cooled. Quick filtration through Celite pad under nitrogen into methanol (10 mL), and removal of solvent gave an oily product, which was charged on a silica gel (30 g) column. Nonpolar products were removed by elution of the column with benzene. Continued elution with the same solvent gave **11** (640 mg, 49%) as an oil and was bulb-to-bulb distilled at 140 °C (1 torr): IR (neat) $\nu_{max}$ 1740 cm$^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.0–3.2 (m, 13 H), 3.36 (s, 3 H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 219.7 (s), 87.3 (s, $COCH_3$), 53.2 (d), 52.5 (q, $OCH_3$), 50.0 (t), 49.6 (d), 45.3 (d), 42.9 (t), 41.7 (t), 38.6 (d), 37.2 (d), 36.6 (d); mass spectrum (70 eV), *m/e* (relative intensity) 192 (molecular ion, 51), 123 (21), 122 (24), 110 (19), 109 (100), 97 (15), 96 (39). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.48; H, 8.30.

Further elution of the column with 5% ethyl acetate–benzene gave the diol **9** (35 mg, 3%), mp 201 °C (lit. mp 202 °C).[10]

**Acid-Catalyzed Cyclization of Tricyclo[6.3.0.0$^{2,6}$]undecane-4,10-dione (6) in Methanol.** A solution of the dione **6** (35 mg, 0.19 mmol) in 5 mL of dry methanol and catalytic amount of *p*-TSA (few crystals) were stirred at room temperature for 30 min. The reaction mixture was diluted with water (5 mL) and extracted with dichloromethane (10 mL × 2). The organic layer was washed with aqueous $NaHCO_3$ and dried. Evaporation of solvent furnished **11** (35 mg, 93%) and was distilled at 140 °C (1 torr). This sample of **11** was identical with the material obtained in the earlier experiment through direct quenching with methanol.

**Sodium Borohydride Reduction of 10-Methoxytetracyclo[6.3.0.0$^{2,6}$.0$^{3,10}$]undecan-4-one (11).** A solution of the methoxy ketone **11** (410 mg, 2.14 mmol) in 15 mL of methanol

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was treated with 65 mg (1.7 mmol, excess) of sodium borohydride at ice temperature for 45 min. Most of the methanol was removed at reduced pressure. The contents of the flask were diluted with water (10 mL) and extracted it with ether (40 mL × 2). The ether layer was washed and dried. Evaporation of solvent gave in quantitative yield **12** (410 mg), which was distilled at 160 °C (1 torr): IR spectrum (neat) $\nu_{max}$ 3500 $cm^{-1}$ (hydroxyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.69–2.57 (m, 13 H), 3.0 (br s, 1 H, COH), 3.29 (s, 3 H, $OCH_3$), 4.51 (m, 1 H, HCOH); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 87.4, 75.0, 52.1, 51.7, 50.1, 46.4, 45.8, 42.4, 41.6, 39.7, 39.6, 33.2. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.54; H, 9.38.

**Acid-Catalyzed Rearrangement of 10-Methoxy-4-hydroxytetracyclo[6.3.0.0$^{2,6}$.0$^{3,10}$]undecane (12).** A solution of **12** (400 mg, 2.06 mmol) and *p*-toluenesulfonic acid (200 mg, 1.16 mmol) in 20 mL of dry benzene was refluxed with a Dean–Stark water separator for 2 h. The reaction mixture was diluted with benzene (30 mL), washed with aqueous $NaHCO_3$ solution, and dried. Evaporation of solvent furnished an oily product, which was charged on a silica gel (20 g) column. Elution with 50% benzene–pet ether gave 70 mg (20%) of tetracyclic olefin **14**. It was further purified by bulb-to-bulb distillation of 130 °C (0.5 torr); IR (neat) $\nu_{max}$ 3040, 1610 $cm^{-1}$ (olefinic); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.6 (m, 4 H), 1.95 (s, 2 H), 2.1–3.2 (m, 5 H), 3.35 (s, 3 H, $COCH_3$), 5.5 (d, 1 H, $J$ = 6 Hz), 5.8 (dd, 1 H, $J_1$ = 6 Hz, $J_2$ = 2 Hz); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 139.0, 128.7, 88.5, 54.7, 53.3, 52.5, 47.7, 44.9, 44.4, 41.2, 36.3, 34.2. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.22; H, 9.19.

Further elution of the column with the same solvent gave keto olefin **13** (190 mg, 57%), which was bulb-to-bulb distilled at 130 °C (0.5 torr): IR spectrum (neat) $\nu_{max}$ 3050, 1730 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.08 (td, 1 H, $J_1$ = 14 Hz, $J_2$ = 8 Hz), 1.8–3.0 (m, 10 H), 3.44 (m, 1 H), 5.6 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 220.3, 131.1, 130.7, 54.0, 42.8 (2 C), 42.7, 42.4, 39.7 (2 C), 39.0; mass spectrum (70 eV), $m/e$ (relative intensity) 162 (molecular ion, 21), 95 (79), 83 (38), 79 (100), 77 (47), 67 (22), 66 (75), 65 (24). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found C, 81.28; H, 8.78.

**Epoxidation of Tricyclo[6.3.0.0$^{2,6}$]undec-3(4)-en-10-one (13).** In a solution of keto olefin **13** (400 mg, 2.47 mmol) in 15 mL of dry dichloromethane was suspended 500 mg of anhydrous sodium carbonate, *m*-Chloroperbenzoic acid (95%, 453 mg, 2.5 mmol) was added at −5 °C, and the reaction mixture was slowly brought to room temperature over a period of 3 h. The reaction mixture was quenched with saturated bicarbonate solution and extracted with dichloromethane (30 mL × 2), and washing and drying gave a viscous residue. This was charged over a silica gel (20 g) column. Elution with benzene gave 70 mg of the starting material. Further elution with 5% ethyl acetate–benzene gave epoxide **17** (250 mg, 69%, based on starting material recovered). It was crystallized from carbontetrachloride–pet ether: mp 64–65 °C; IR (KBr) $\nu_{max}$ 1740 (carbonyl), 1400, 1180, 840 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.8–3.3 (m, 12 H), 3.4 (s, 1 H), 3.6 (s, 1 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 219.4, 60.3, 59.2, 49.9, 44.7, 43.7, 42.5 (2 C), 40.4, 38.8, 37.9. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.25; H, 7.99.

**Base Treatment and Pyridinium Chlorochromate Oxidation of 3,4-Epoxytricyclo[6.3.0.0$^{2,6}$]undecan-10-one (17).** To a freshly sublimed sample of potassium *tert*-butoxide (40 mg, 0.34 mmol) in 5 mL of dry THF and 0.2 mL of dry *tert*-butyl alcohol was added 42 mg (0.23 mmol) of **17**, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with 5 mL of 30% HCl and extracted with ethyl acetate (10 mL × 2). Removal of solvent and filtration through a small silica gel (5 g) column gave 15 mg (35%) of hydroxy compound. This was directly treated with pyridinium chlorochromate (30 mg, 0.14 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at room temperature for 1 h. At the conclusion of this period, the reaction mixture was passed through a small silica gel (5 g) column. Evaporation of solvent gave 13 mg of **20** as a crystalline residue. It was recrystallized from dichloromethane–pet ether: mp 73–74 °C; IR ($CCl_4$) $\nu_{max}$ 1750, 1760 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.0–1.4 (m, 1 H), 1.6–2.4 (m, 8 H), 2.6 (s, 1 H), 2.8 (s, 2 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 217.8, 212.7, 59.2, 49.5, 46.6, 46.5, 46.1 (some carbon signals are of double intensity), 37.7, 33.9. Anal. Calcd: for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.21; H, 7.03.

**Dichloroketene Addition[9] to Tricyclo[6.3.0.0$^{2,6}$]undec-3-(4)-en-10-one (13).** A 50-mL, three-necked round-bottom flask equipped with nitrogen inlet and pressure-equalizing addition funnel was charged with olefin **13** (100 mg, 0.61 mmol) and 119 mg (1.8 mmol) of zinc and 10 mL of anhydrous ether. The flask was then partially submerged in the sonicator water bath in a place that produced maximum agitation. To this suspension 0.1 mL (1.5 equiv) of trichloroacetylchloride in 10 mL of anhydrous ether was added during a 30-min period while sonication continued. After the reaction was kept under sonication condition for another 90 min it was quenched with wet ether and was filtered through Celite. The filtrate was washed with water (2 × 10 mL), saturated sodium bicarbonate solution (2 × 10 mL), and brine (10 mL). After the ethereal solution was dried over anhydrous $Na_2SO_4$, the solvent was removed, and the crude product was charged on a silica gel (10 g) column. Elution with 10% ethylacetate–pet ether gave 50 mg of the starting keto olefin **13**. Continued elution of the column gave 45 mg (55%) of an adduct which is a mixture of two regioisomers **15a** and **15b**: IR (neat) $\nu_{max}$ 1800, 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.0–3.1 (m, 24 H), 3.24 (d, 1 H, $J$ = 8 Hz), 3.5 (t, 1 H, $J$ = 8 Hz), 3.9 (d, 1 H, $J$ = 8 Hz), 4.2 (t, 1 H, $J$ = 8 Hz). The $^1H$ NMR signals at $\delta$ 3.24, 3.5, 3.9, and 4.2 correspond to the ring junction protons of the $\alpha,\alpha'$-dichlorocyclobutanone ring and therefore are of equal intensity. Therefore we conclude the regioisomers **15a** and **15b** are present in equal amount.

***cis-syn-cis-anti*-Tetracyclo[6.6.0.0$^{2,6}$.0$^{10,14}$]-tetradecane-4,12-dione (16).** To a solution of the dichloroketene adduct mixture (40 mg) of **15a** and **15b** in 10 mL of ether was added ethereal solution of diazomethane at ice temperature, and the resulting mixture was kept at room temperature for 2 h. At the end of this time the excess diazomethane was destroyed by addition of a few drops of acetic acid, and the ethreal solution was washed successively with water and 5% aqueous $NaHCO_3$ and dried. Removal of solvent furnished 40 mg of crude ring expanded product, which showed characteristic IR absorption at 1750 $cm^{-1}$ ($\alpha,\alpha'$-dichlorocyclopentanone) and was directly used for dechlorination without any purification. The above sample (40 mg) was magnetically stirred with zinc dust (40 mg, 0.61 mmol) in 2 mL of glacial acetic acid at room temperature for 2 h. The reaction mixture was diluted with 10 mL of water, suspended zinc salts were removed by filtration, and the filtrate was concentrated at reduced pressure. The residue was diluted with cold water (5 mL) and extracted with dichloromethane (10 mL × 2). The organic layer was washed with aqueous $NaHCO_3$ solution and dried. Removal of solvent gave tetracyclic dione **16** (20 mg, 62%) as a solid residue. This material was recrystallized from dichloromethane–pet ether to give **16**: mp 78–79 °C; IR (KBr) $\nu_{max}$ 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.8–1.2 (m, 2 H), 1.68 (m, 2 H), 1.8–3.0 (m, 14 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 218.8 (2 C?), 53.5, 47.1 (2 C?), 44.4, 43.6 (2 C?), 43.3 (2 C?), 42.3, 39.7, 39.1, 37.2. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.40; H, 8.58.

**Zinc–Acetic Acid Reduction of 1,9-Dimethylpentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-8,11-dione (21).** To 300 mg (1.48 mmol) of **21**[2b] in 50 mL of glacial acetic acid was added 1.5 g (23 mmol) of zinc, and the mixture was refluxed for 24 h with stirring. An additional 3.0 g (46 mmol) of zinc was added and the mixture refluxed for another 24 h. The insoluble material was removed by filtration, and the filtrate was diluted with cold water. Extraction with chloroform (15 mL × 2), washing with aqueous $NaHCO_3$ solution, and removal of solvent gave an oily product, which was charged on a silica gel (10 g) column. Elution with benzene first gave unreacted starting material (100 mg). Further elution of the column with 15% ethyl acetate–benzene gave **23** (100 mg, 50%, based on recovery of the starting material). Crystallization from dichloromethane–pet ether mixture gave pure **23**: mp 102–103 °C; IR (KBr) $\nu_{max}$ 1745 $cm^{-1}$ (carbonyl). $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.1 (d, 3 H, $J$ = 7 Hz), 1.14 (s, 3 H), 1.4–3.2 (m, 10 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 220.3, 218.5, 66.8, 53.4, 45.6 (2 C), 43.8, 39.8, 37.0, 33.4, 19.5, 17.3. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 75.95; H, 7.97.

**Na–K Alloy Reduction of 3,8-Dimethyltetracyclo[6.3.0.0$^{4,11}$.0$^{5,9}$]undecane-2,7-dione (23).** Tetracyclic dione **23** (235 mg, 1.15 mmol) was treated with 500 mg of Na–K alloy

(prepared from 80 mg of sodium and 420 mg of potassium as described in the earlier experiment) and 5 mL of trimethylchlorosilane in toluene (50 mL). The mixture was refluxed for 2.5 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad into *tert*-butyl alcohol under nitrogen atmosphere. Concentration of the filtrate and column chromatography over silica gel gave tricyclic dione **24** (70 mg, 29%) as a mixture of methyl epimers: IR (KBr), $\nu_{max}$ 1735 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.12 (d, 6 H, $J$ = 7 Hz), 1.6–3.2 (m, 12 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 220.6, 220.3, 219.0, 51.7, 50.5, 50.1, 49.9, 48.0, 46.6, 44.5, 42.9, 40.0, 39.5, 39.0, 38.8, 38.0, 35.0, 15.5, 15.4, 15.0, 10.5 (some carbon signals are of double intensity due to overlap of resonances); mass spectrum (70 eV), $m/e$ (relative intensity) 206 (molecular ion, 100), 204 (20), 188 (12), 163 (22), 149 (28), 135 (24), 122 (23), 109 (85), 96 (64), 68 (75). Anal. Calcd for $C_{13}H_{18}O_2$: $m/e$ 206.1307. Found: $m/e$ 206.1309.

**Zinc–Acetic Acid Reduction of 1,7-Dimethylpentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-8,11-dione (22).** To 300 mg of pentacyclic dione **22**[2b] (1.48 mmol) in 50 mL of glacial acetic acid was added 1.5 g (23 mmol) of zinc, and the reaction mixture was kept at reflux temperature for 24 h with vigorous stirring. An additional amount of zinc (3 g, 46 mmol) was added and the refluxing continued for another 24 h. The insoluble salts were removed by filtration. The filtrate was diluted with cold water and extracted with chloroform. The organic extract was washed with saturated $NaHCO_3$ solution and dried. Removal of solvent gave a thick oily product, which was charged on a silica gel (15 g) column. Elution with benzene gave 50 mg (16%) of the starting pentacyclic dione **22**. Further elution with 10% ethyl acetate–benzene gave hydroxy ketone **25**, as a solid residue. Recrystallization from pet ether–carbon tetrachloride gave **25**: mp 88–89 °C; IR (KBr) $\nu_{max}$ 3400 (hydroxyl), 1750 $cm^{-1}$ (carbonyl); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.08 (d, 3 H, $CHCH_3$, $J$ = 7 Hz). 1.1 (s, 3 H), 1.47 (d, 1 H, $J$ = 8 Hz), 1.58 (d, 1 H, $J$ = 8 Hz), 1.86 (br s, 1 H), 2.06 (m, 2 H), 2.14 (AB q, 1 H, $J$ = 5 Hz), 2.26 (t, 1 H, $J$ = 5 Hz), 2.43 (t, 1 H, $J$ = 5 Hz), 2.46 (br s, 1 H), 2.55 (br s, 1 H); $^{13}C$ NMR (25.0 MHz, $CDCl_3$) $\delta$ 218.0 (s), 83.9 (s, COH), 53,3 (s), 51.0 (d), 49.9 (d), 49.4 (d), 47.8 (d), 46.3 (d), 45.4 (d), 40.6 (d), 36.9 (t), 12.4 (q, $CH_3$), 10.2 (q, $CH_3$); mass spectrum (70 eV), $m/e$ (relative intensity) 204 (molecular ion, 72), 189 (20), 161 (13), 135 (10), 110 (100), 109 (67), 108 (44), 107 (11), 96 (43), 95 (44), 91 (23), 77 (23). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.09; H, 8.05.

**Na–K Alloy Reduction of 5-Hydroxy-4,6-dimethylpentacyclo[6.3.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecan-7-one (25).** In a flame-dried three-necked flask, 1.2 g of Na–K alloy (from 200 mg of sodium and 1.0 g of potassium) was prepared as described in the earlier experiment. Hydroxy ketone **25** (500 mg, 2.45 mmol) in 15 mL of dry toluene and 6 mL of trimethylchlorosilane were sequentially injected, and the reaction mixture was stirred and refluxed for 3.5 h. After cooling, the reaction mixture was quickly filtered through Celite pad under nitrogen atmosphere into *tert*-butyl alcohol (10 mL) solution. Removal of solvent furnished a dark oily product, which was charged on a silica gel (20 g) column. Elution of the column with benzene removed substantial impurities of nonpolar products. Continued elution with the same solvent furnished diketone **26** (200 mg, 40%). Recrystallization from pet ether–dichloromethane furnished **26** as white needles: mp 85 °C; IR (KBr) $\nu_{max}$ 1740 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.16 (d, 6 H, $J$ = 7 Hz, $CHCH_3$), 1.9–2.6 (m, 12 H); $^{13}C$ NMR ($CDCl_3$, 67.89 MHz) $\delta$ 220.1 (s), 51.2 (d), 44.7 (d), 42.7 (t), 41.1 (t), 39.8 (d), 15.6 (q, $CH_3$); mass spectrum (70 eV), $m/e$ (relative intensity) 206 (molecular ion, 57), 109 (95), 96 (61), 82 (90), 79 (61), 68 (52), 67 (100), 55 (33), 53 (47), 41 (95). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.75; H, 8.86.

Further elution of the column with 10% ethyl acetate–benzene gave **27** (70 mg, 14%). Crystallization from pet ether–dichloromethane gave pure **27**: mp 107–108 °C; IR (KBr) $\nu_{max}$ 3500 (hydroxyl), 1730 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.0 (d, 3 H, $J$ = 7 Hz, $CHCH_3$), 1.16 (s, 3 H, $CCH_3$), 1.25–2.9 (m, 12 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 225.5, 83.6, 57.6, 55.9, 50.8, 49.5, 46.7, 41.4, 38.2, 37.2, 36.3, 19.3, 10.6.

**Acid-Catalyzed Cyclization of 3,11-Dimethyltricyclo[6.3.0.0$^{2,6}$]undecane-4,10-dione (26).** A solution of dione **26** (100 mg, 0.48 mmol) and *p*-toluenesulfonic acid (100 mg, 0.58 mmol) in 10 mL of dry methanol was refluxed for 12 h. The reaction mixture was diluted with water and extracted with dichloromethane (10 mL × 2), washed with aqueous $NaHCO_3$, and dried. Evaporation of solvent and filtration through a small silica gel column furnished **28** (60 mg, 50%). Crystallization from carbon tetrachloride–pet ether gave **28**: mp 119–120 °C; IR (KBr) $\nu_{max}$ 1735 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.94 (d, 3 H, $J$ = 7 Hz, $CHCH_3$), 1.16 (s, 3 H, $CCH_3$), 1.2–2.9 (m, 11 H), 3.4 (s, 3 H, $OCH_3$); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 225.0 (s), 88.5 (s, $COCH_3$), 59.3 (s), 57.8 (d), 54.5 (q, $COCH_3$), 50.0 (d), 49.7 (t), 48.0 (d), 41.8 (t), 38.4 (t), 36.2 (d), 33.0 (t), 20.1 (q, $CH_3$), 11.1 (q, $CH_3$). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.73; H, 9.23.

**Zinc–Acetic Acid Reduction of Hexacyclo[7.4.2.0$^{1,9}$.0$^{3,7}$.0$^{4,14}$.0$^{6,15}$]pentadecane-2,8-dione (29).** A mixture of hexacyclic dione **29**[13] (1.0 g, 4.38 mmol) and zinc (3 g, 45.8 mmol) in 50 mL of glacial acetic acid was stirred at room temperature for 12 h. The insoluble metal and salts were removed by filtration. The filtrate was concentrated and diluted with acid with cold water (25 mL). Extraction with dichloromethane (50 mL × 2), washing with saturated $NaHCO_3$ solution, drying, and removal of solvent gave hydroxyketone **30** (800 mg, 80%). Crystallization from carbon tetrachloride–pet ether mixture gave **30**: mp 119–120 °C; IR (KBr) $\nu_{max}$ 3450 (hydroxyl), 1745 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.0–2.8 (m, 17 H), 3.25 (s, 1 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 218.1 (s), 85.3 (s, COH), 56.4 (s), 52.2 (d), 50.0, 49.4, 49.0, 48.4, 47.0, 40.8 (d), 36.7 (t), 28.6 (t), 25.8 (t), 24.6 (t, 2 C). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.16; H, 7.86.

**Na–K Alloy Reduction of 7-Hydroxyhexacyclo[7.5.1.0$^{1,7}$.0$^{6,13}$0.$^{8,12}$.0$^{10,14}$]pentadecan-15-one (30).** Of hydroxy ketone **30** (400 mg, 1.75 mmol) in 10 mL of dry toluene and trimethylchlorosilane (10 mL) were sequentially injected into a 250-mL flask containing 720 mg of Na–K alloy (prepared from 120 mg of Na, 600 mg of K) in dry toluene (60 mL). The reaction mixture was refluxed for 3 h and cooled. Quick filtration through a Celite pad under nitrogen into *tert*-butyl alcohol (10 mL) and removal of solvent gave an oily product, which was charged on silica gel (20 g) column. Elution with benzene removed nonpolar material. Further elution with 5% ethyl acetate–benzene gave **31** (150 mg, 38%). Crystallization from pet ether–dichloromethane gave pure, crystalline **31**: mp 107–108 °C; IR (KBr) $\nu_{max}$ 1735 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.9–3.0 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 67.89 MHz) $\delta$ 219.2 (s), 50.0 (d), 48.9 (d), 41.0 (t), 40.6 (t), 40.0 (d), 29.2 (t), 25.6 (t); mass spectrum (70 eV), $m/e$ (relative intensity) 232 (molecular ion, 70), 191 (30), 178 (100), 149 (24), 131 (30), 119 (34), 95 (38), 93 (36), 91 (58), 79 (64), 69 (90), 41 (64). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.34; H, 8.66. Continued elution with the same solvent gave **32** (33 mg, 8%), which was crystallized from pet ether–dichloromethane: mp 115 °C; IR (KBr) $\nu_{max}$ 3350 (hydroxyl), 1720 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 1.0–3.2 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 84.0, 61.2, 56.3, 56.1, 51.2, 49.5, 43.7, 41.0, 38.8, 37.7, 33.3, 29.0, 27.3, 24.0; mass spectrum (70 eV) $m/e$ (relative intensity) 232 (molecular ion, 100), 214 (38), 95 (40), 79 (35), 67 (23). Anal. Calcd for $C_{15}H_{20}O_2$: $m/e$ 232.1463. Found: $m/e$ 232.1442.

**Acid-Catalyzed Cyclization of Tetracyclo[10.2.1.0$^{4,14}$.0$^{9,13}$]pentadecane-3,10-dione (31).** A solution of tetracyclic dione **31** (20 mg, 0.086 mmol) and *p*-toluenesulfonic acid (100 mg, 0.58 mmol) in 5 mL of dry methanol was refluxed for 32 h. The reaction mixture was diluted with water (5 mL) and extracted with dichloromethane (10 mL × 2). The organic phase was washed with aqueous $NaHCO_3$ solution and dried. Evaporation of solvent furnished **33** (21 mg, 100%), which was bulb-to-bulb distilled at 160 °C (1 torr): IR ($CCl_4$) $\nu_{max}$ 1735 $cm^{-1}$ (carbonyl); $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.8–3.2 (m, 19 H), 3.36 (s, 3 H, $COCH_3$); $^{13}C$ NMR ($CDCl_3$, 25.0 MHz) $\delta$ 223.8 (s), 88.5 (s, $COCH_3$), 62.3 (s), 56.7 (q, $OCH_3$), 53.2 (d), 52.5 (d), 50.8 (d), 49.7 (t), 41.1 (t), 38.6 (d), 37.6 (d), 36.1 (t), 33.3 (t), 29.1 (t), 27.2 (t), 24.0 (t). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.00; H, 9.06.

**Pentacyclo[10.2.1.0$^{4,8}$.0$^{4,10}$.0$^{9,13}$]pentadec-5-ene-3,10-dione (36).** Dione **34**[14] (600 mg, 2.65 mmol) was treated with 600 mg of Na–K alloy (prepared from 100 mg of sodium and 500 mg of potassium as described earlier) and 10 mL of trimethylchlorosilane

in toluene (50 mL). The mixture was refluxed for 2.5 h. After cooling to room temperature, the reaction mixture was filtered through Celite pad into *tert*-butyl alcohol (10 mL) under nitrogen atmosphere. Concentration of the filtrate and column chromatography gave **36** (300 mg, 50%) as a white solid. It was recrystallized from methanol: mp 150 °C; IR (KBr) $\nu_{max}$ 3060, 1735 (carbonyl), 1610 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 100 MHz) $\delta$ 0.9 (q, 1 H, $J$ = 12 Hz), 2.0–3.0 (m, 11 H), 3.1–3.5 (m, 2 H), 5.4 (m, 1 H), 5.8 (m, 1 H); $^{13}$C NMR ($CDCl_3$, 25.0 MHz) $\delta$ 220.9 (s), 219.3 (s), 132.6 (d), 131.7 (d), 77.7 (s), 63.0 (d), 58.7 (d), 54.1 (d), 53.8 (d), 45.2 (t), 44.5 (t), 41.2 (d, 2 C), 40.8 (t), 39.5 (t); mass spectrum (70 eV) $m/e$ (relative intensity) 228 (molecular ion, 100), 210 (14), 200 (13), 160 (26), 147 (25), 132 (35), 130 (32), 121 (42), 105 (97), 91 (34). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.99; H, 6.80.

**6-Methoxypentacyclo[10.2.1.0$^{4,8}$.0$^{4,10}$.0$^{9,13}$]pentadecane-3,10-dione (37).** Dione **35**[14] (1.2 g, 4.65 mmol) was treated with 1.2 g of Na–K alloy (prepared from 200 mg of sodium and 1.0 g of potassium as described earlier) and trimethylchlorosilane (10 mL) in 100 mL of dry toluene. The mixture was refluxed for 1 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad into *tert*-butyl alcohol (10 mL) under nitrogen atmosphere. Concentration of the filtrate and column chromatography gave **37** (720 mg, 60%) as a white solid. It was recrystallized from pet ether–carbon tetrachloride: mp 97–98 °C; IR (KBr) $\nu_{max}$ 1730 cm$^{-1}$ (carbonyl); $^1$H NMR ($CDCl_3$, 100 MHz) $\delta$ 0.8 (q, 1 H, $J$ = 12 Hz), 1.4–3.0 (m, 13 H), 3.2 (s, 3 H, $OCH_3$), 3.3–3.8 (m, 3 H); $^{13}$C NMR ($CDCl_3$, 25.0 MHz) $\delta$ 222.8 (s), 220.4 (s), 87.3 (d, $HCOCH_3$), 72.5 (s), 62.1 (d), 57.7 (q, $OCH_3$), 55.9, 54.9, 53.8, 45.9 (t), 44.9 (t), 41.0 (d, 2 C), 39.3 (d), 30.7 (t), 30.6 (t); mass spectrum (70 eV) $m/e$ (relative intensity) 260 (molecular ion, 54), 245 (19), 232 (30), 228 (46), 189 (95), 161 (6), 117 (22), 105 (25), 91 (43), 79 (23), 72 (100). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.74; H, 7.56.

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# 2-Alkenyl-Substituted Methyl 2-Siloxycyclopropanecarboxylates as Masked Vinyl Ketones: Efficient Syntheses of Highly Functionalized Michael Adducts

Erich L. Grimm, Ruth Zschiesche, and Hans-Ulrich Reissig*

*Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG*

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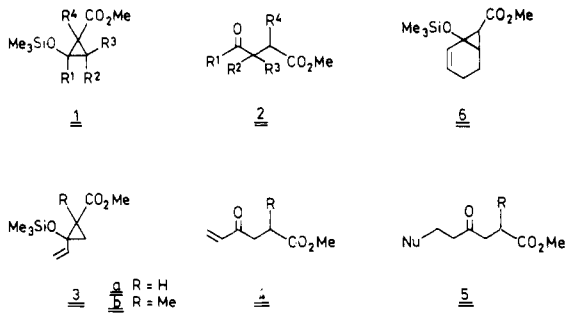
2-Alkenyl-substituted methyl 2-siloxycyclopropanecarboxylates **3a**, **3b**, and **6**—easily available from the corresponding silyl enol ether—react with a variety of O-, N-, S-, and C-nucleophiles under mild acidic or basic conditions providing polyfunctionalized products **7–19** in good to excellent yields via 1,4-addition to vinyl ketones formed in situ. Due to the versatility of the nitro group, nitroalkane adducts **15–19** are of special interest for further transformations.

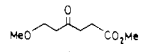
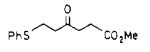
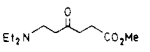
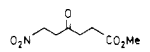
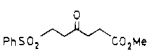
Michael addition of nucleophiles toward $\alpha,\beta$-unsaturated carbonyl compounds is a key reaction to construct polyfunctional carbon skeletons.[1] Numerous examples demonstrate the utility of this basic step in synthetic strategy.

We have shown that the easily available[2] methyl 2-siloxycyclopropanecarboxylates **1** are versatile intermediates for the high-yield synthesis of several 4-oxoalkanoate derivatives (e.g., **2**).[3] If $R^1$ is an alkenyl group as in **3** these




cyclopropanes are masked vinyl ketones since **4** can be liberated by ring opening with fluoride or acid.[3a] We therefore looked for efficient one-pot procedures allowing generation of 4-type acceptors and trapping of these intermediates with nucleophiles. This straightforward

**Table I. Conversion of Vinylcyclopropane 3a to 6-Heterosubstituted 4-Oxoalkanoates 7–11**

| entry | nucleophile | solvent | "catalyst" | product | yield |
|---|---|---|---|---|---|
| a | MeOH | MeOH | $K_2CO_3$ |  7 | 91 % |
| b | PhSH | – | Triton B |  8 | 69 %[a] |
| c | $Et_2NH$ | THF | $NEt_3 \cdot 3HF$ |  9 | 98 % |
| d | $NaNO_2$ | THF | AcOH |  10 | 55 % |
| e | $NaSO_2Ph$ | $CH_2Cl_2/H_2O$ | HCl |  11 | 54 % |

[a] This material contains traces of $Ph_2S_2$ which can be removed by chromatography. Participation of a free radical path forming **8** cannot be excluded.

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