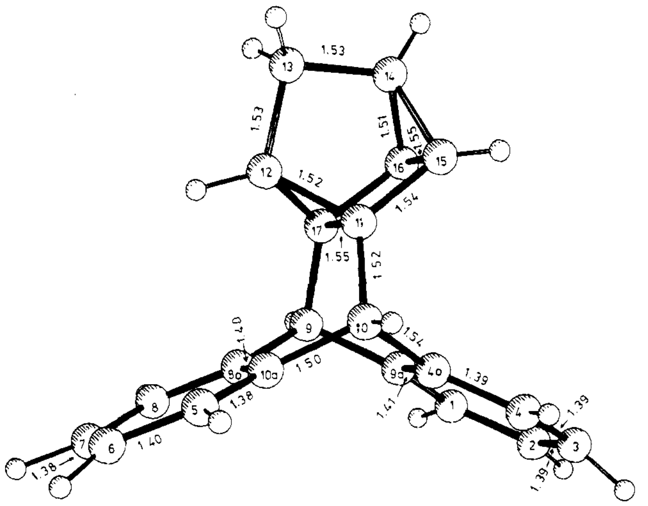

Figure 1. A perspective view of **12**. Values for the CC bond lengths (ångstroms) are displayed.

Table I. Selected CCC Bond Angles of **12**

∠C-C-C	degree	∠C-C-C	degree
9-17-11	113	11-15-14	104
9-17-12	125	12-13-14	100
9-17-16	128	13-14-16	111
11-12-17	60	14-15-16	58
11-17-12	60	15-14-16	62
11-15-16	90	15-11-17	89

(d), 125.74 (d), 141.26 (s), 144.71 (s)). The latter excludes **13**, the Diels-Alder adduct of **11** and anthracene, the ^{13}C NMR spectrum of which should show only five different signals for aliphatic C atoms.[8]

The X-ray analysis of the Diels-Alder adduct definitely proved structure **12** which is depicted in detail in Figure 1. Selected bond angles are given in Table I.[9]

Note that the bond C-11-C-17 is the central bond of a [4.2.1]propellane system. Furthermore, the centers of the propellane subunit, C-11 and C-17, show the phenomenon of the "inverted tetrahedron".[10,11]

The outcome of the trapping experiment with the formation of the adduct **12** is in accordance with Scheme I. However, at present it is not clear why the expected isomer **13** could not be detected. Attempts are underway to establish fully the intermediacy of the proposed reactive species **10** and **11**.

Acknowledgments. This work was supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie, and by Fonds de la Recherche Fondamentale Collective. One of us (J.-P. D.) is indebted to the Fonds National de la Recherche Scientifique for a fellowship.

References and Notes

(1) (a) G. Szeimies, J. Harnisch, and O. Baumgärtel, *J. Am. Chem. Soc.*, **99**, 5183 (1977); (b) G. Szeimies, J. Harnisch, and K.-H. Stadler, *Tetrahedron Lett.*, 243 (1978); (c) U. Szeimies-Seebach and G. Szeimies, *J. Am. Chem. Soc.*, **100**, 3966 (1978); (d) J. Harnisch, H. Legner, U. Szeimies-Seebach, and G. Szeimies, *Tetrahedron Lett.*, 3683 (1978); (e) U. Szeimies-Seebach, J. Harnisch, G. Szeimies, M. Van Meerssche, G. Germain, and J.-P. Declercq, *Angew. Chem., Int. Ed. Engl.*, **17**, 848 (1978).

(2) IUPAC name: tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane. S. J. Cristol and R. L. Snell (*J. Am. Chem. Soc.*, **80**, 1950 (1958)) coined this ring system "quadricyclene", which most, but not all, users silently changed to "quadricyclane" (H. Hogeveen and B. J. Nusse, *ibid.*, **100**, 3110 (1978); Y. Sugiyama, T. Kawamura, and T. Yonezawa, *ibid.*, **100**, 6525 (1978); T. Sasaki, K. Kanematsu, I. Ando, and O. Yamashita, *ibid.*, **99**, 871 (1977); D. S. Kabakoff, J.-C. G. Bünzli, J. F. M. Oth, W. B. Hammond, and J. A. Berson, *ibid.*, **97**, 1510 (1975); R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *ibid.*, **97**, 812 (1975); H. K. Hall, Jr., C. D. Smith, and J. H. Bald, *ibid.*, **95**, 3197 (1973)). Here, we follow this latter practice. On this basis, **10** and **11** could be named 1,7- and 1,5-dehydroquadricyclane, respectively.

(3) C. D. Smith, *Org. Synth.*, **51**, 133 (1971).

(4) G. Szeimies, F. Philipp, O. Baumgärtel, and J. Harnisch, *Tetrahedron Lett.*, 2135 (1977).

(5) D. I. Davies, *J. Chem. Soc.*, 3669 (1960).

(6) The spectral data of this compound are consistent with the proposed structure.

(7) The norbornadienes **5**, **6**, and **7** were separated by preparative GLC (20% Carbowax 20M on Kieselguhr; retention times for **5-7** were in the order **6** < **7** < **5**) and the compounds were identified by the chemical shifts of the olefinic and bridgehead protons in the respective ^1H NMR spectra ($CDCl_3$, δ scale): **5**, 6.04 (narrow m, 2 H), 2.90 (narrow m, 1 H), 3.25 (narrow m, 1 H); **6**, 6.63 (narrow m, 2 H), 3.09 (narrow m, 1 H), 3.17 (narrow m, 1 H); **7**, 6.01 (narrow m, 2 H), 3.04 (m, 2 H).

(8) Judging from the NMR spectra of the raw material, **13** could not have been formed in a yield >5%.

(9) Space group $P2_1/n$; $Z = 8$; $a = 18.407\ (19)$, $b = 14.244\ (5)$, $c = 11.153\ (10)$ Å; $\beta = 105.99\ (7)°$. The intensities of 4159 reflexions were measured on a Syntex $P2_1$ automated diffractometer (Mo $K\alpha$ radiation; $2\theta_{max} = 47°$) and 1293 were used for the resolution with the program MULTAN 77 (P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J.-P. Declercq, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University of York, England, and University of Louvain-la-Neuve, Belgium) and refined to $R = 0.075$ with the X-RAY 72 SYSTEM (Technical Report TR-192. Computer Science Center, University of Maryland, College Park, 1972).

(10) K. B. Wiberg, G. J. Burgmaier, K. W. Shen, S. J. La Placa, W. C. Hamilton, and M. D. Newton, *J. Am. Chem. Soc.*, **94**, 7402 (1972); C. S. Gibbons and J. Trotter, *Can. J. Chem.*, **51**, 87 (1973).

(11) The distance of C-11 to the nearest tetrahedral plane (C-10-C-12-C-15) is 0.05 Å. This plane intersects the C-11-C-17 bond.

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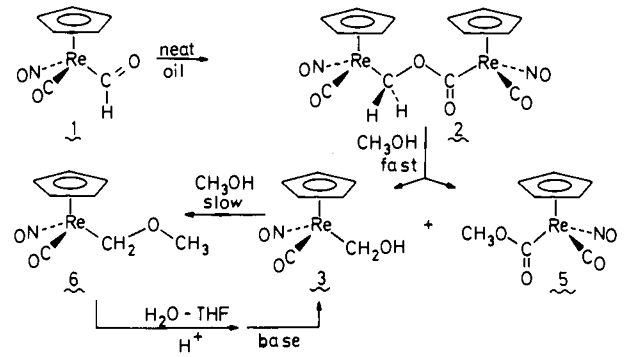
Disproportionation of a Neutral Metal-Formyl Complex and Synthesis of a Stable Hydroxymethyl-Metal Compound

Sir:

The projected petroleum shortage has caused renewed interest in alternative sources of liquid fuels and petrochemical feedstocks. One such alternative that is now being widely investigated is the reduction of coal-derived carbon monoxide-hydrogen mixtures via the Fischer-Tropsch and related reactions.[1] Little is known, however, about the course of these reactions, and proposed mechanisms are essentially only intelligent speculations. For the past several years, we have been studying some of the unusual intermediates and reactions which have been proposed to occur in CO reduction.[1-3] We,[1,2] and others,[4] have synthesized and studied the reactions of metal-formyl complexes which may be important intermediates in the initiation step of CO reduction. We have also studied the hydrogenation of metal-carbene complexes,[3] a reaction which may be related to the chain termination step in CO reduction. Here we report (a) the Cannizzaro-like disproportionation of the neutral formyl complex $(C_5H_5)Re(CO)(NO)(CHO)$ (**1**)[1] to give the dimeric metallo ester $(C_5H_5)(CO)(NO)ReCH_2OC(O)Re(CO)(NO)(C_5H_5)$ (**2**) and (b) the indirect hydrolysis of this ester to give the first stable authentic hydroxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OH)$ (**3**) (Scheme I). Hydroxymethyl-metal complexes have been considered as intermediates in CO reduction but have previously been unavailable for study.[5-7]

Ester **2** was discovered during our attempts to understand the unusual behavior of $(C_5H_5)Re(CO)(NO)(CHO)$. This neutral formyl complex is only moderately air sensitive and is relatively stable in solution under nitrogen, decomposing over several days to give $(C_5H_5)Re(CO)(NO)(H)$ (**4**) as the pri-

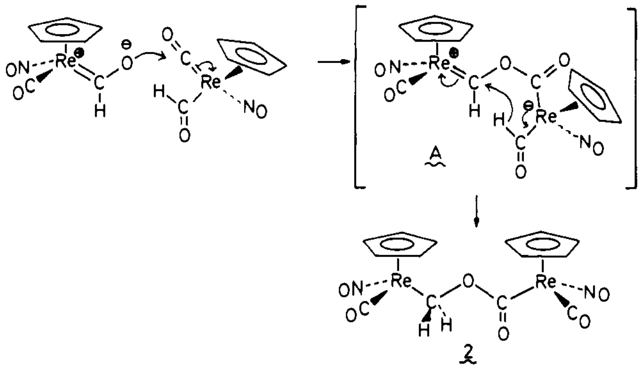
Scheme I



mary product.[1] Despite this apparent stability, attempts to rigorously purify **1** were unsuccessful. When rapidly isolated at 0 °C, **1** can be obtained as an orange oil.[1] Upon sitting at room temperature under a nitrogen atmosphere, however, the oil soon darkens and then forms a deep red solid over a period of 12-48 h. Surprisingly, the red solid does not contain significant amounts of hydride **4**. Recrystallization of the benzene-soluble extract of the red solid from toluene-heptane gave a 45-55% isolated yield[8] of the dimeric metallo ester $(C_5H_5)(CO)(NO)ReCH_2OC(O)Re(CO)(NO)(C_5H_5)$ (**2**, red-orange powder, mp 105-115 °C) as a ~1:1 mixture of the two possible diastereomers (each pseudotetrahedral rhenium atom is a chiral center). The IR spectrum (tetrahydrofuran) of **2** shows two terminal CO stretching modes at 1986 and 1966 cm^{-1}, two NO stretching modes at 1722 and 1702 cm^{-1}, and bands at 1626 and 1010 (Nujol mull) cm^{-1} due to the ester linkage (cf. $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$[5]). The presence of two diastereomers is clearly evident from the ^1H NMR spectrum (C_6D_6). A total of four C_5H_5 resonances (two from each diastereomer) are seen at 270 MHz at δ 4.956, 4.958, 5.032, and 5.034. In addition, two AB quartets, one due to the diastereotopic CH_2 group of each diastereomer, are seen at δ 5.89, 6.49 (J = 9.7 Hz) and 5.99, 6.42 (J = 9.7 Hz). Although the mass spectrum of **2** lacks a parent ion, $(P - CO)^+$ and $(P - NO)^+$ peaks are observed as well as other fragments consistent with **2**. In particular, the base peak is $(C_5H_5)Re(CO)_2(NO)^+$ resulting from a typical ester fragmentation pattern.

The differing behavior of formyl complex **1** in solution vs. the neat oil is apparently the result of competing unimolecular and bimolecular decomposition pathways. In dilute solution, unimolecular decomposition predominates yielding $(C_5H_5)Re(CO)(NO)(H)$. In the highly concentrated neat oil, on the other hand, a bimolecular pathway predominates giving ester **2**. In overall appearance, this redox disproportionation of formyl complex **1** to ester **2** resembles the Cannizzaro and Tischenko reaction of organic aldehydes.[9] The formation of metallo ester **2** is suggested to proceed by the two-step mechanism shown in Scheme II. Initially, the formyl oxygen atom of one molecule of **1** could attack the coordinated carbonyl ligand of a second molecule of **1** to form intermediate **A**. The low stretching frequency of the formyl CO bond (1619 cm^{-1}) of **1**[1] indicates a high contribution from a zwitterionic resonance structure ($Re^+{=}CH{-}O^-$) and thus a moderate nucleophilicity for the formyl oxygen atom. The susceptibility of the coordinated CO of **1** to nucleophilic attack was demonstrated earlier in the reaction of **1** with $LiBH(C_2H_5)_3$ to give the diformyl anion $(C_5H_5)Re(NO)(CHO)_2^-$.[1] Intermediate A is ideally situated for internal hydride transfer from the formyl ligand attached to the negatively charged rhenium center to the carbene carbon atom of the positively charged rhenium center. The ability of metal-formyl compounds to act as hydride donors has previously been established.[2,4c] In particular, the reduction of the carbene complex $(CO)_5WC(OCH_3)(C_6H_5)$ to $(CO)_5WCH(OCH_3)(C_6H_5)^-$ by $Fe(CO)_3[P(OC_6H_5)_3](CHO)^-$ has been observed.[10]

Scheme II



Scheme III

$$2\ MH + 2\ CO \rightleftharpoons 2\ MCHO \qquad (1)$$

$$2\ MCHO \longrightarrow MCH_2OC(O)M \qquad (2)$$

$$MCH_2OC(O)M + H_2O \rightleftharpoons MCH_2OH + MCO_2H \qquad (3)$$

$$MCH_2OH + H_2 \longrightarrow MH + CH_3OH \qquad (4)$$

$$MCO_2H \longrightarrow MH + CO_2 \qquad (5)$$

$$2\ CO + H_2O + H_2 \longrightarrow CH_3OH + CO_2$$

Metallo ester **2** appeared to be an ideal precursor for the preparation of an authentic sample of the hydroxymethyl complex **3**.[5] In a model experiment, it was found that the methyl ester $(C_5H_5)Re(CO)(NO)(CO_2CH_3)$ (**5**)[5] readily transesterifies with ethanol under exceedingly mild conditions: 2 h in C_6D_6 without added catalyst. ^1H NMR suggested that the methanolysis of the metallo ester **2** in C_6D_6 proceeded similarly to give hydroxymethyl complex **3** and methyl ester **5**. Although complex **3** could not be isolated from this reaction mixture,[11] its presence was verified by NMR following its successful isolation (vide infra). Continued NMR monitoring of the methanolysis of dimer **2** showed that the peaks attributed to hydroxymethyl complex **3** slowly disappeared and were replaced by new ones which could be assigned to a methoxymethyl complex $(C_5H_5)Re(CO)(NO)(CH_2OCH_3)$ (**6**).[12] Complex **6** was subsequently isolated[8,13] and characterized.[14,15]

An attempt was then made to hydrolyze ether **6** by dissolution in water-tetrahydrofuran (2:1). While little reaction occurred in the absence of acid, addition of 0.1 equiv of CF_3CO_2H, stirring for 2.5 h, concentration, and extraction with toluene yielded an orange solid on evaporation. Spectral data strongly suggest that the orange substance is not hydroxymethyl complex **3**, but its acid-catalyzed, self-condensation product $(C_5H_5)(CO)(NO)ReCH_2OCH_2Re(CO)(NO)(C_5H_5)$ (**7**).[12,16,17] The desired hydroxymethyl complex **3** was finally obtained when the acid-catalyzed hydrolysis of ether **6** described above was quenched with 0.15 equiv of $N(C_2H_5)_3$ prior to workup. Evaporation of the toluene extract yielded an orange powder (80%)[8] conclusively identified as hydroxymethyl complex **3**. The ^1H NMR (C_6D_6) shows a cyclopentadienyl resonance at δ 4.78, an AB quartet due to the diastereotopic CH_2 group at 5.83, 5.11 (J = 10 Hz), and a singlet at 0.88 which exchanges with D_2O and is assigned to the OH proton. The IR spectrum in toluene shows ν_{CO} at 1967 cm^{-1} and ν_{NO} at 1699 cm^{-1} and in Fluorolube mull shows ν_{OH} at 3215 (br) cm^{-1} which is shifted to 2390 (br) cm^{-1} in the D_2O exchanged material. The higher melting point (97-100

°C with slow heating from 25°C, 105 °C with heating from 95 °C) and air stability of **3** clearly distinguish it from the material purported to have the same structure as **3** isolated by Nesmeyanov et al. (mp 69-71 °C, rapidly oxidized).[5] While the multistep synthesis required for the preparation of **3** (seven steps from $Re_2(CO)_{10}$, 7% overall yield) has so far limited our study of its chemistry, we note here the rather surprising observation that **3** is stable toward $N(C_2H_5)_3$ in C_6D_6.

The results reported here suggest that mechanisms similar to that shown in Scheme III should be considered as possible routes for metal-catalyzed CO reduction. While the metal-formyl complex formed in step 1 is probably thermodynamically unstable relative to metal hydride,[10] reactions proceeding through the formyl intermediate might still occur at reasonable rates. The formyl disproportionation (step 2) and metallo ester hydrolysis (step 3) have been demonstrated here. The hydrogenation of metal alkyls (step 4) and the decarboxylation of metal-carboxy complexes (step 5) are well known. (Obviously, chain extension by CO insertion could precede hydrogen cleavage of the hydroxymethyl metal complex.) Finally, it should be noted that the suggested scheme also includes a variant on the water gas shift reaction.[18] Half of the CO is oxidized to CO_2 via disproportionation of the formyl species, while water supplies half of the hydrogen for reducing the other mole of CO.

Note Added in Proof. The reduction of $C_5H_5Re(NO)(CO)_2{}^+PF_6{}^-$ with $Na^+H_2Al(CH_2CH_3)_2{}^-$ in THF provides a more direct synthesis of $C_5H_5Re(NO)(CO)CH_2OH$, **3**, in 45% isolated yield. Graham has similarly observed that reduction of $C_5H_5Re(NO)(CO)_2{}^+BF_4{}^-$ with 2 equiv of $NaBH_4$ in THF-H_2O gives **3**: W. A. G. Graham and J. R. Sweet, *J. Organomet. Chem.*, in press.

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Supplementary Material Available: Experimental details for the synthesis of complexes **2**, **3** and **6** (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741, and references therein. For a review see Olivé, G. H.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–141.

(2) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544–2545; **1976**, 98, 5395–5396.

(3) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 1651–1652.

(4) (a) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089–4090. (b) Winter, S. R.; Cornett, G. W.; Thompson, E. A. *J. Organomet. Chem.* **1977**, *133*, 339–346. (c) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545–2547, and references therein. (d) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73–89.

(5) While the preparation of hydroxymethyl complex **3** has been claimed by Nesmeyanov et al. (Nesmeyanov, A. N.; Krasnoslobodskaya, L. L. *Bull. Acad. Sci. USSR* **1970**, 807–811), we have recently shown[1] that this work is probably in error—a conclusion verified by the present work.

(6) The bistrifluoromethyl derivative of a hydroxymethyl complex, $(C_5H_5)Fe(CO)_2[C(OH)(CF_3)_2]$ has been reported: Blackmore, T.; Bruce, M. I.; Davidson, P. J.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3153–3158.

(7) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766–6768.

(8) Experimental details are available as supplementary material.

(9) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill Book Co.: New York, 1968.

(10) Neumann, S. M. Ph.D. Thesis, University of Wisconsin at Madison, 1978.

(11) Removal of solvent from the reaction mixture containg hydroxymethyl complex **3** and methyl ester **5** simply leads to reverse transesterification and the regeneration of dimer **2**.

(12) This unusually rapid ether formation by alcohol condensation is suggested to proceed via the cationic carbene complex $(C_5H_5)Re(CO)(NO)(CH_2)^+$.

(13) Dimer **2** was dissolved in methanol and stirred for 4–5 days and the methanol evaporated. The residue was extracted with heptane (leaving behind methyl ester **5**) and the heptane evaporated to give **6** as an orange oil which gradually solidified to red-orange crystals (85%).

(14) IR (heptane): ν_{CO} 1976, ν_{NO} 1715 (br) cm^{-1}. ^1H NMR (C_6D_6): δ 3.24, s (3 H) 4.80 (s, 5 H), 5.14, 5.30 (AB quartet, $J = 9.5$ Hz, 2 H).

(15) Other methoxymethyl complexes are known. See, for example, the following. (a) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910–1918. (b) Green, M. L. H.; Ishaq, M.; Whitely, R. N. *J. Chem. Soc. A.* **1967**, 1508–1515. (c) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5045.

(16) IR (THF): ν_{CO} 1961, ν_{NO} 1697 cm^{-1}. ^1H NMR (C_6D_6): δ 4.85 (s, 5 H), 4.87 (s, 5 H), 5.06, 5.16, 5.34, 5.49 (pair of AB quartets, $J = 9$ Hz, 4 H).

(17) Dimeric ether **7** is also formed when isolated hydroxymethyl complex **3** is treated with catalytic CF_3CO_2H in C_6D_6.

(18) See ref 1 and references therein. For a review see "Catalyst Handbook", Springer-Verlag: London, 1970.

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A New Strategy for Gibberellin Synthesis

Sir:

Although many elegant and ingenious methods have been developed for the preparation of the individual structural features of gibberellic acid (**1**), the total synthesis of the complete molecule has not yet been realized.[1,2] This is presumably due to the lack of a sufficiently efficient and reliable overall strategy. In this paper we describe the preparation of the gibbane derivative **9** by a very efficient sequence, which is sufficiently flexible to be used in the elaboration of **1** itself. The synthesis (Scheme I), which begins with the readily prepared naphthoic acid **2**,[3] is notable for the complete utilization of all the latent functionality contained in the anisole synthon,[6] for the generation of the remaining carbon skeleton from one functional center (C-8), and for its stereoselectivity.

The diazo ketone **3**[7] was the pivotal intermediate in the sequence leading to **9** and was cyclized in trifluoroacetic acid[8] to the dienone **4**, which then underwent an intramolecular Michael reaction to give the tetracyclic diketone **5**.[9] From ^1H NMR spectra it was apparent that one ester methoxyl (δ 3.54) lay in the shielding zone of the 7-carbonyl group,[9a] but that the 15-exo proton (δ 3.24, d, $J = 20$ Hz) was deshielded by it.[10] These data were consistent only with the diastereomer **5**, and although this stereochemistry differed from the natural gibberellins, it was expected to ensure the development of the correct relative chirality at C-4, C-5, C-9, and C-10.[11,12] Lactonization of the diketo acid, mp 178-180 °C, derived (*n*-PrSLi, HMPA)[13] from **5** was not productive, but the corresponding $7\alpha,16\alpha$-dibenzoate, mp 199-200 °C, was converted quantitatively to lactone **6**; the stereochemistry assigned to **6** is expected to be favored both kinetically, and thermodynamically.[11] In preparation for the final stage of the synthesis, **6** was reduced[14] to the C-18 alcohol (*p*-nitrobenzoate, mp 219-220 °C), protected as the methoxymethyl ether,[15] mp 193-194 °C, the C-7 hydroxyl function selectively liberated, and then oxidized to the ketone **7**, mp 169-170 °C. Functionalization of the hindered C-6 position is clearly mandatory for any ring contraction procedure, but all traditional procedures (e.g., acylation, nitrosation, thallation[16]) were completely unsuccessful. The diazo ketone **8** was finally obtained (66% yield) by a novel phase-transfer method,[17] and induced to undergo the photochemical Wolff rearrangement, affording acid **9**, mp 214-215 °C (45% yield, not optimized), as well as a minor amount (10%) of the 6α epimer. Comparison of the ^{13}C NMR spectrum of **9** methyl ester with that of the gibberellin derived **10**[18] and analogous compounds (with allowance for substituent effects) substantiated the assignment of structure **9**.[19] In ^1H NMR spectra H-6 gave rise to a doublet ($J_{5,6} = 7$ Hz) at δ 2.62 for both **9** and **10**; the 6-epimer of **9** methyl ester showed a doublet ($J_{5,6} = 11$ Hz) at δ 2.40.[22]

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