$CHCH_2Cl$) were essentially the only compounds observed by GC analysis. For example, the reaction of 1,4-dichloro-2-butyne (1) and *m*-chlorophenylmagnesium bromide gave a product distribution of 15% m-$ClC_6H_4CH_2C\equiv CCH_2Cl$ and 85% biaryl, according to GC–MS analysis. However, the *p*-bromo- and *p*-fluoroaryl Grignards gave a significant number of side products. Apparently, these para electron-withdrawing groups repress the desired electron transfer in favor of other competitive processes. For example, the product distribution for the reaction of 2 and the Grignard made from *p*-dibromobenzene in ether was 14% $CH_2{=}CHCH(p\text{-}BrC_6H_4)CH_2Cl$ (from an S_N2'-like reaction on 1,4-dichloro-2-butene), 8% p-$BrC_6H_4CH_2CH{=}CHCH_2Cl$, 12% 4-bromobiphenyl, 62% 4,4′-dibromobiphenyl, and 4% of a tribromobiphenyl.

The product mixture was even more complex for the reaction between 2 and the Grignard reagent made from *p*-bromofluorobenzene. Product composition was 8% $CH_2{=}CHCH(p\text{-}BrC_6H_4)CH_2Cl$, 14% p-$BrC_6H_4CH_2CH{=}CHCH_2Cl$, 68% 4,4′-difluorobiphenyl, 6% of a difluorobromobiphenyl, 1.5% of a bromofluorobiphenyl, and 2% of an unidentified compound.

We believe this chemistry may be useful as a probe for electron-transfer phenomena and are therefore investigating the reaction mechanism and ways of improving the coupling yields of alkyl Grignards.[13] In a separate paper we describe the use of this chemistry to prepare aromatic polymers[16] in high yields.

Experimental Section

Infrared spectra were obtained with Perkin-Elmer 137 and Beckman IR 10 spectrophotometers. Gas chromatographic analyses were obtained on a Hewlett-Packard 5712 TC detector instrument. Integration of peak areas was done on a Hewlett-Packard 3380 A integrator–recorder. NMR spectra were recorded on a Varian EM-360 spectrometer. Low-resolution mass spectra were obtained on a Varian MAT A GC/MS. Melting points are uncorrected and were obtained on a Mel-Temp apparatus. All chemicals were commercially obtained in reagent purity.

General Procedure for Coupling of Aryl Grignard Reagents. The Grignard reagent was typically prepared in 20 mL of ether from 0.53 g of magnesium (0.022 mol) and 0.022 mol of aryl bromide. Then, to the ice–water-cooled Grignard was added a solution of 0.020 mol of the dihalobutene (2 or 3) or butyne (1) in 5 mL of dry ether. After a 3-h reflux, the mixture was cooled with an ice–water bath, and a small amount of 4% HCl was added to make the solution just acidic to litmus. The aqueous layer was separated and the organic layer (if coupler 1 was used, the organic layer was filtered) was washed with 5% sodium bicarbonate and water and dried ($MgSO_4$). Air or rotary evaporation in vacuo then normally left a solid biaryl product. Liquids obtained (3,3′-biaryls) were distilled by using a 9-in. Vigreux column (see Table I). Product comparisons were made by NMR, melting point, and GC or GC–MS (with authentic samples). Three Grignards were prepared in THF (see Table I) instead of ether.

3,3′-Dichlorobiphenyl by means of 1,4-Dichloro-2-butyne (1) Promoter. A Grignard was prepared in 20 mL of ether from 0.54 g (0.022 mol) of magnesium and 4.30 g (0.022 mol) of 3-bromochlorobenzene. Then 2.48 g (0.02 mol) of 1,4-dichloro-2-butyne in 5 mL of ether was added dropwise over 15 min. The resulting mixture was refluxed for 3 h and then workup was done as above. A brown liquid (2.26 g) was obtained, which was 15% m-$ClC_6H_4CH_2C\equiv CCH_2Cl$ and 85% 3,3′-dichlorobiphenyl (1.92 g, 86% yield). Retention times were 6.9 and 14.1 min, respectively (6 ft × 0.125 in. 10% polyphenyl ether column at 225 °C). In GC–MS (6 ft × 0.125 in. 3% OV 17 column, 100–300 °C at 10 °C/min), the former compound's retention time was 7.4 min: m/z (relative intensity) 202 (1), 200 (9), 198 (12), 163 (55), 128 (100), 127 (90). The 3,3′-dichlorobiphenyl eluted at 8.8 min: m/z (relative intensity) 226 (10), 224 (54), 222 (100), 152 (99), 76 (30), 75 (25). The product distilled at 318–319 °C (lit.[3] bp 320).

4,4′-Difluorobiphenyl by means of *cis*-1,4-Dichloro-2-butene (2) Promoter. The reaction was performed as described above only with the Grignard from *p*-bromofluorobenzene and 2 as the promoter. The solid product was recrystalized twice from ethanol [mp 87–88 (lit.[3] mp 91–92 °C)]. The crude product (1.77 g) was 68.1% pure (63%) as determined by GC–MS analysis (5% SE-30 column, 160 °C, 6.12 min). Other products were 8% $CH_2{=}CHCH(p\text{-}FC_6H_4)CH_2Cl$ (3.5 min) 14% p-$FC_6H_4CH_2CH{=}CHCH_2Cl$ (5.0 min), 6% unknown compound (7.2 min), 1.5% of a difluorobromobiphenyl (11.1 min), 0.5% bromofluorobiphenyl (11.8 min), and 2% unknown compound (13.2 min).

Acknowledgment. We thank Peter Kovacic, Michael P. Doyle, and the Purdue University Organic Chemistry Faculty for helpful discussions. M. Beeny provided valuable GC–MS assistance. We also thank Research Corporation (C1108) and the National Science Foundation (CDP-8006131) for supporting this work.

Registry No. 1, 821-10-3; 2, 1476-11-5; 3, 110-57-6; bromophenylmagnesium, 100-58-3; bromo-*p*-tolylmagnesium, 4294-57-9; bromo-*m*-tolylmagnesium, 28987-79-3; bromo(*p*-methoxyphenyl)magnesium, 13139-86-1; bromo(*p*-chlorophenyl)magnesium, 873-77-8; bromo(*m*-chlorophenyl)magnesium, 36229-42-2; bromo(*p*-fluorophenyl)magnesium, 352-13-6; bromo(*p*-bromophenyl)magnesium, 18620-02-5; bromo-1-naphthylmagnesium, 703-55-9; 4-biphenylylbromomagnesium, 3315-91-1; biphenyl, 92-52-4; 4,4′-dimethylbiphenyl, 613-33-2; 3,3′-dimethylbiphenyl, 612-75-9; 4,4′-dimethoxybiphenyl, 2132-80-1; 4,4′-dichlorobiphenyl, 2050-68-2; 3,3′-dichlorobiphenyl, 2050-67-1; 4,4′-difluorobiphenyl, 398-23-2; 4,4′-dibromobiphenyl, 92-86-4; 1,1′-binaphthyl, 604-53-5; 4,4′-quaterphenyl, 135-70-6; tribromobiphenyl, 51202-79-0; difluorobromobiphenyl, 77029-20-0; $CH_2{=}CHCH(p\text{-}BrC_6H4)CH_2Cl$, 77028-08-1; ($Z$)-$p$-$BrC_6H_4CH_2CH{=}CHCH_2Cl$, 77028-09-2; m-$ClC_6H_4CH_2C\equiv CCH_2Cl$, 77028-10-5; $CH_2{=}CHCH(p\text{-}FC_6H_4)CH_2Cl$, 77028-11-6; ($Z$)-$p$-$FC_6H_4CH_2CH{=}CHCH_2Cl$, 77028-12-7.

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Formation of Dioxolanes from Carbonyl Compounds: Favored 5-Trigonal Cyclizations[1a]

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A few years ago, a series of rules was formulated which permitted predictions to be made regarding the ease with which certain cyclizations may occur.[2] Particularly important among these, in a predictive sense, has been that, in a chain of five first row atoms, attack by a nucleophilic atom at one end (atom 1) onto atom 5 of a 4,5-double bond is a "disfavored" path to a five-membered ring. In contrast, similar attack on atom 5 of a 5,6-double bond in a six-atom chain is "favored". These processes, which were denoted 5-endo-trig and 5-exo-trig, respectively, are depicted in eq 1 and 2. The rules were based on empirical data rather than on theory, and a critical consideration was the importance of the direction of approach of a nucleophile toward a double bond that had been deduced from crystallographic studies.[3] This approach vector is dis-

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[1] (a) Issued as NRCC Publication No. 18897. (b) Chelsea College. (c) National Research Council.

[2] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

[3] Burgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

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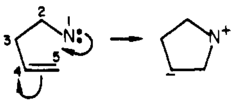
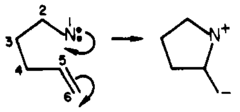


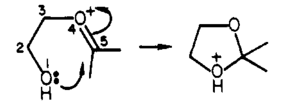
(1)



(2)

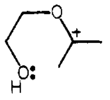
placed slightly from the perpendicular (Figure 1). Consideration of the precise direction of attack has proved to be especially valuable in the "approach vector analysis" of conjugate addition of nucleophiles to α,β-unsaturated carbonyl compounds,[4] but a different effect is, we believe, of vital importance in determining the relative ease of the 5-endo- and 5-exo-trig processes. Very simply, it is that in eq 1 only atoms 1 and 2 can easily be displaced out of the plane of the double bond until a relatively late stage along the reaction coordinate is reached. Thus considerable strain is necessary to bring atom 1 above atom 5. In contrast, in eq 2 ready displacement out of the plane of the double bond commences with atom 3, and models show that positioning of atom 1 above atom 5 incurs relatively little penalty in terms of strain energy.

The above distinction between eq 1 and 2 may have been implicit in the earlier work,[2] but its explicit consideration is important in the following analysis of what has sometimes been regarded as an exception to the rule disfavoring 5-endo-trig reactions. This exception is the formation of ethylene ketals,[5] for which the key "disfavored", but successfull, step is generally written as eq 3.



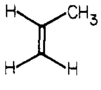
(3)

While it is formally possible to raise only atoms 1 and 2 out of the plane of the alkylideneoxonium ion, the barrier to raising atom 3 [i.e., to twisting about the C(5)–O bond] should be much smaller than that for the corresponding operation in eq 1. This is due to the carbonium ion contribution (1), in which there is a formal single bond between C(5) and oxygen.

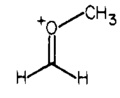


1

To adduce support for this hypothesis, we have now used MNDO calculations[6] to compare the energy requirements for twisting of the simple systems 2 and 3 about their respective double bonds.



2



3

Somewhat similar considerations are applicable to the observation that 4 cyclizes to 5 under conditions of acid catalysis, but that the reaction cannot be effected by base.[7] The inference drawn, namely, that there is a larger kinetic barrier to cyclization of 6 than 7, can, we believe, be accounted for in part by the greater ease of rotation about the α,β-C–C bond in 7 (cf. structure 7A). This has been examined by computing the ease of rotation about the α,β-bond in each of the model systems 8 and 9.

Figure 1. Direction of approach of nucleophilic reagent to a double bond inclined at angle θ to vertical.

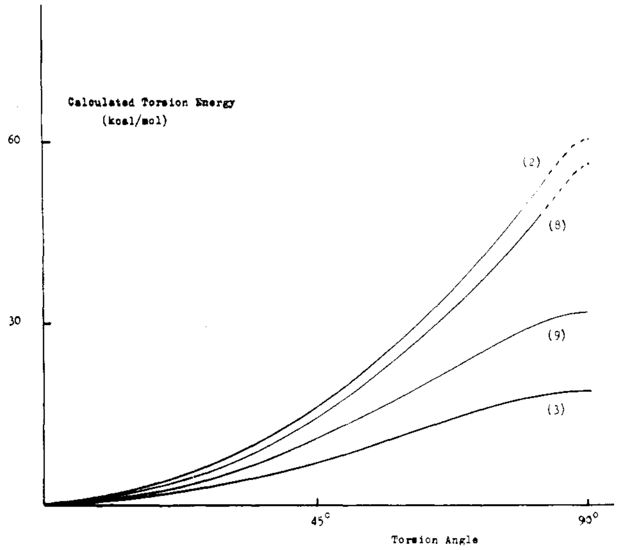
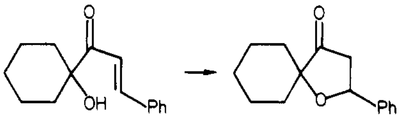
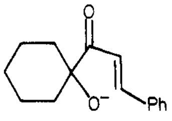


Figure 2. Calculated torsion energy profiles for rotation about double bonds in structures 2, 3, 8, and 9.



4 5



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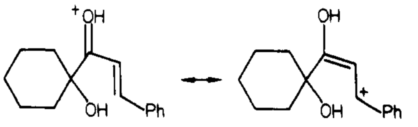
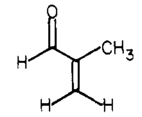


7 7A



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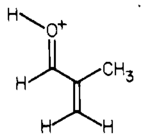

9

Method of Calculation

All computations were performed on an IBM 360 computer using the MNDO method[6] with the single determinantal restricted Hartree-Fock SCF procedure. In calculating the torsion barriers, the substituents on the doubly bonded atoms were held in planes while the double bond was twisted. Calculations were carried out at torsion increments of 15°. The bond lengths and angles were fully optimized for both propylene (2) and the *O*-methylformaldehyde cation (3) at each point, except that the COC angle in 3 was held at the value obtained for the planar structure in order to prevent it from opening to 180° as the torsion angle was increased to 90°. Only selective optimizations were performed for 2-methylpropenal (8) and protonated 2-methylpropenal (9).

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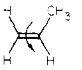
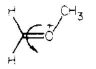
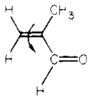
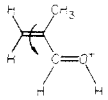
Table I. Calculated Energy Requirement for Rotation of Molecules about Formal Double Bonds

				
calcd/ΔH_f, kcal mol^{-1} [a]	4.93	155.89	−23.25	148.25
	Torsional Strain, kcal mol^{-1}			
torsional angle, μg				
0	0.00	0.00	0.00	0.00
15	1.78	1.01	1.39	1.21
30	7.10	3.88	6.13	4.81
45	15.90	6.72	14.53	10.63
60	28.03	13.05	25.67	18.23
75	42.83	15.76	40.01	26.37
90	60.33	18.77	56.24	31.83

[a] Calculated for the most stable geometry.

Results and Discussion

The calculated heats of formation and the torsion energies for the double bonds (indicated) of **2**, **3**, **8**, and **9** are summarized in Table I; Figure 2 shows the variation of torsion energy as a function of twist angle for each of the four species. The heat of formation and the bond parameters found for propylene (**2**) are the same as the reported values.[8] The calculated twisting barrier for **2** is 60.33 kcal mol^{-1}. This is in good agreement with the experimental (61.3 ± 1.2 kcal mol^{-1})[9] and theoretical (62 kcal mol^{-1})[10] twisting barriers for ethylene.

As expected, the calculated torsion barrier for the *O*-methylformaldehyde cation (methoxymethyl cation, **3**) is rather low (18.77 kcal mol^{-1}); the calculations confirm that the doubly bonded carbon atom of **3** has significant carbonium ion character.

When the COC angle in **3** was not held constant, a linear structure was reached which was only 11.98 kcal mol^{-1} above the planar ground state. This figure is in excellent agreement with the experimental[11] (11.9 kcal mol^{-1}) barrier for geometrical isomerization of the methoxymethyl cation and with an ab initio[11,12] estimate (at the 4-31G level) of the energy required to attain the linear geometry (12.0 kcal mol^{-1}). The ab initio rotational barrier for **3** was calculated to be 20.8 kcal mol^{-1},[11,12] also in good agreement with our MNDO results.

While the calculations leave little doubt that the geometrical isomerization of methoxymethyl cation observed by NMR[11] proceeds by inversion at oxygen, rather than by rotation, this is immaterial for present purposes, since the cyclization of eq 3 evidently cannot involve a linear oxonium oxygen.

Although the comparison of **8** and **9** yields a less dramatic difference in torsion barriers, the effect is still substantial. Furthermore, in the systems studied experimentally the effect may be enhanced by further conjugation with the aryl substituent; this point was emphasized in the original report[7] in connection with the preferred approach vector.

The torsion barrier calculated for **9** is 31.83 kcal mol^{-1}. This is appreciably higher than the experimentally observed barriers (21–26 kcal mol^{-1}) for the stereomutation of the partial α,β double bond in protonated α,β-unsaturated aldehydes and ketones.[13] Our value therefore lends some support to the conclusion[13] that such stereomutations involve lower energy paths than rotation.

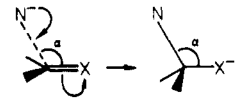
The calculated twisting barrier for 2-methylpropenal (**8**) is about 4 kcal mol^{-1} lower than that for **2**. This is expected since the additional double bond stabilizes the biradical-like perpendicular ethylene. Our value is slightly higher than the value estimated for cycloheptenone (30–50 kcal mol^{-1}).[14]

Conclusion

Among several factors which need to be taken into account when considering the ease of ring formation by nucleophilic attack on an "endo" double bond, one which should not be neglected is the barrier to torsion about that double bond. Since this is very low in an alkylideneoxonium ion, the acid-catalyzed formation of ethylene ketals should no longer be considered to have a "disfavored" step.

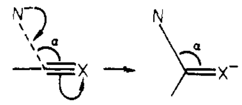
Addendum

In the analysis of these reactions,[2] it was suggested that "the subtended angle, α, between the three interacting atoms is maintained during the reaction pathway", e.g., eq 4.

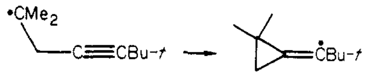


(4)

Extrapolation of this qualitative picture to triple bonds should, in our view, be represented as and not as in the original. This picture accords better with simple frontier orbital considerations and with theoretical treatment[15] of reactions of acetylenes. (Reference 15 shows very clearly the similarity of the π^* orbitals of ethylene and acetylene.) It satisfactorily accommodates the example of a 3-exo-dig reaction observed recently in free-radical chemistry and shown in eq 6.



(5)



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Although it might be argued that an illustration from radical chemistry is of doubtful relevance here, the transition states calculated by ab initio methods for hydride addition to acetylene[15] and for hydrogen atom addition to acetylene[17] are remarkably similar.

An example[18] which has been cited[2] of a 4-endo-dig reaction, the ready occurrence of which seems unreasonable on the present argument, notwithstanding the predicted[15] bending of the acetylene at the transition state for nucleophilic addition, may well involve a larger ring transition state incorporating a molecule of water.

Acknowledgment. We are indebted to Professor R. F. Hudson, Dr. D. Griller, and Dr. M. C. Grossel for helpful comments. M.J.P. also thanks NATO for a travel grant, during the tenure of which in 1978 he gave a seminar at NRCC which led to the present work, as well as Dr. K. U. Ingold for his hospitality at NRCC.

Registry No. 2, 115-07-1; **3**, 41879-84-9; **8**, 78-85-3; **9**, 71298-09-4.

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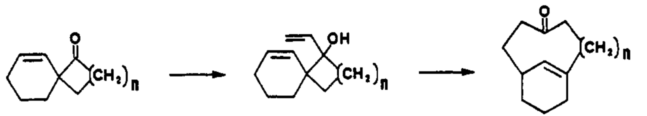
Communications

Oxy-Cope Rearrangement Route to Bridgehead Olefins[1]

Summary: Bicyclic bridgehead olefins, with a carbonyl group included in the largest bridge, may be synthesized by oxy-Cope rearrangement of easily accessible spirocyclic precursors.

Sir: Our interest in the influence of through-space interactions on the reactivity of functional groups[2] has led us to develop a general method for the construction of bicyclic bridgehead olefins in which a carbonyl group is included in the largest bridge. This method is based on the anionic oxy-Cope rearrangement[3] of vinyl carbinols of type **2** to the δ,ε-unsaturated ketones **3**.



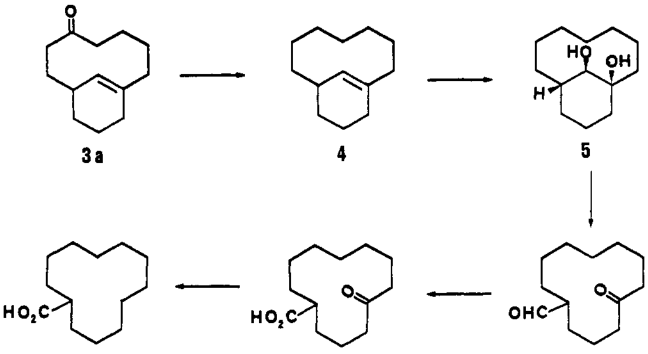
1a, n=3
1b, n=2
1c, n=1

2a
2b
2c

3a
3b
3c

The vinyl carbinol **2a**,[4] obtained by vinylmagnesium bromide addition to the spiroannulated cyclohexanone **1a**,[4,5] was converted (KH in THF) to the potassium salt and then heated under reflux for 4 h. Normal workup and purification by distillation gave the unsaturated ketone **3a** in 79% yield. The structure of ketone **3a**[7] was verified by the degradation sequence given in Scheme I. Wolf-Kishner reduction to **4** followed by osmium tetroxide oxidation gave diol **5**,[4] mp 109–109.5 °C, which was oxidized ($Pb(OAc)_4$ followed by Jones oxidation) to keto acid **7**,[4] mp 126.5–127.5 °C. A second Wolf-Kishner reduction then provided the known cyclododecanecarboxylic acid **8**,[4] mp 93.5–95.0 °C (lit.[8] mp 93–95 °C). Bridgehead olefin **4** was also subjected to hydroboration–oxidation; the major product (65%) was a secondary alcohol, mp 133.0–135.5 °C, whose ^{13}C NMR spectrum revealed only eight different carbon resonances as expected for the symmetrical structure **9**.[4,9]

Scheme I



The vinyl carbinol **2b**,[4] derived from spiroannulated cyclopentanone **1b**,[6] when subjected, as above, to the anionic oxy-Cope rearrangement conditions provided oxocycloalkene **3b**[10] in 83% yield.

The vinyl carbinol **2c** (from cyclobutanone **1c**[11]), as the potassium salt, was found to undergo rearrangement in THF solution at an appreciable rate at room temperature. After 12 h, normal workup and purification by chromatography on silica gel gave the unstable oxocycloalkene **3c**[12,13] in 47% yield. Catalytic hydrogenation of **3c** afforded

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(1) Presented in part at the 1980 American Chemical Society Combined Southeast–Southwest Regional Meeting, New Orleans, LA, Dec 10–13, 1980.

(2) S. G. Levine, R.-C.L. Hsu, and M. L. Miles, *Tetrahedron Lett.*, 3347 (1980).

(3) D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.*, **97**, 4765 (1975).

(4) A satisfactory elemental analysis was obtained for this product.

(5) Ketone **1a** was prepared from methyl cyclohex-2-enecarboxylate by alkylation with ethyl 5-bromopentanoate, Dieckmann cyclization, and decarboethoxylation. These reactions were carried out essentially as described[6] for the five-membered ketone **1b**.

(6) E. J. Corey, M. Petrzilka, and Y. Ueda, *Tetrahedron Lett.*, 4343 (1975); *Helv. Chim. Acta*, **60**, 2294 (1977).

(7) IR (CS_2) 3005, 1697 cm^{-1}; ^1H NMR ($CDCl_3$ δ 5.10 (s, 1 H); ^{13}C NMR ($CDCl_3$) 213.3, 138.6, 128.2, 44.4, 37.7, 37.4, 35.6, 34.0, 29.4, 28.1, 25.7, 23.1, 22.3 ppm; mass spectrum (70 eV), *m/e* 192 (14%), 174 (100%), 131 (26%), 120 (45%), 91 (80%), 79 (100%).

(8) A. P. Krapcho and R. G. Johanson, *J. Org. Chem.*, **36**, 146 (1971).

(9) The slightly more polar diastereomeric secondary alcohol was also isolated (7% yield) and gave 13 signals in its ^{13}C NMR spectrum.

(10) IR ($CHCl_3$) 3020, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–2.60 (m, 17 H), 5.40 (d, *J* = 5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 213.8, 140.6, 129.2, 43.7, 41.3, 36.4, 34.3, 30.0, 27.9, 27.6, 26.6, 17.7; mass spectrum (70 eV), *m/e* 178 (5%), 160 (100%).

(11) B. M. Trost, D. E. Keeley, H. C. Arndt, J. H. Rigby, and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **99**, 3080 (1977).

(12) IR (CS_2) 1695 cm^{-1}; ^1H NMR ($CDCl_3$) 1.00–3.20 (m, 15 H), 5.20 (br s, 1 H); mass spectrum, *m/e* 164 (64%), 79 (100%); ^{13}C NMR ($CDCl_3$) 217.4, 142.2, 128.8, 48.2, 38.7, 38.2, 36.4, 33.8, 29.6, 25.8, 21.6 ppm.

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