

7.9 ($k^{16}/k^{18} = 1.0403 \pm 0.0034$; $k^{12}/k^{13} = 1.0020 \pm 0.0003$) of methyl benzoate in aqueous solution at 25 °C.

- (9) S. A. Shain and J. F. Kirsch, *J. Am. Chem. Soc.*, **90**, 5848 (1968).
 (10) Four precautions served to eliminate most of this background. (1) All water used in these experiments was doubly distilled; the last distillation was from alkaline permanganate in an all-glass fractional distillation apparatus. (2) All glassware was cleaned in alkaline permanganate and rinsed with the above water. (3) Norit was purified by heating to 1000 °C in a quartz tube under high vacuum. (4) Large sample sizes (greater than 120 μ mol) were generated to reduce the effect of any possible contamination.
 (11) S. L. Johnson, *Adv. Phys. Org. Chem.*, **5**, 237 (1967).
 (12) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).
 (13) This research was supported by Grants PCM 75-15315 and PCM 77-00812 from the National Science Foundation.

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Received November 7, 1977

A New and Efficient Total Synthesis of (\pm)-Longifolene

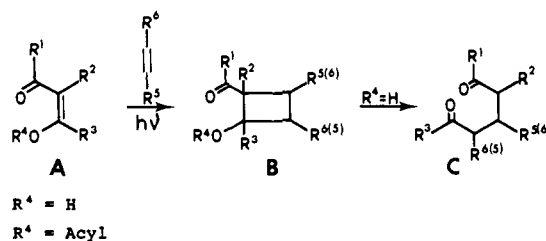
Sir:

Despite the well-documented synthetic power of the bimolecular photoaddition-retroaldol reaction sequence (de Mayo reaction), depicted in Scheme I,¹ the potential of intramolecular variants starting from 1,3 diketones or their enol derivatives A, bearing olefinic substituents R¹, R², or R³, has been neglected so far.² We now report the first example of one of these intramolecular alternatives which constitutes the key reaction leading to a ready synthesis of (\pm)-longifolene (11) (Scheme II).³ The intricate carbon network of this sesquiterpene has served as a challenging test case for synthetic methodology⁴ and planning⁵ throughout the past 15 years.

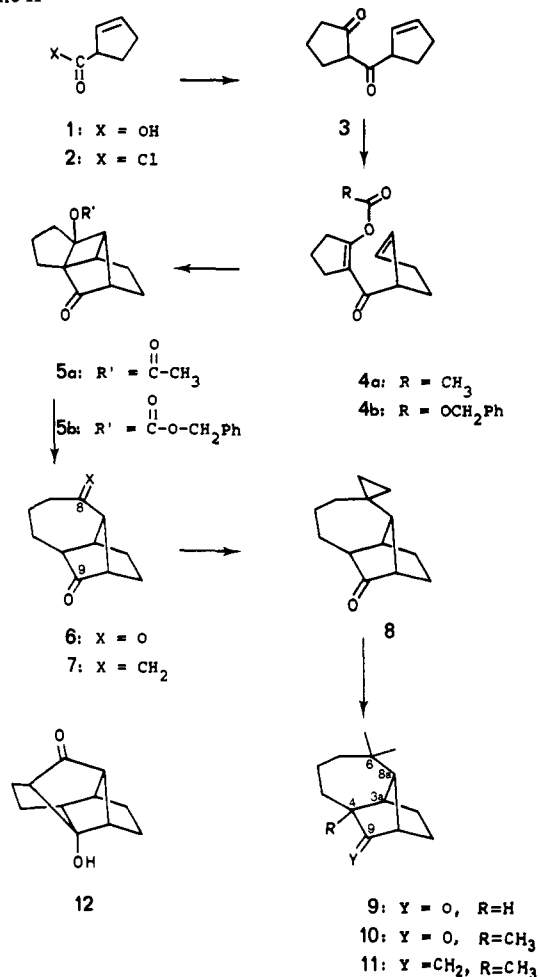
To realize our objective, the acid chloride 2^{6,7} (bp 66 °C (28 Torr)) was treated with 1-morpholino-1-cyclopentene under the usual conditions⁸ to give the 1,3 diketone 3⁷ (bp 63 °C (0.05 Torr), 82%), which on O-acetylation (1.5 equiv of acetyl chloride, pyridine, 0 °C, 4 h) furnished a crude enol acetate⁷ (IR (CCl₄) 1770, 1718 (m), and 1640 cm⁻¹; NMR (CDCl₃) δ 2.22 (s, 3 H); UV (hexane) 243 nm (log ϵ 4.05); 80%) to which structure 4a has been assigned.⁹ Irradiation of the crude acetate 4a (mercury high-pressure lamp, cyclohexane, Pyrex filter, 15–30 °C) afforded regioselectively in high yield (78%) the adducts 5a^{7,11} (1:3 mixture of stereoisomers). Hydrolytic cleavage of the acetoxy group, however, required heating of 5a with 4% KOH in dioxane/water, 1:1, at 100 °C for 20 min to give directly the aldol 12^{7,11} (72%), presumably via the transient retroaldol intermediate 6. As a way of avoiding the undesired secondary reaction 6 \rightarrow 12,¹² 3 was first converted to its benzyloxycarbonyl derivative 4b^{7,9} (2.7 equiv of benzyloxy chloroformate/pyridine, 5 °C, 8 h, 88%) which under the above-mentioned irradiation conditions furnished the adducts 5b⁷ (2:3 mixture of stereoisomers, 83%). Hydrogenolysis of 5b (3 atmH₂, Pd/C (10%), HOAc, 25 °C 18 h) resulted in clean retroaldol cleavage giving the 1,5 diketone 6^{7,11} (mp 63–64 °C, 83%).

Having achieved a simple and efficient entry to the skeleton of longifolene (11), 6 was functionalized by initially converting the less hindered 8-carbonyl to a geminal dimethyl group¹³ as follows. Regioselective Wittig methylenation of 6 to 7^{7,11} (5.8 equiv of methyltriphenylphosphonium bromide, 5.0 equiv of sodium *tert*-amylate, toluene, 14–25 °C, 1.5 h, 88%), followed by a modified Simmons–Smith cyclopropanation of 7 to 8^{7,11} (6 equiv of zinc/silver couple,¹⁵ 3 equiv of diiodomethane, refluxing ether, 60 h, 78%) and selective cyclopropane hydrogenolysis¹⁶ (2 to 3 atmH₂, PtO₂, HOAc, 25 °C 18 h, 96%) gave the ketone 9^{7,11} which reveals superimposable ¹H NMR and IR spectra on those of (\pm)-9, obtained by another route.^{4c} The previously described α -methylation of 9^{4c} furnished 10

Scheme I



Scheme II



(94%), which was identified by comparison with a sample of naturally derived longicamphenylone (10) using GC (coinjection), ¹H NMR, ¹³C NMR, IR, and mass spectral evidence.¹⁷ Finally, using known reaction conditions,⁴ 10 was converted into (\pm)-longifolene (11) (80%), the identity of which followed from similar comparison with the natural product.

In summary, this approach affords (\pm)-longifolene (11) in a nonoptimized overall yield of 25% from the acid chloride 2.¹⁸ The key step 4b \rightarrow 5b involves the formation of two C–C bonds, one of which (C(8)–C(8a)) has not been regarded as a particular strategic one;⁵ furthermore, the asymmetric center of 4b induces correctly the other three chiral centers of longifolene. The enantioselective synthesis of (\pm)-longifolene, as well as further exploration of intramolecular de Mayo reactions, are presently under study in our laboratory.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique, Sandoz Ltd, Basel, and Givaudan SA, Vernier, for financial support of this work. We also record our gratitude to Professor W. S. Johnson for kindly providing spectra of (\pm)-9, as well as the detailed procedure for its methylation to longicamphenylone (10). We are indebted to

Dr. P. Ochsner, Givaudan SA, for a generous sample of (+)-longifolene. (a)

References and Notes

- (1) For recent reviews, see P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971); (b) H. Meier in "Houben-Weyl, Methoden der Organischen Chemie," Vol 4/5b, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1975, p 924.
- (2) We know only of the related photoaddition-hydrolysis sequence of alkenylamino- and alkenyloxy-2-cyclohexenones: Y. Tamura, Y. Kita, H. Ishibashi, and M. Ikeda, *Tetrahedron Lett.*, 1977 (1972); *J. Chem. Soc., Chem. Commun.*, 101 (1973).
- (3) For the structure elucidation of (+)-longifolene (11), a constituent of the essential oil of many *Pinus* species, see (a) G. Ourisson, *Bull. Soc. Chim. Fr.*, 895 (1955), and references cited therein; (b) J.-C. Thierry and R. Weiss, *Tetrahedron Lett.*, 2663 (1969).
- (4) For successful total syntheses of longifolene, see (a) E. J. Corey, M. Ohno, R. B. Mitra, and P. Vatakcherry, *J. Am. Chem. Soc.*, **86**, 478 (1964); (b) J. E. McMurry and S. J. Isser, *ibid.*, **94**, 7132 (1972); (c) R. A. Volkmann, G. C. Andrews, and W. S. Johnson, *ibid.*, **97**, 4777, (1975). Unsuccessful attempts are cited in ref 4b; see also G. Brieger, *J. Am. Chem. Soc.*, **85**, 3783 (1963).
- (5) For longifolene as a subject for synthetic planning and strategy, see ref 4a and E. J. Corey, W. J. Howe, H. W. Orf, D. A. Pensak, and G. Petersson, *J. Am. Chem. Soc.*, **97**, 6116 (1975).
- (6) The acid chloride **2** was prepared from the carboxylic acid **1** (SOCl₂, reflux, 1 h, 90%) which is accessible from cyclopentadiene in 52% overall yield: S. Branner-Jørgensen and A. Berg, *Acta. Chem. Scand.* **20**, 2192 (1966).
- (7) IR, ¹H NMR, and mass spectra are in full agreement with the assigned structure.
- (8) S. Hünig and W. Lendle, *Chem. Ber.*, **93**, 909 (1960).
- (9) The spectral data did not permit the rigorous exclusion of the presence of the corresponding exocyclic enol esters; however, this point appears to be of little relevance as far as the subsequent photoaddition to **5** is concerned. It can thus be expected that light-induced isomerization of the exocyclic (*E*- and *Z*-) enol esters, followed by spontaneous 1,5-acyl migration of the latter, gives an equilibrium concentration of **4**; for a close analogy, see E. Wachsen and K. Hartke, *Chem. Ber.*, **108**, 683 (1975). **4** should then be selectively trapped by photoaddition (4 → 5) owing to the endocyclic nature of the conjugated olefinic bond which is also favorably placed with respect to the isolated double bond.¹⁰
- (10) For a review on photoadditions of alicyclic conjugated enones to olefins, see P. E. Eaton, *Acc. Chem. Res.*, **1**, 50 (1968).
- (11) The ¹³C NMR spectrum agrees fully with the assigned structure.
- (12) Although the conversion of **12** into **10** can be envisaged by approaches involving a fragmentation step,^{4b} the preparation and selective functionalization of **6**, as described below, provides a more direct route to longifolene.
- (13) The longifolene framework is numbered here as in *Chemical Abstracts*.
- (14) J.-M. Conia and J.-C. Limasset, *Bull. Soc. Chim. Fr.*, 1936 (1967).
- (15) J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 549 (1972).
- (16) (a) C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968). (b) C. Gröger and H. Musso, *Angew. Chem.*, **88**, 415 (1976); *Angew. Chem. Int. Ed. Engl.*, **15**, 373 (1976).
- (17) We thank Mr. K. Bättig for carrying out these comparison studies.
- (18) Reported by one of us (W.O.) at the Chemische Gesellschaft Zürich on Dec 7, 1977.

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Received December 6, 1977

Metal Carbene Chemistry. Formation and Reactions of (η⁵-C₅H₅)Fe(CO)_n(CH₂)⁺ (n = 1, 2) in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Sir:

It is often possible to prepare and characterize species in the gas phase whose exceptional reactivity leads only to a fleeting existence in solution, where their presence is more often inferred than demonstrated. Transition metal carbenes are an important class of intermediates for which this is the case.¹⁻³ We wish to report studies, using the techniques of ion cyclotron resonance spectroscopy,⁴ of the formation and reactions of several of these interesting species in the gas phase.⁵

Jolly and Pettit² report the attempted preparation of (η⁵-C₅H₅)Fe(CO)₂(CH₂)⁺BF₄⁻ by cleavage of the ether (η⁵-C₅H₅)Fe(CO)₂(CH₂OCH₃) with HBF₄. While the cationic complex could not be isolated, its presence was postulated to

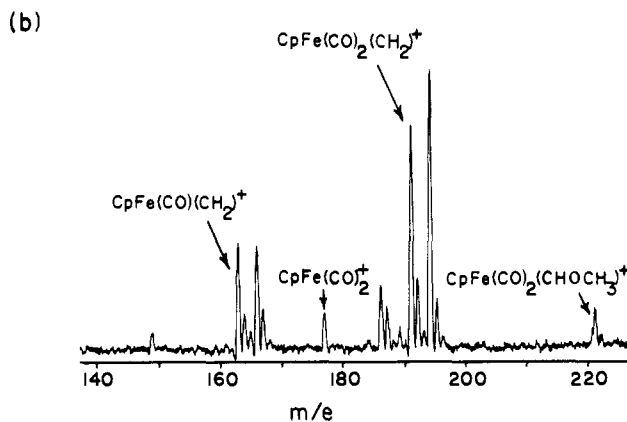
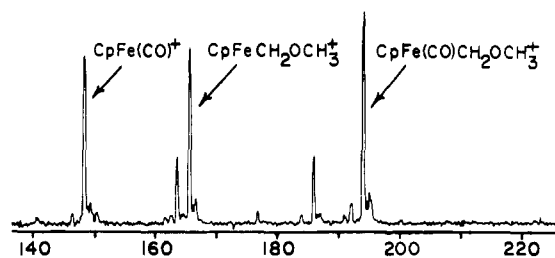
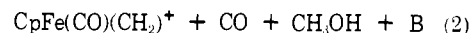
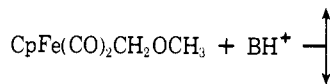


Figure 1. (a) Partial mass spectrum of CpFe(CO)₂CH₂OCH₃ observed in the drift mode at 10⁻⁷ Torr with 70-eV electron energy. (b) Spectrum of products observed after 30-ms reaction time in a mixture of CpFe(CO)₂CH₂OCH₃ (10⁻⁷ Torr) and CH₄ (10⁻⁶ Torr) ionized by a 10-ms 70-eV electron beam pulse. Several ionic species pertinent to the discussion in the text are identified.

account for methylene transfer to produce norcarane from cyclohexene and *cis*- and *trans*-1,2-dimethylcyclopropane from *cis*- and *trans*-2-butene, respectively. This system struck us as ideally suited for acidic ionization by proton transfer in the gas phase to produce the isolated CpFe(CO)₂(CH₂)⁺ ion.

The electron impact mass spectrum of CpFe(CO)₂CH₂OCH₃⁶ (over the range of 12 to 70 eV) shows major fragment ions CpFe(CO)CH₂OCH₃⁺ and CpFeCH₂OCH₃⁺, arising from sequential loss of CO; the parent ion is not observed. The ions CpFe(CO)₂(CH₂)⁺, CpFe(CO)(CH₂)⁺, and CpFe(CO)₂(CHOCH₃)⁺ are present, but in very low abundance.

The ions CpFe(CO)₂(CH₂)⁺ and CpFe(CO)(CH₂)⁺ show dramatic increase in abundance when the acids BH⁺ = NH₄⁺, C₂H₅⁺, CH₅⁺, and H₃⁺⁷ are used as protonation agents (reactions 1 and 2). The spectra shown in Figure 1 contrast the



abundant ionic species observed with 70-eV electron impact (Figure 1a) and with the addition of CH₄ (Figure 1b, reaction time 30 ms⁸). Not unexpectedly, as the exothermicity of reaction 1 increases over the series BH⁺ = NH₄⁺, C₂H₅⁺, CH₅⁺, H₃⁺,⁴ there is a concomitant increase in the abundance of CpFe(CO)(CH₂)⁺ relative to CpFe(CO)₂(CH₂)⁺. Double resonance⁹ identifies the carbene CpFe(CO)₂(CHOCH₃)⁺ being produced at longer times or higher pressures, mainly from CpFe(CO)₂(CH₂)⁺, reaction 3.¹⁰

