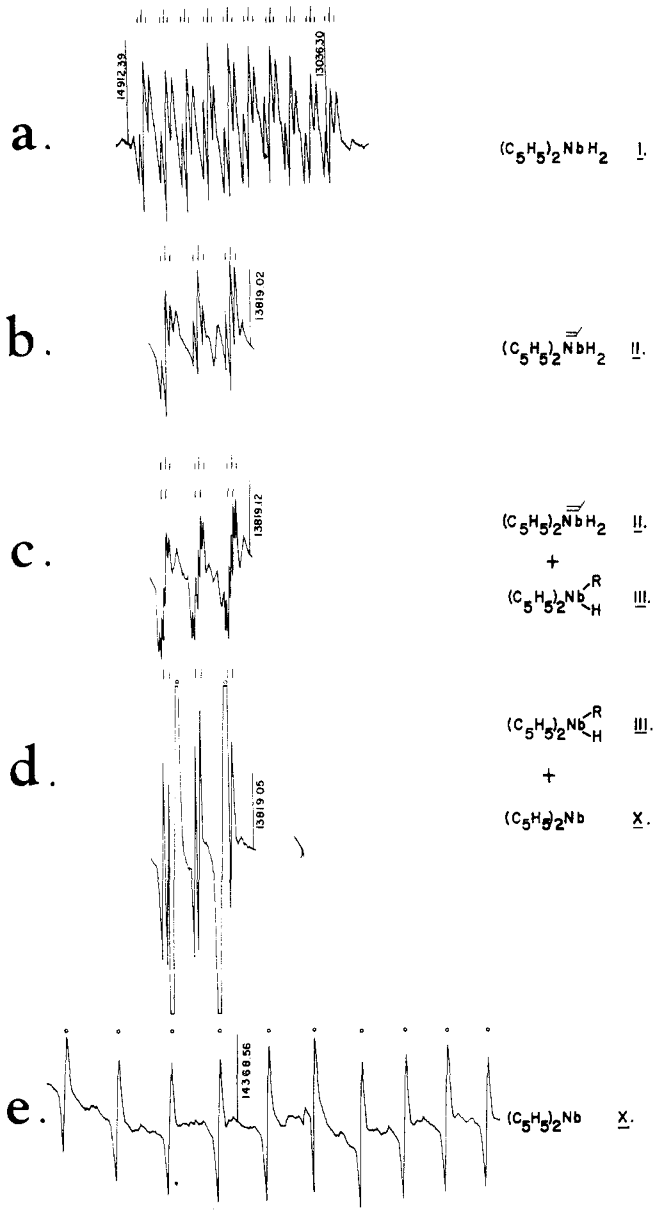

Figure 1. ESR spectral changes occurring during the reaction of $(C_5H_5)_2NbH_2$ with isobutylene at (a) −70°, (b) −37°, (c) −10°, (d) 25°, and (e) on standing. For clarity only selected lines corresponding to $m_I = 1/2, 3/2$, and $5/2$ of the decet Nb splitting are shown in (b), (c), and (d). Sweep widths are the same in all the spectra. Proton NMR field markers are in kHz. In (d) and (e) lines marked with open circles are due to species X.

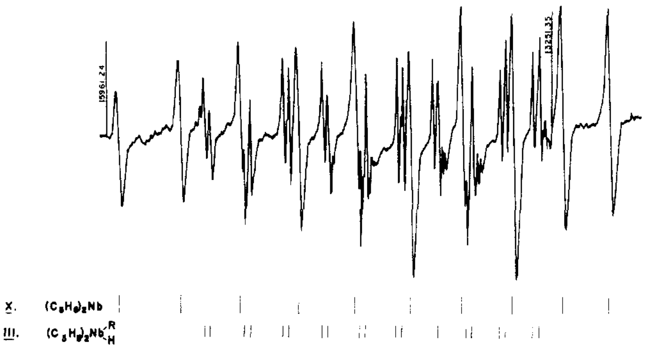

Figure 2. ESR spectrum obtained during the thermal reaction of Cp_2NbH_3 and isobutylene at 25° in cyclopropane–benzene solution. Two species clearly present are IIIb and X, in addition to minor amounts of other niobium(IV) species.

the information obtained from these ESR studies will provide us with optimum conditions for its eventual isolation, either as a crystalline substance or in an inert matrix.[16]

References and Notes

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(3) F. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc.*, **93,** 3792 (1971); F. B. Tebbe, *ibid.*, **95,** 5823 (1973).
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(5) (a) In addition to a species showing Nb splitting of 127 G (g = 1.95) formed only in the presence of di*tert*-butyl peroxide and assigned to $(C_5H_5)_2Nb(O\text{-}t\text{-}Bu)_2$ (vide infra). (b) The reversible addition of molecular hydrogen to titanocene and its analogs has been described by J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **94,** 1219 (1972).
(6) The unresolved deuterium splitting of 1/6, the proton splitting is within the linewidth (7.6 G).
(7) Depending on the location of the coordinated olefin in II, the pair of hydrogens attached to Nb will or will not be magnetically equivalent. Any differences in the latter case are not resolved within the spectral linewidths.
(8) We were unable to observe the corresponding equilibrium for $(C_5H_5)_2Nb(CH_3)_2$ and were unable to induce any such changes with ultraviolet radiation.
(9) Species III could be formed from II by loss of hydrogen. Deuterium labeling studies show that only one of the hydrogens attached to Nb is lost; the other may be lost from the allylic position of the olefin. However, except for slight differences in linewidths, the data are insufficient to distinguish III from IV rigorously. Since there is more precedence for the pathway via IV,[3] it may be necessary to change the spectral assignments from III to IV, if a choice is necessary. The failure to observe the species from ethylene may then be attributed to its instability.
(10) Propylene and I also produce a species V (which we ascribe to $CpNb(Pr)_2$ by comparison with the g factors of other $Cp_2Nb(alkyl)_2$ in Table I) derivable from IV by addition of a second propylene.
(11) The stability of alkyl- and dialkylniobium(IV) species was examined in the metathesis of $(C_5H_5)_2NbCl_2$ and alkyllithium reagents. Although the dimethyl derivative is sufficiently stable to isolate,[4] ethyl and *tert*-butyl analogs were not. Instead the reaction of $(C_5H_5)_2NbCl_2$ and *tert*-butyl Grignard or *tert*-butyllithium afforded a species with a single niobium and proton which could be $(C_5H_5)_2NbH(Cl)$, derived by β-elimination of the chlorobutyl intermediate.
(12) What is more significant is that the g factors for the hydrides of tantalum and niobium are greater than the free-spin value g_e of 2.0023, whereas the g factor of the dimethyl species is less than free spin. Theoretically, the difference Δg (where $g_{obsd} = g_e + \Delta g$) is inversely related to the difference in orbital energies.[13] The large positive deviation in Δg observed in the hydrides can be attributed, thus, to the mixing between the half-filled orbital and a bonding Nb–H σ orbital of *lower* energy. Such an interaction could lead to increased lability of the hydride ligands. On the other hand, the low g factors in the dialkyl and dichloro species is attributable to excitation of the odd electron into an empty orbital of *higher* energy and not into a bonding metal–alkyl or metal–chloro orbital. In this respect the behavior of tantalum and niobium differs markedly from that of the isoelectronic analogs of titanium.[14]
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(14) H. H. Brintzinger, *J. Am. Chem. Soc.*, **89,** 6871 (1967); J. E. Bercaw and H. H. Brintzinger, *ibid.*, **91,** 7301 (1969).
(15) The spectrum ascribed to niobocene X is not observed if organic halides and reactive peroxides are present. For example, in the presence of vinyl fluoride, vinylidene fluoride, tetrafluoroethylene, methyl chloride, and bis(trifluoromethyl) peroxide, the spectrum of X is not observed but is replaced by those of other paramagnetic species.
(16) Acknowledgment. We wish to thank the National Science Foundation for financial support and Dr. F. N. Tebbe for samples of Cp_2NbH_3 and Cp_2NbD_3.

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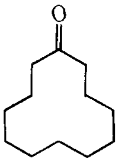
A Synthesis of *d,l*-Muscone from Cyclododecanone

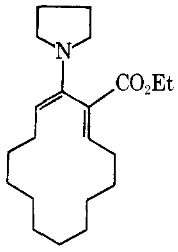
Sir:

We wish to disclose here an efficient synthesis of *d,l*-muscone (V) from the readily available cyclododecanone (I).[1] The ring expansion sequence employs consecutive two- and one-carbon ring homologations and allows the controlled introduction of substituents on the final macrocycle.

Our approach generates cyclotetradecenone (III), which we succeeded in obtaining in 70% yield as a 1:1 $\alpha,\beta:\beta,\gamma$ mixture[2] from the C_{12} ketone by hot aqueous hydrochloric acid hydrolysis of the known reaction product II[3] of 1-pyrrolidinocyclododecene with ethyl propiolate. Treatment of the enone mixture with triethylsilane in refluxing glyme containing a catalytic amount of chloroplatinic acid afforded 1-triethylsiloxycyclotetradecene (III)[4] (92%; ν_{max} 1675^{-1} (C=C); NMR δ 4.42 quintet, J = 7.0 Hz, 1 H; 2.0, b s, 4 H). Addition of dichlorocarbene (sodium trichloroacetate (2 equiv) in refluxing glyme–tetrachloroethylene (1:4) for 18 hr, followed by aqueous 1 N hydrochloric acid–tetrahydrofuran (1 hr, room temperature), gave 2-chloro-2-cyclopentadecenone (V) in 66% yield (ν_{max} 1700, 1625 cm^{-1}; NMR δ 6.83, t, J = 7.0 Hz, 1 H; 2.60, m, 4 H). Conjugate addition of dimethylcopper lithium in ether (−10°, 30 min), followed by saturated ammonium chloride workup and subsequent chromium(II) perchlorate reduction of the resulting α-chloro ketone in dimethyl formamide[5] yielded *d,l*-muscone (VI) as a light yellow oil (89%) which was identical with an authentic sample[6] in spectral and analytical characteristics. The overall yield of *d,l*-muscone from cyclododecanone is about 36%.



I



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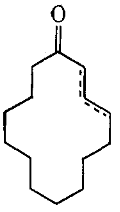
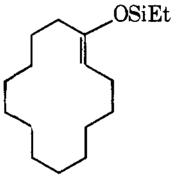
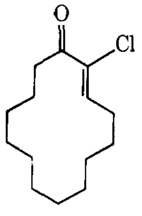


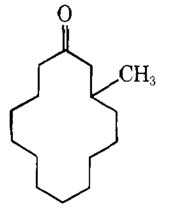
III



IV



V



VI

This synthesis demonstrates that, as we anticipated, rapid equilibration of an α,β-β,γ mixture of unsaturated ketones takes place under the platinum-catalyzed silylation conditions,[7] thus allowing the clean formation of IV from III. Further, the dichlorocyclopropanation of enol silyl ethers (which can often be prepared regiospecifically), followed by hydrolysis, offers an efficient alternative to current methods[8] for the transformation of ketones into specifically homologated α-chloroenones. It should be noted that cyclopentadecenone derivatives are known to be equilibrated to mixtures rich in the β,γ isomer.[9] Thus, the α-chloro substituent helps to stabilize the unsaturated C_{15} ketone in the α,β-enone configuration required for conjugate addition. The compatibility of the α-chloroenone system with alkyl copper reagents is due to the fact that the chlorine becomes a relatively unreactive vinyl chloride in the enolate resulting from 1,4-addition.[10]

References and Notes

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(2) The α,β isomer has ν_{max} 1691, 1620 cm^{-1} (C=C—C=O); NMR δ 6.90 (d, t, J = 15.5, 7.0 Hz, 1 H), 6.18 (m, 1 H). The β,γ isomer has ν_{max} 1718 (C=O), 1650 cm^{-1} (C=C); NMR δ 5.4–5.6 m, 2 H, 2.95, m, 2 H. Infrared spectra were taken neat and NMR spectra in deuteriochloroform for all compounds reported in this communication.

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(4) All new compounds gave satisfactory infrared, NMR, and mass spectra.

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(6) The authors thank Drs. W. I. Taylor and B. Mookherje of International Flavors and Fragrances for an authentic sample of *d,l*-muscone.

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(9) See ref 1j for a brief study. Note, however, that conjugate 1,4-addition to kinetically generated 2-cyclopentadecenone has been used successfully as a route to *d,l*-muscone.[1c]

(10) We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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Correlation between Acidities of Carboxylic Acids and Core Ionization Potentials

Sir:

It has recently been shown by Martin and Shirley[1] and by Davis and Rabalais[2] that there is a strong correlation between core-electron binding energies and proton affinities. For a series of alcohols, Martin and Shirley have found that the change in oxygen 1s binding energy from one alcohol to the next in the series is nearly identical with the change in proton affinity. The reason for this remarkable result is that the removal of an electron from the oxygen is electrically equivalent to the addition of a proton at the same site.

Martin and Shirley also suggested that there should be a correlation between the oxygen 1s ionization potentials and the gas-phase acidities of these compounds and noted that the results obtained by Brauman and Blair[3,4] on a series of alcohols are in accord with their expectation. No quantitative comparison was possible since only relative acidities were measured by Brauman and Blair. The acidities for alcohols in aqueous phase are the reverse of what they are in the gas phase because of solvent effects. The aqueous-phase acidities of the alcohols do not, therefore, correlate in the expected way with the core-electron ionization potentials.

If, however, we direct our attention to substances in which the relative aqueous-phase acidity is largely determined by the charge distribution in the original molecule (i.e., by inductive effects) rather than by either solvent or internal polarization effects, we may expect to find acid strength increasing with increasing core-electron binding energy. An electrostatic potential from which it is relatively difficult to remove an electron is one from which it is relatively easy to remove a proton.

In the course of some research unrelated to this problem, we have measured the ionizatiion potentials for iodine 3d electrons in the compounds RI (R = CH_3, CF_3, C_6H_5, and C_6F_5). We compare these here with the acidities of the cor-