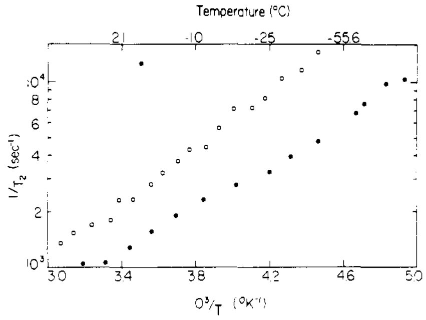

Figure 2. Semilog plots of $1/T_2$ of ^{87}Rb in methanol solutions of RbCNS *vs.* reciprocal absolute temperature. The measurements correspond to 19.5 MHz (14 kG). The open circles are for a solution containing 0.64 *M* RbCNS and 0.11 *M* DBC, while the closed circles correspond to a solution containing 0.7 *M* RbCNS but no DBC.

at −13°, and ΔE = 11.7 kcal/mol) but are considerably different from those for rubidium, for which the exchange rate is much faster. This behavior is consistent with the known structure of the corresponding complexes in the solid state as determined by X-ray crystallography.[6] These studies show that both Na^+ and K^+ fit nicely into the cavity of the crown form of DBC, while the much larger rubidium ion sticks out from it and consequently is probably less tightly bound to the DBC molecule.

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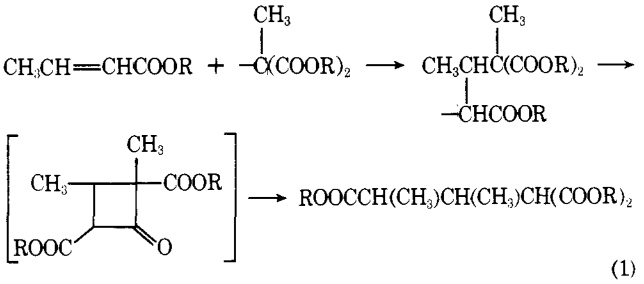
Mechanism of the Abnormal Michael Reaction between Ethyl Cyanoacetate and 3-Methyl-2-cyclohexenone

Sir:

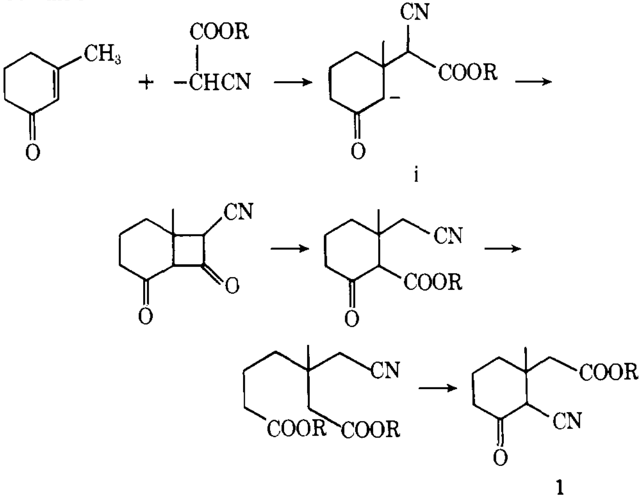
The incursion of an abnormal pathway into the normal base-catalyzed Michael addition of acyclic acceptors, frequent with monosubstituted malonates or cyanoacetates,[1] is attributed to cyclization of the initial adduct to a cyclobutanone intermediate followed by base cleavage in the opposite direction, allowing equilibration to the more acidic abnormal product; an example[2] is shown in eq 1. This mechanism, proposed early by Holden and Lapworth,[3] has been substantiated by ^{14}C and ^{18}O tracer studies.[4]



(1)

There are also reports of abnormal Michael products, particularly from cyclohexenones, which cannot be explained by the Holden-Lapworth mechanism alone. Johnson and coworkers[5] proved in 1953 that the abnormal product from ethyl cyanoacetate and 3-methyl-2-cyclohexenone, prepared originally by Farmer and Ross,[6] had structure **1**, and proposed the mechanism shown in Scheme I for its formation.

Scheme I

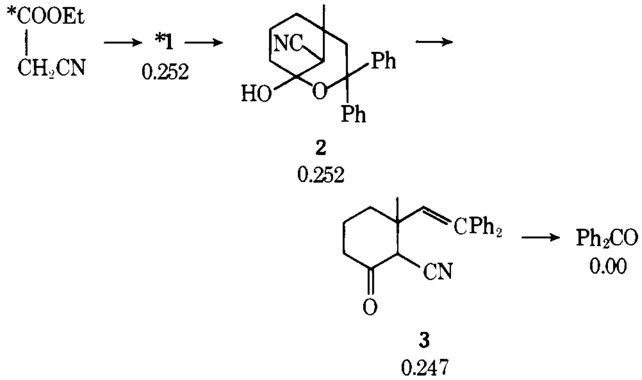


We present here the results of a ^{13}C and ^{14}C tracer study of the formation of **1** which rule out the published mechanism[5] and establish an alternate route to abnormal Michael products from cyclohexenones.

Use of ethyl cyanoacetate-*1*-^{14}C in the Michael reaction with 3-methyl-2-cyclohexenone led to radioactive **1**. The Johnson mechanism predicts that the label should be located at the ester carbonyl; liberation of this carbon was achieved by the Barbier-Wieland degradation. As anticipated, the β-ketonitrile moiety is apparently protected from Grignard addition by enolization, so that reaction of **1** with excess phenylmagnesium bromide led to hemiketal **2**, mp 158-160°, in 77% yield. Compound **2**[7] showed hydroxyl and nitrile absorption but no carbonyl bands in the ir, and the nmr spectrum revealed two aromatic rings but only one hydroxyl. Dehydration of **2** with iodine in refluxing acetic acid gave olefin **3**,[7] mp 107-109°, which showed nitrile (2240 cm^{-1}) and ketone (1710 cm^{-1}) bands in the ir, a vinyl proton in the nmr, and a strong uv absorption at 267 nm. Ozonolysis of **3** gave benzophenone in good yield. As shown in Scheme II, the benzophenone was nonradioactive.

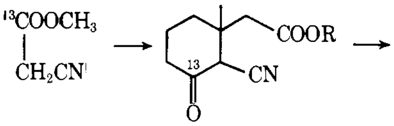
The location of the label was revealed by repeating the abnormal Michael reaction with methyl cyanoacetate-*1*-^{13}C, giving **1** containing 5.5% excess atom % ^{13}C. The adduct was converted to the known[5] imide **4** and thence to its ethylene ketal[7] **5**, mp 203.5-204°. Comparison of the cmr

Scheme II

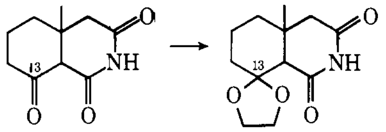


(figures represent specific molar activity in mCi/mol)

spectra of these enriched samples with the natural abundance spectra of **1**, **4**, and **5**, to which unambiguous assignments could be made,[8] showed that only one carbon in each compound was enriched: the ketone carbonyl of **1** (δ 201.075) and **4** (δ 173.33) and the corresponding ketal carbon of **5** (δ 109.10). Confirming the ^{14}C results, no enrichment was detected in the ester carbonyl (δ171.09) of **1**.



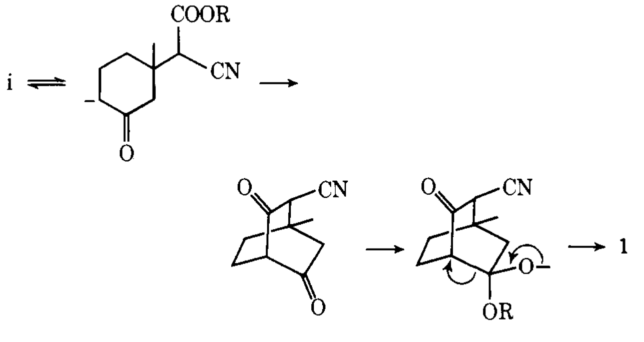
1



4 5

These findings invalidate the Johnson mechanism[5] as well as a reasonable alternative in which the cyano group is transferred directly from i to **1** through an iminocyclobutane intermediate and also several other mechanisms proposed for abnormal Michael additions.[9,10] They are consistent only with the bicyclo[2.2.2]octane intermediate shown in Scheme III, the so-called "para-bridged" mechanism suggested originally by Farmer and Ross[11] and considered[5] for the ethyl cyanoacetate adduct but judged unlikely (there being no opportunity for stabilization of the intermediate bridged β-diketone as the enolate anion).

Scheme III



Our tracer studies provide the first unambiguous evidence that the bicyclo[2.2.2]octane route is not only a viable mechanism but apparently the sole pathway for formation of abnormal Michael products from 3-methyl-2-cyclohexenone.[12] The present case provides another illustration of the importance of subjecting even those mechanisms which appear obvious to experimental test.

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(8) We are particularly indebted to Professor R. H. Cox for his aid in obtaining and interpreting the cmr spectra. The Fourier transform nmr spectrometer on which the spectra were obtained was purchased with the aid of a grant from the National Science Foundation, to whom we express our warm appreciation.
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An Electron Spin Resonance Study of the Oxidative Homolytic Cleavage of Metal–Metal and Metal–Carbon Bonds

Sir:

The metal–metal bonds of a variety of transition metal binuclear carbonyl complexes can be readily cleaved by the action of one-electron oxidizing agents ($NOPF_6$, ferric complexes, etc.) with the production of diamagnetic cationic species containing a solvent molecule in the coordination sphere of the metal.[1] One-electron oxidants can also cleave the metal–metal bonds of organoditin compounds[2] as well as the metal–carbon bonds of many metal alkyls.[3] The latter reactions are traditionally referred to as electrophilic substitutions although a single-electron mechanism has been established in a few instances.[3] A single electron transfer from a neutral diamagnetic organometallic compound must necessarily lead in the primary mechanistic step to a cationic paramagnetic intermediate[4] which can undergo fragmentation into a diamagnetic cation and a reactive metal- or carbon-centered radical. We wish to present esr evidence for the formation of such radicals from a variety of organometallic compounds containing metal–metal or metal–carbon σ bonds using tetracyanoethylene (TCNE) as the one-electron oxidizing agent and for their further reactions.

A 10^{-3} *M* tetrahydrofuran solution of manganese decacarbonyl and TCNE displays, in the absence of oxygen, a complex esr spectrum which is the superposition of the spectra of the TCNE radical anion,[5] indicative of a one-electron transfer from $Mn_2(CO)_{10}$, and of another species. A large excess of $Mn_2(CO)_{10}$ eradicates the $TCNE\cdot^-$ lines yielding the unencumbered spectrum of the second species (Figure 1) which can be analyzed in terms of a hyperfine structure due to four distinct nitrogens, of which two are almost equivalent, and to only one manganese atom (Table I). The small manganese splitting (a^{Mn} = 2.163 G), the *g* value (Table I), the narrow line widths (0.25 G), and the absence