product. It is likely that none of the 1,1-difluoro-2-vinylsilacyclopropane-^{31}Si survives as a final product because of its inherent instability and because of the excess energy deposited during its formation. Attempts thus far to synthesize a silacyclopropane have failed,[21] presumably due to excessive ring strain introduced by the silicon atom. Skell and Goldstein[22] observed vinylsilanes rather than silacyclopropanes under conditions which should have produced the latter.

The resulting 1,1-difluoro-2-vinylsilacyclopropane-^{31}Si from (4) is likely to be excited.[23] Even though being formed by two successive fluorine abstraction reactions, the reacting $^{31}SiF_2$ might still retain part of the original excitation of the hot ^{31}Si atom. Some energy could also have been released during the formation of two extra silicon–carbon bonds. Nevertheless, the major reason that (5) is expected to go to completion is the instability of the reactant rather than its excitation.

Between the two mechanisms (a) direct 1,4 addition by singlet $^{31}SiF_2$ and (b) 1,2 addition followed by isomerization, we favor the latter process. However, it is impossible to rule out the possibility that SiF_2, being larger than its carbene analog, might have the right geometry to participate in a direct 1,4 addition process.

Acknowledgments. We wish to express our appreciation to the Texas A & M Cyclotron Institute for providing the facilities used in this experiment. We are also grateful to Professor Jaan Laane and Professor E. A. Schweikert, and their research groups, for technical assistance and helpful cooperation.

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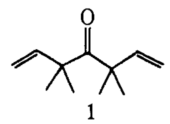
The Photochemistry of an Acyclic Bis β,γ-Unsaturated Ketone

Sir:

The photochemistry of β,γ-unsaturated ketones is currently a topic of lively interest. Direct irradiation of acyclic compounds results in α cleavage to an acyl and an allyl radical.[1-4] When the structure allows it, γ-hydrogen abstraction[2,3] and cis-trans isomerization of the double bond[1,5] are also observable. Triplet photosensitization of an acyclic β,γ-unsaturated ketone[4] led to oxa-di-π-methane rearrangement, a reaction now familiar in cyclic compounds.[6]



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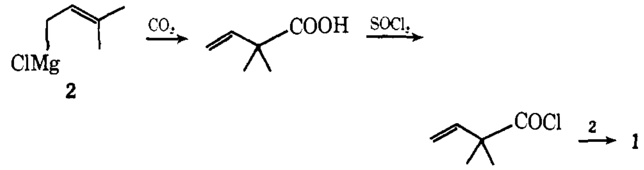
We report here a study of the first acyclic bis β,γ-unsaturated ketone, 3,3,5,5-tetramethylhepta-1,6-dien-4-one (**1**). Although this work was originally undertaken to determine the fate of allylic radicals[7] produced by decarbonylation,[8] the photochemistry of the ketone itself has proven to be intriguing. The dimethyl groups in **1** serve to stabilize it against positional isomerization and to distinguish the ends of the allylic radicals formed.



The synthesis of **1** was based upon the preferential reaction of allylic Grignard reagents at the more hindered end.[9] Thus, carbonation of the Grignard reagent **2** derived from 1-chloro-3-methyl-2-butene[10] gave 2,2-dimethyl-3-butenoic acid. Reaction of its acid chloride with more Grignard reagent provided **1**, a clear oil (bp 75° (18 mm)).[11] The ir spectrum of **1** showed bands at 1696 (C=O), 1635 (C=C), 918, and 988 cm^{-1} (terminal vinyl), while the nmr spectrum in CCl_4 appeared as follows: δ 1.28 (s, 12 H), 5.13 (m, 4 H), 6.22 (q, 2 H). The mass spectrum gave a molecular ion at m/e 166 and a base peak at 69 ($C_5H_9^+$). The uv spectrum of **1** revealed an enhanced n-π* transition in hexane at λ_{max} 292 nm (ε 100).

Irradiation of 0.1 *M* **1** in toluene at 313 nm gave a 90% yield of CO and the three possible allylic radical recombination products. Designating the dimethyl end of the radical as the head (h) end, one can identify these products as hh, ht, and tt. They were formed in relative yields of 14, 27, and 59%, virtually the same distribution as observed from the analogous azo compound.[7] The formation of all three products in amounts characteristic of free radicals rules out an appealing seven-membered cyclic decomposition mechanism, which would produce only the tt product. The CO quantum yield from **1** was 0.30, less than half that of di-*tert*-butyl ketone ($\Phi = 0.62$)[12] and of dibenzyl ketone ($\Phi = 0.70$).[8] Since cis-trans isomerization is known in related systems[1,5] it is likely that the relatively low efficiency of decarbonylation is caused by degenerate isomerization of the double bonds of **1**. In fact decarbonylation of the saturated analog of **1** in toluene occurs with a substantially higher efficiency[13] ($\Phi = 0.50$).

When **1** was irradiated to low conversions, the presence of a new product was noted by vpc. Moreover, this material was formed to the complete exclusion of

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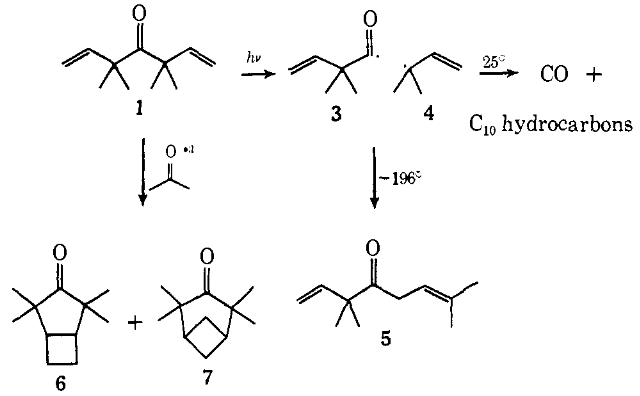
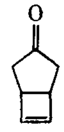
C_{10} hydrocarbons when irradiation was carried out at −196° in an ethanol–ether glass. Its spectral properties suggested that the new product was **5** and this assignment was confirmed by comparing it with the compound formed from **2** and 4-methyl-3-pentenoyl chloride.[14] Two schemes which would rationalize this behavior are the following. (a) Decarbonylation of the intermediate acyl radical **3** is completely suppressed at low temperature and high viscosity in favor of recombination with the allyl radical **4**. (b) The concerted 1,3-acyl shift[15] has a lower activation energy than simultaneous fission of both bonds to the carbonyl group. We tentatively favor (a) because **3** is analogous to $C_6H_5CH_2CO\cdot$, an intermediate in the photolysis of dibenzyl ketone.[16] Furthermore, the existence of acyl radicals is consistent with the fact that the efficiency of decarbonylation in solution always falls short of unity.[17] We have shown that although decarbonylation is approximately thermoneutral, some 20% of the acyl radicals **3** survive long enough to recouple at the tail end of **4** in solution at ambient temperature. If it is assumed that only steric effects determine the extent of recombination at each end of **4**,[7] greater than 10% of the acyl–allyl radical pairs must revert to ketone **1**. This process would operate in compounds which cannot form isomers of starting material only by imposing a maximum on the quantum yield for ketone disappearance. It is interesting that this maximum is roughly 0.7, equal to the observed value for di-*tert*-butyl ketone.[12]



The decarbonylation of **1** is not quenched by 1.0 *M* piperylene and **1** does not sensitize the dimerization of cyclohexadiene.[18] These results indicate either that intersystem crossing does not occur or else that the triplet state is extremely short lived. Photosensitization experiments support only the former, however, for the products of triplet sensitization are entirely different from those of direct irradiation.

The fact that **1** does not quench the type II elimination of butyrophenone[19] demonstrates that its triplet energy is above 74.7 kcal. However, acetone proved to be an efficient photosensitizer (Φ for ketone disappearance = 0.19), placing an upper limit of 80 kcal on the triplet energy of **1**. The high quantum yield of ketone disappearance in this case is significant because it proves that **1** does not undergo intersystem crossing. A low quantum yield would leave open the possibility that the intersystem crossing yield is fairly high but that no triplet products are seen under direct irradiation because of the low efficiency with which the triplet state forms products.[20]

Surprisingly, the products of acetone sensitization did not arise from a di-π-methane rearrangement but instead were two isomeric materials (ratio 3:1) which showed no olefinic protons in the nmr. The major product was identical with **6** prepared by hydrogenation and methylation of **8**.[21] It showed a carbony band at 1731 cm^{-1} and two nmr singlets at δ 1.03 and 1.06. The rest of the nmr spectrum consisted of a multiplet extending to 2.8 ppm. The minor product, although of considerably shorter vpc retention time than **6** was a solid (mp 50–52°), suggesting the highly symmetrical structure **7**.[22] This was supported by its mass spectrum[23] ($M\cdot^+$ *m/e* 166), the ir (ν_{CO} 1737 cm^{-1}), and the nmr which showed δ 0.93 (s), 1.07 (s), and 1.8 (br).



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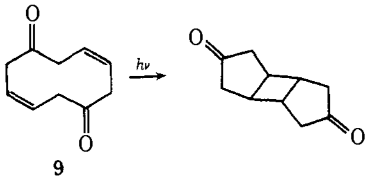
The closest analogy for the formation of **6** is the cyclization of dienedione **9** which occurs either upon acetone sensitization or by two successive photoreactions, double bond isomerization and ring closure.[24] Although it bears a formal resemblance to the mercury-sensitized cyclization of 1,6-heptadiene,[25] ring closure of **1** is a clean, high yield (>60%) reaction. In fact, the facility with which cyclization occurs to give both normal and crossed adducts leads us to speculate that the bulky methyl groups favor a conformation which places the double bonds in proximity. Intramolecular cycloaddition in **1** is clearly faster than oxa-di-π-methane rearrangement and at least competitive with double bond isomerization.



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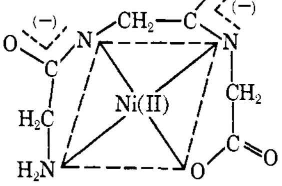
Reaction of Cyanide Ion with Nickel Triglycine. An Example of the Kinetic Trans Effect in Low-Spin Nickel(II)

Sir:

There have been many reported examples of the trans effect in Pt(II) and Pd(II) substitution reactions;[1] however, the same cannot be said for low-spin nickel(II). Triglycine forms a yellow, low-spin complex with nickel(II) in which the deprotonated nitrogen atoms are coordinated.[2-4] This complex, $\mathrm{NiH_{-2}L^-}$ (shown in structure I), reacts with cyanide ion through a series



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of mixed complexes to form $\mathrm{Ni(CN)_4^{2-}}$. It is through the formation of the mixed complex $\mathrm{NiH_{-2}L(CN)_2^{3-}}$ that cyanide is capable of labilizing the trans imide groups and thus increasing the rate of the substitution reaction.

The rate equation for the formation of $\mathrm{Ni(CN)_4^{2-}}$ at pH 11 is shown in eq 1.

$$\frac{d[\mathrm{Ni(CN)_4^{2-}}]}{dt} = \left\{k_{1.0}[\mathrm{CN^-}] + \frac{K_2[\mathrm{CN^-}]}{1 + K_2[\mathrm{CN^-}]}k_{2.0}[\mathrm{CN^-}]\right\}[\mathrm{NiH_{-2}L(CN)^{2-}}] \qquad (1)$$

The mixed complex $\mathrm{NiH_{-2}L(CN)^{2-}}$ forms rapidly and completely as evidenced by the fact that no $\mathrm{Ni(CN)_4^{2-}}$ is produced when the molar ratio of $\mathrm{CN^-}$ to $\mathrm{NiH_{-2}L^-}$ is equal to or less than 1. The visible spectra of $\mathrm{NiH_{-2}L^-}$ and $\mathrm{NiH_{-2}L(CN)^{2-}}$ also exhibit an isosbestic point at 406 nm. Cyanide probably replaces the coordinated carboxylate group. The reaction was studied under pseudo-first-order conditions and the observed rate constant is shown in eq 2.

$$k_{\mathrm{obsd}} = k_{1.0}[\mathrm{CN^-}] + K_2[\mathrm{CN^-}]k_{2.0}[\mathrm{CN^-}]/(1 + K_2[\mathrm{CN^-}]) \qquad (2)$$

At $[\mathrm{CN^-}] < 9 \times 10^{-4}\ M$ the value of $K_2[\mathrm{CN^-}]$ is negligible compared to 1 and thus $k_{\mathrm{obsd}} = k_{1.0}[\mathrm{CN^-}] + K_2k_{2.0}[\mathrm{CN^-}]^2$. This equation indicates that a plot of $k_{\mathrm{obsd}}/[\mathrm{CN^-}]$ *vs.* $[\mathrm{CN^-}]$ should be linear with a slope of $K_2k_{2.0}$ and an intercept of $k_{1.0}$. From a plot of this type, the value of $k_{1.0} = 5.9\ M^{-1}\ \mathrm{sec}^{-1}$ and $K_2k_{2.0} = 1.3 \times 10^3\ M^{-2}\ \mathrm{sec}^{-1}$. The relevant kinetic data are summarized in Table I.

Table I. Rate Constants for the Reaction of Cyanide Ion with Nickel(II) Triglycine[a]

$10^6[\mathrm{NiH_{-2}L^-}]$, M	$10^4[\mathrm{CN}]$, M	pH	10^3k_{obsd}, sec^{-1}
9.59	1.63	10.94	0.93
9.57	3.25	10.99	1.98
9.54	6.39	10.98	4.20
9.49	9.56	10.98	6.79
9.24	31.3	11.09	29.8
9.17	37.3	11.04	39.1
9.06	46.1	11.06	49.7

[a] Temperature, 25.0°; $\mu = 0.10\ M\ \mathrm{NaClO_4}$.

At $[\mathrm{CN^-}] > 9 \times 10^{-4}\ M$ the value of $K_2[\mathrm{CN^-}]$ is not small compared to 1. Equation 2 can be rearranged to the form shown in eq 3. This equation indicates

$$\frac{[\mathrm{CN^-}]}{(k_{\mathrm{obsd}} - k_{1.0}[\mathrm{CN^-}])} = \frac{1}{k_{2.0}} + \frac{1}{K_2k_{2.0}[\mathrm{CN^-}]} \qquad (3)$$

that a plot of $[\mathrm{CN^-}]/(k_{\mathrm{obsd}} - k_{1.0}[\mathrm{CN^-}])$ *vs.* $1/[\mathrm{CN^-}]$ should be linear with a slope of $1/K_2k_{2.0}$ and an intercept of $1/k_{2.0}$. From a plot of this type, $k_{2.0} = 25\ M^{-1}\ \mathrm{sec}^{-1}$ and $K_2 = 52\ M^{-1}$. The relevant kinetic data are summarized in Table I.

The reaction of cyanide with $\mathrm{NiH_{-2}L^-}$ at pH 11 proceeds through a two-path mechanism (see eq 4–6).

$$\mathrm{NiH_{-2}L^-} + \mathrm{CN^-} \rightleftharpoons \mathrm{NiH_{-2}L(CN)^{2-}} \text{ rapid and complete} \qquad (4)$$

$$\mathrm{NiH_{-2}L(CN)^{2-}} + \mathrm{CN^-} \xrightarrow{k_{1.0}} \text{products (path I)} \qquad (5)$$

$$\mathrm{NiH_{-2}L(CN)^{2-}} + \mathrm{CN^-} \overset{K_2}{\rightleftharpoons} \mathrm{NiH_{-2}L(CN)_2^{3-}} \xrightarrow[+\mathrm{CN^-}]{k_{2.0}} \text{products (path II)} \qquad (6)$$

However, the rate-determining step for each path involves the breakage of the first nickel–imide bond. The difference between the two paths lies in the degree of the mixed complex formed prior to the rate-determining step. Path I carries the reaction at low cyanide concentration, requiring a total of two cyanide molecules in the activated complex. The first cyanide adds to $\mathrm{NiH_{-2}L^-}$ rapidly and completely to form $\mathrm{NiH_{-2}L(CN)^{2-}}$. The second cyanide then reacts with concurrent breakage of the imide bond near the carboxylate end of triglycine. This is the step that is rate determining and has a rate constant $k_{1.0} = 5.9\ M^{-1}\ \mathrm{sec}^{-1}$. Previous studies with $\mathrm{NiH_{-2}L^-}$ and $\mathrm{CuH_{-2}L^-}$ indicate that the carboxylate coordination is more labile than the imide coordination.[5,6] Cyanide is not capable of exerting any trans labilization in this path since the imide bond trans to the coordinated cyanide does not break during the rate-determining step.

At high cyanide concentration path II carries the reaction through the formation of a second mixed complex, $\mathrm{NiH_{-2}L(CN)_2^{3-}}$, which is believed to have cyanide occupying both of the planar positions trans to the imide coordination sites. This complex reacts with another cyanide during the rate-determining step. Since cyanide is trans to both of the imide bonds it is capable of labilizing these bonds. This labilization is

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