2897 (1971).

(19) Camille and Henry Dreyfus Teacher-Scholar Award Recipient, 1976-1981. A. P. Sloan Foundation Fellow, 1975-1977.

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Nucleophilic Substitution in Organomercury Halides by a Free-Radical Chain Process ($S_{RN}1$)[1]

Sir:

The free-radical chain nucleophilic substitution process (reactions 1-3) has been observed in aliphatic[2,3] and aromatic systems[4] and has been labeled $S_{RN}1$.[5] In aliphatic systems all substrates (RX) described to date contain a nitro or *p*-nitrophenyl substituent at the reaction center.[6,7] With the exception of *p*-nitrobenzyl derivatives only tertiary substrates have been successfully employed, generally with the structure $(R)_2C(X)NO_2$, where X = Cl, Br, NO_2, CN, CO_2R, COAr, SO_2R.[8]

$$RX^{-}\cdot \rightarrow R\cdot + X^{-} \tag{1}$$

$$R\cdot + A{:}^{-} \rightarrow RA^{-}\cdot \tag{2}$$

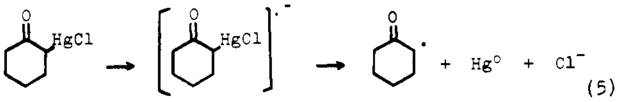
$$RA^{-}\cdot + RX \rightarrow RX^{-}\cdot + RA \tag{3}$$

$$\overline{RX + A^{-} \rightarrow RA + X^{-}}$$

We have found that primary or secondary alkylmercury chlorides or bromides will participate in the $S_{RN}1$ process with nitronate anions in Me_2SO or DMF (reaction 4).

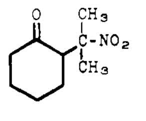
$$RHgX + R'_2C{=}NO_2^{-} \xrightarrow[N_2]{h\nu} RC(R')_2NO_2 + X^{-} + Hg^0 \tag{4}$$

We selected **1** as a substrate for the $S_{RN}1$ process with the idea that the carbonyl group would facilitate the formation of $RX^{-}\cdot$ in reaction 3, and that the radical anion **2** would decompose readily as shown in reaction 5. Reactions of the anions of 2-nitropropane or nitrocyclohexane with **1** gave the expected products (**3**) of the $S_{RN}1$ reaction in 60-70% yield when deoxygenated solutions were illuminated with a sun lamp through Pyrex. The reaction showed the characteristics of a free-radical chain process. Not only was the reaction induced by light, but it was completely inhibited by 5 mol % di-*tert*-butyl nitroxide. The reaction when illuminated started immediately only if the solution was completely deoxygenated. When the deoxygenation was incomplete, inhibition periods were observed.

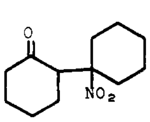


(5)

1 2



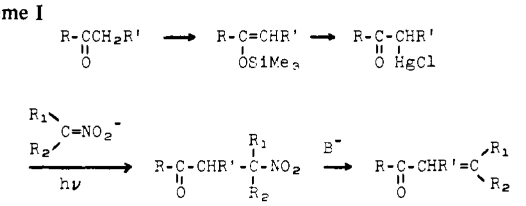
3a, mp 69-70°C



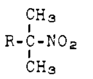
3b, mp 66-68°C

The *β*-nitro ketones (**3**) readily undergo E_2 elimination of the elements of HNO_2 in basic solution to give the *α*-alkylidene ketones. The reaction sequence is thus an *α*-alkylidenation process for a ketone (Scheme I).[9]

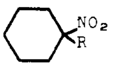
Scheme I



Further experiments demonstrated that the carbonyl function is not necessary for the $S_{RN}1$ reaction of an alkylmercury halide. Thus, benzyl-, cyclohexyl-, or *n*-hexylmercury chloride all react with the anion of 2-nitropropane or nitrocyclohexane in a light-catalyzed process at 25 °C to give the coupling products **4** and **5**.[10]



4a, R = benzyl, mp 25° C, 2 h, 99%
4b, R = cyclo-C_6H_{12}, mp 46-47°C, 34 h, 76%
4c, R = n-hexyl, 37 h, 90%
4d, R = 2-methoxycyclohexyl, 47 h, 8:1 ratio of trans and cis isomers

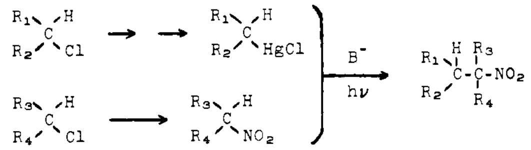


5a, R = benzyl, mp 68.5-69° C, 2 h, 87%
5b, R = cyclohexyl, mp 55-56° C, 60 h, 84%

The rate of the reaction under standard conditions decreases from R = benzyl to R = alkyl. Apparently resonance stabilization of R· formed by reaction 1 is an important consideration. In line with this we have been unable to bring about the coupling of phenyl- or vinylmercury halides with the nitronate anions in reaction 4. Apparently a nitronate anion is required as the anion (A^-) in reaction 2 when R· is a simple alkyl radical. The nitro group stabilizes and thus facilitates the formation of $RA^{-}\cdot$ in reaction 2. We have been unable to observe coupling when **1** or other organomercury halides are irradiated in the presence of diethyl methylmalonate anions.

This reaction not only makes available a wide variety of new tertiary nitroalkanes, but when combined with an E_2 elimination of nitrite ions furnishes a wide variety of substituted alkenes from readily available precursors (Scheme II).

Scheme II



In a typical experiment a solution of *α*-bromomercuricyclohexanone[11] (5.72 mmol, mp 130-131 °C) in 30 mL of DMF was purged of oxygen by a stream of prepurified nitrogen in a 100-mL flask at room temperature. After addition of 6.21 mmol of lithium 2-nitropropanate,[12] the solution was stirred for 1 h at a distance of 8 in. from a 275-W sun lamp. Mercury precipitated in a greenish gray form, which was removed by filtration through Celite after quenching of the reaction mixture with 25 mL of 2% hydrochloric acid. The filtrate was diluted with 100 mL of H_2O and extracted with three 75-mL portions of ethyl ether. The ether extract was washed, dried, and concentrated on a rotary evaporator to give 0.54 g of **3a** (68%): mp 69-70 °C from pentane; bp 98 °C (0.3 Torr); ^{1}H NMR (CCl_4) δ 1.53 (s, 3 H), 1.62 (s, 3 H), 1.67-2.10 (m, 6 H), 2.16-2.50 (m, 2 H), 3.1-3.4 (m, 1 H).

Acknowledgment. The benzyl- and *n*-hexylmercury chloride were supplied by Professor R. Larock. We thank the National Science Foundation for funds which allowed the purchase of the Finnigan 4023 GC-mass spectrometer used in this work (CHE 76-80362).

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(1) Electron Transfer Processes. 16.
(2) (a) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88,** 5663 (1966); **90,** 347 (1968). (b) G. A. Russell, R. K. Norris, and E. J. Panek, *ibid.*, **93,** 5839 (1971).
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(4) D. E. Bartok, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35,** 1206 (1970).
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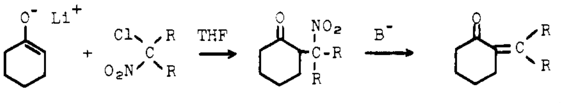
(6) The nitro group is usually retained in the radical. However, in the case of $[R_2C(NO_2)CN]^{-}\cdot$, $[R_2C(CO_2Et)NO_2]^{-}\cdot$ or $[R_2C(COAr)NO_2]^{-}\cdot$ the nitro group is lost as nitrite ion.[2b,3b] α-Nitrocumene itself also undergoes the $S_{RN}1$ reaction: N. Kornblum, S. C. Carlson, J. Widmer, M. J. Fifelt, B. N. Newton, and R. G. Smith, *J. Org. Chem.*, **43,** 1394 (1978).
(7) Electron transfer between anions and alkyl halides not containing an α-nitro group can lead to free radicals or free-radical pairs, but apparently not to the $S_{RN}1$ chain substitution process. See, for example, G. A. Russell, E. G. Janzen, and E. T. Strom *J. Am. Chem. Soc.*, **86,** 1807 (1964); C. Y. Myers, A. M. Malte, and W. S. Mathews, *ibid.*, **91,** 7510 (1969); J. S. Filippo, Jr., J. Silbermann, and P. J. Fagan, *ibid.*, **100,** 4834 (1978).
(8) Among the leaving groups observed in the *p*-nitrobenzyl or *p*-nitro-α,α-dimethylbenzyl system are Cl, NO_2, SO_2Ar, N_3, OAr, SOAr, $O_2CC_6Cl_5$, Me_2S^+, $Me_3N^+\cdot$: N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14,** 734 (1975); G. A. Russell, *Int. Cong. Pure Appl. Chem., 23rd, 1971*, **4,** 67 (1971).
(9) A synthetically more attractive route is the controlled crossed aldol condensation using an α-halonitroalkane as a ketone equivalent: G. A. Russell and M. Jawdosiuk, *J. Am. Chem. Soc.*, submitted for publication.



(10) The reactions are clearly chain processes. Reaction does not occur in the dark. With illumination (sun lamp) the reactions can be completely inhibited by 5 mol % of di-*tert*-butyl nitroxide. Finally, a photochemical process involving S_N2 substitution or the generation of an alkyl cation from the alkylmercury halide would lead to O-alkylation: N. Kornblum, P. Pink, and R. V. Vorka, *J. Am. Chem. Soc.*, **83,** 2779 (1961).
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(13) National Science Foundation Undergraduate Research Participant, summer 1978.

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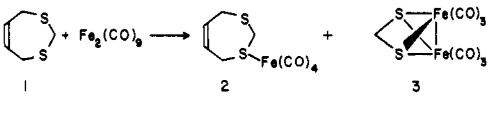
Reductive Decyclization of Organosulfur Compounds. Preparation and Crystal Structure of *μ,μ'*-Dithiolato-methanehexacarbonyldiiron(I)

Sir:

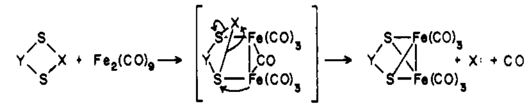
Desulfurization with organometallic complexes is a topic of current interest and development.[1] During a study on the coordination chemistry of cyclic organosulfur compounds, we have discovered a decarbasulfurization reaction. The parent molecules undergo novel cleavage reactions whereby organosulfur fragments are incorporated in complexes of general formula $(RS_2)(CO)_6Fe_2$. We are prompted to communicate these unexpected results because of the importance of the two classes of molecules involved. In addition, organometallic complexes of novel structures have been prepared.

1,3-Dithia-5-cycloheptene[2] (**1**) has two potential ligating sites: the olefin and the sulfur atoms. Upon reaction with $Fe_2(CO)_9$ in tetrahydrofuran, at room temperature, a complex mixture resulted. Chromatography on alumina permitted **2**[3] and **3**[4] to be isolated as oils which were crystallized from hexane. The structure of **2**, an expected product, was assigned by comparison of its spectroscopic properties to those of the analogous complexes $LFe(CO)_4$.[5] The structure of the unexpected product, **3**, was assigned by comparison of its spectroscopic properties with those of $[(RS)(CO)_3Fe]_2$.[6,7] Unbridged complexes such as $[(C_2H_5S)(CO)_3Fe]_2$ (**4**) have stereochemically nonrigid $Fe(CO)_3$ groups.[8] Compound **3** is also fluxional at room temperature, showing only one line[9] in the carbonyl region of the ^{13}C NMR spectrum. At −85 °C, two lines, approximately in the intensity ratio 2:1, are observed, consistent with the symmetrical structure expected for **3.**



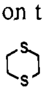
1 2 3

Scheme I



The preparation of **3** was quite unexpected, involving the cleavage of two carbon-sulfur bonds. Little, if any, **3** is formed when $Fe(CO)_5$ is used in the reaction, while a large excess of $Fe_2(CO)_9$ raises the yield. An atmosphere of CO prevents formation of **3** with **2** being the major product. This implies that an unsaturated dimeric carbonyl species is required. Possible precursors, such as dithiacyclopropane[10] or methanedithiol,[11] are unlikely to be produced from **1** under the reaction conditions. We propose that **3** may be produced via reductive decyclization of an intermediate such as $(XYS_2)(CO)_7Fe_2$ (Scheme I). Complexes of the type $(L\text{-}L)Fe_2(CO)_7$ are known in iron carbonyl chemistry.[12] Such a complex containing 1,3-dithiacyclohexane has been reported but not characterized.[13]

Compounds **5** and **6** undergo decarbasulfurization to give **7** in addition to products analogous to **2.**[14a] In **8** there is the possibility of cleaving either two carbon-sulfur bonds or two sulfur-sulfur bonds to give **9** or **10**, respectively. Only **10** is isolated,[14b] which suggests that sulfur-sulfur bond cleavage is preferred. Scheme I is consistent with previously unrelated reactions such as the preparation[15] of **11** from **12** and **13.** In addition, complex **14,** which has aryl groups replacing the methylene hydrogens of **3,** has been isolated from reactions of diaryl thioketones and $Fe_2(CO)_9$.[16] It was proposed that these thioketones may rearrange in solution to give **15** which falls into the general category. Finally, the recently reported[17] synthesis of **16** from **17** indicates that this reaction may be applicable to other classes of cyclic sulfur compounds.



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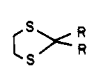
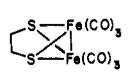


6 a R = H
b R = CH_3



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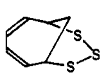

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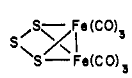

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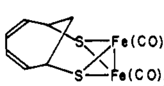

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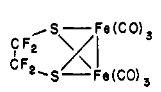

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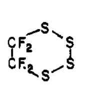

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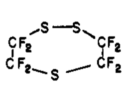

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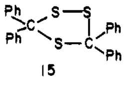

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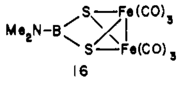

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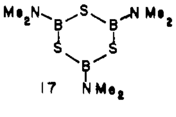

17

The structure of **3**, with its bridging methylene group, is particularly relevant to unbridged complexes of the general formula $[(RS)(CO)_3Fe]_2$.[18] Three different isomers can exist depending on the arrangement of the R groups. The presence of two of the three isomers can be detected in solution.[6] For R = C_2H_5 (**4**)[19] and C_6H_5[20] and for the structural analogue