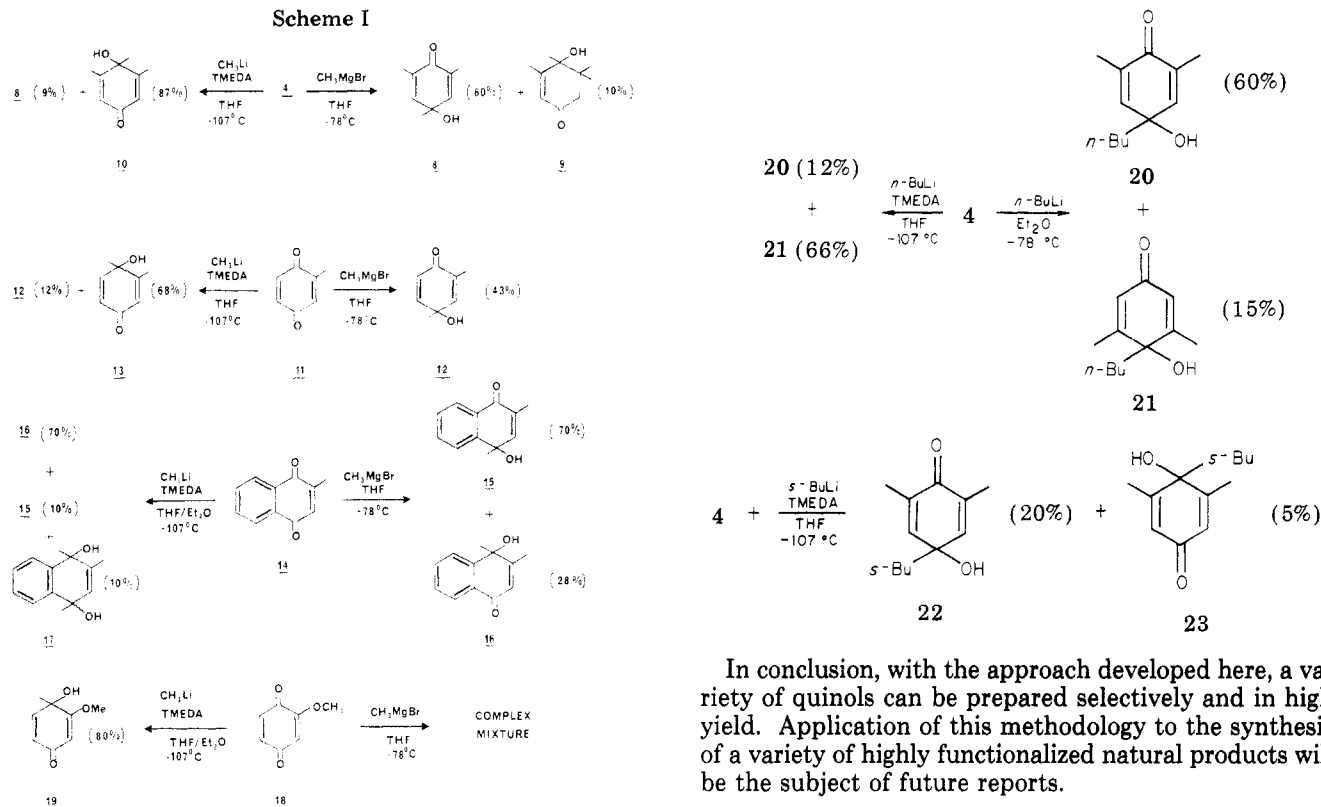


Scheme I



addition of 1 equiv of methyl lithium, containing 6 equiv of tetramethylethylenediamine (TMEDA) in THF at -107°C , produces 8 and 10 in 9% and 87% isolated yields, respectively. Under these conditions the methyl carbanion is in a nonaggregated, weakly solvated state and reacts in accord with the electronic model discussed above. Thus, by altering the nature of the methyl carbanion, one can effect an almost total reversal of the regioselectivity of the process.

Similar reversals can also be achieved with the other quinones (see Scheme I).^{15,16} This is especially noteworthy for the additions of methyl carbanions to 11, where both the steric and electronic differences between the two carbonyl carbons are quite small. When electronic differences between the carbonyl carbons are very large, as is the case in 18, only monoadditions to the more electrophilic carbonyl carbon can be achieved, irrespective of the conditions employed. Attempts to force 18 to react in accord with the steric model resulted only in the formation of complex mixtures, consisting primarily of hydroquinones.

These reversals of regioselectivity are not simply limited to methyl carbanions. For example, 4 reacts with *n*-butyllithium in ether at -78°C to produce 20 and 21 in a 4:1 ratio. However, by carrying out the reaction in THF in the presence of TMEDA at -107°C , the ratio of 20 to 21 becomes 1:5.5.

When the steric requirements of the carbanion become very large, selective attack at the more electrophilic carbonyl carbon is no longer possible. Thus, addition of *sec*-butyllithium to 4 in THF/TMEDA at -107°C results in a 4:1 mixture of 22 and 23, respectively.

(15) All new materials exhibited satisfactory combustion analysis and/or precise mass measurements.

(16) Cases involving intermediate degrees of solvation and/or aggregation result in poor regioselectivity (vide infra): 4 + CH₃Li (Et₂O, -78°C) → 8 (55%) + 9 (42%) and 11 + CH₃Li (Et₂O, -78°C) → 12 (42%) + 13 (36%).

In conclusion, with the approach developed here, a variety of quinols can be prepared selectively and in high yield. Application of this methodology to the synthesis of a variety of highly functionalized natural products will be the subject of future reports.

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

Registry No. 4, 527-61-7; 8, 16404-66-3; 9, 52103-92-1; 10, 55776-84-6; 11, 553-97-9; 12, 51770-93-5; 13, 55153-54-3; 14, 58-27-5; 15, 78127-78-3; 16, 78127-79-4; 17, 78127-80-7; 18, 2880-58-2; 19, 78127-81-8; 20, 78127-82-9; 21, 78127-83-0; 22, 78127-84-1; 23, 78127-85-2.

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Electron Transfer Induced Decomposition of Diazoacetophenone

Summary: Triarylamine radical cations are shown to induce the decomposition of diazoacetophenone by a second-order rate process directly related to their redox potentials.

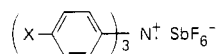
Sir: Interest in electron-transfer processes of organic reactions is increasing as the scope and extent of these phenomena become appreciated. Recently, a number of papers have appeared describing experimental observations of organic reactions which occur by electron-transfer mechanisms.^{1,2} Several subsequent papers have dealt with the theoretical and mechanistic interpretation of these data.^{1,2,3}

(1) Leonhardt, H.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1963**, *67*, 791-795.

(2) Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *101*, 5851-5853, and references therein.

We have found that the triarylamine radical cations, which, though quite stable in air and in a number of solvents, readily induce the decomposition of a variety of compounds, including diazo ketones. Several reports have appeared which suggest that triarylamine radical cations may be synthetically useful as mild oxidants.⁴ One report describes the thermal oxygenation of dienes, a reaction mimicking photochemical singlet oxygenation.⁵ However, the mechanism of these reactions has not been understood.⁶ Herein we report evidence for the triarylamine radical cation induced decomposition of diazoacetophenone by an electron-transfer process. In addition, we demonstrate that the triarylamine radical cations, because of their ease of preparation,^{5,7} well-characterized electrochemical⁸ and spectral⁹ properties, and their remarkable stability, are useful as mechanistic probes as well as synthetic reagents.

Upon mixing samples of tris(*p*-bromophenyl)ammonium antimonyhexafluoride, **1a**, and a large excess of diazo-



- 1a - Br
 b - Cl
 c - F
 d - CH₃
 e - CH₃O

acetophenone, **2**, in CH₂Cl₂, we noted rapid fading of the intense blue color due to **1a**. Upon stoichiometric addition of the above reagents, fading of the blue color, evolution of nitrogen, and formation of tris(*p*-bromophenyl)amine were observed. Upon mixing the tris(*p*-methoxy) derivative, **1e**, and large excesses of **2**, virtually no fading of the blue color was noted (visually) after 15 min. It seemed likely that the loss of color for **1a** was due to reduction of the radical cation with concomitant oxidation of diazoacetophenone. Since **1a** is much more easily reduced than the tris(*p*-methoxy) derivative, **1e**,⁸ our preliminary observations were consistent with the expected relative rates resulting from an electron-transfer process.

Since the role of a one-electron-transfer process has been speculated upon in diazoalkane chemistry¹⁰ and since the redox properties⁸ of triarylamines and their radical cations have been well documented, we were prompted to study the rates of **2** with **1a-e**. Good pseudo-first-order rate constants were obtained for several half-lives of the reaction by following the disappearance of triarylamine radical cations in the presence of a large excess of diazoacetophenone.¹¹ As shown in Figure 1, the observed first-order

rate constants vary linearly with diazoacetophenone concentration, and the slopes (k_2) of these lines are affected by the structure of the triarylamine radical cation. Figure 2 shows that $\ln k_2$ varies linearly with the redox potentials of **1a-e** as expected for an electron-transfer process.

Induced decomposition by metals (most notably copper)¹² and aromatic hydrocarbons (tetraphenylethylene)¹⁰ has been observed, and products arising from carbene and carbenoid intermediates often result. In the present reaction system, no products of carbenoid origin were observed. That is, decomposition of **2** by **1a** in the presence of methanol produced no α -methoxyacetophenone, **3**, or methyl phenylacetate, **4**, decomposition of **2** by **1a** in the presence of cyclohexene produced no benzoincarane, **5** (Scheme I), and decomposition of **2** by **1a** in CH₂Cl₂ produced no dibenzoyl ethylene.¹³ In fact, only high molecular weight (polymeric) material was observed.¹⁴

Scheme I outlines the proposed fate of diazoacetophenone upon oxidation. The mechanism is similar to that used by Schuster¹ and Walling² in their descriptions of electron-transfer reactions. When A is one of the triarylamine radical cations, electron transfer is as described by Schuster's case iii—endergonic and irreversible. The kinetics are consistent with k_2 being the rate-determining step. Loss of N₂ may occur in the rate-determining step (k_2) or in a subsequent step (k_3).

As shown in Scheme I, the nature of the new redox couple formed after the rate-determining step (k_2) and after irreversible loss of nitrogen (k_3) may govern the appearance and identity of the products. If back electron transfer (k_4) is favored and competes effectively with diffusion apart of the redox pair (k_5), carbene or carbenoid intermediates and their subsequent products are expected. However, if back electron transfer is not favored and diffusion apart dominates, such products would not be expected. When A is Cu^I or tetraphenylethylene, products resulting from carbenoid intermediates are observed, though never quantitatively.^{10,12} Thus back electron transfer is at least competitive with diffusion apart. When A is **1a-e** or Cu^{II,12} no such carbenoid products are observed. This suggests that back electron transfer is not favored at all over diffusion in these cases.

The mechanism as described in Scheme I is of significant interest because it generally describes induced decomposition of diazo compounds by a variety of oxidants. The present work uniquely provides evidence for such a process. In addition, it provides a reasonable explanation for the differences in reactivity and product observations from oxidants such as Cu^I and Cu^{II,12}

Triarylamine radical cations have been well studied in the past for their unique electrochemical and spectroscopic (visible and ESR) properties. Their ease of preparation and selective redox properties has only recently stirred synthetic interest. They have proved particularly useful in the present study for providing kinetic evidence to demonstrate a one-electron oxidation of diazoacetophenone. We have also observed that triarylamine radical

(3) Walling, C. *J. Am. Chem. Soc.* **1980**, *101*, 6854-6855.

(4) (a) Schmidt, C. W.; Steckhan, E. *Angew. Chem. IE* **1979**, *18*, 801-802; (b) Schmidt, C. W.; Sterkhan, E. *Angew. Chem. IE* **1979**, *18*, 802-803; (c) Belleville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718-720.

(5) Barton, D. H. R.; Haynes, R. K.; Leclerc, G.; Magmes, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055-2065.

(6) A spin-pairing argument was used to explain dark oxygenation and additional arguments involving electrophilicity of the triarylamine radical cation were invoked to explain the (rate) reactivity of the system.⁵ A simpler explanation would involve straightforward oxidation of the diene followed by reaction with oxygen—a mechanism analogous to Foote's observation of photooxygenation of stilbene in the presence of methylene blue: Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *99*, 4275-4277.

(7) Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999-6002.

(8) Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087-1093.

(9) Linkletter, S. J. G.; Pearson, G. A.; Walter, R. I. *J. Am. Chem. Soc.* **1977**, *99*, 5269-5272.

(10) Ho, C.-T.; Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1974**, *96*, 8109-8111.

(11) The reaction was run in degassed CH₂Cl₂. No differences in reaction rates were observed if O₂ was not excluded. The reactions were followed by the disappearance of the absorption of the radical cations **1a-e**.

(12) (a) Salomon, R. G. Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300-3310; (b) Bethell, D.; Eeles, M. F. *J. Chem. Soc., Perkin Trans. 2* **1974**, 704-710.

(13) By confirmation with authentic samples (GC and NMR), carbene(oid) products **3**, **4**, **5**, and dibenzoyl ethylene were not observed ($\leq 1\%$) in the reactions of **1a** with **2**.

(14) A brown, tarry substance with only aromatic and carbonyl NMR absorptions (¹H and ¹³C) was obtained.

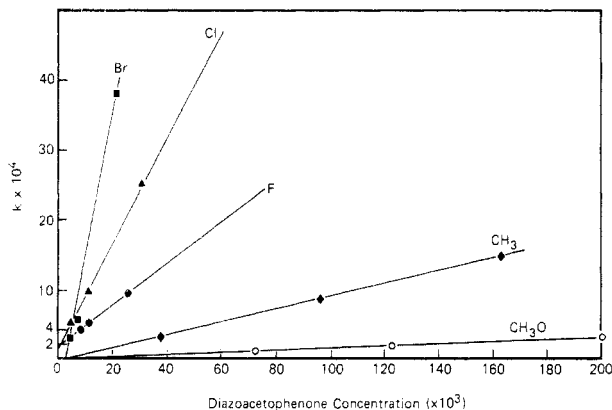


Figure 1. Pseudo-first-order rates observed for 1a-e with excess diazoacetophenone.

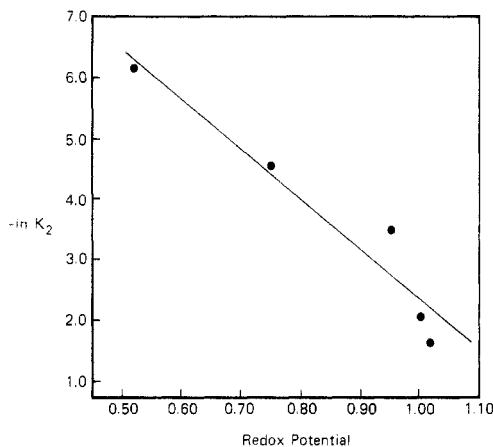
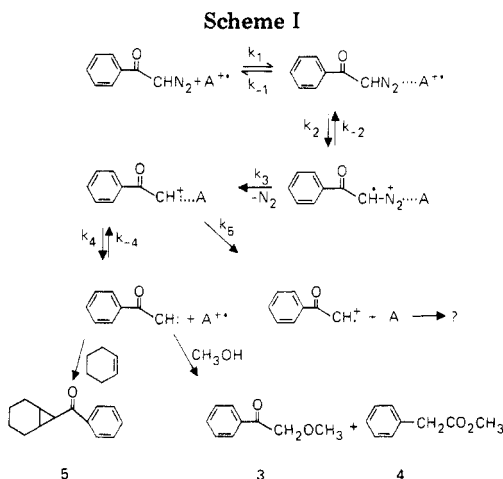


Figure 2. Relationship of second-order rate constant of the reaction of 1a-e and 2 to redox potentials of 1a-e.



cations are very reactive with a variety of functional groups including carbonyl, epoxy, and olefinic compounds. We are currently investigating these reactions at greater length as well as looking into the synthetic exploitation of these reagents as selective oxidants.

Registry No. 1a, 78065-12-0; 1b, 78065-13-1; 1c, 78065-14-2; 1d, 78090-05-8; 1e, 78065-15-3; 2, 3282-32-4.

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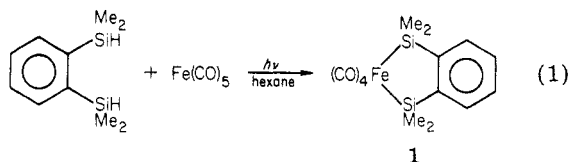
A Disilylated Iron Carbonyl Complex as Reagent for the Conversion of Nitriles into Aldehyde-Enamines

Summary: A readily available disilylated iron carbonyl complex converted nitriles into aldehyde-enamines. This chemical transformation is proved to be useful for the reduction of nitriles into aldehydes and for the protection of nitriles.

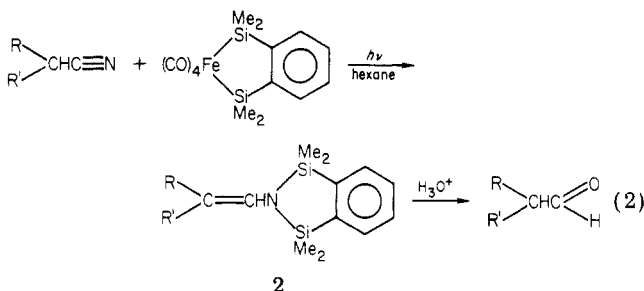
Sir: Our current interest in the use of organometallic compounds in organic synthesis has led us to investigate the reactivity of organosilyl transition-metal complexes.¹ These compounds are potential reagents for organic syntheses.²

In a previous communication, we mentioned the formation of a silylated vinylamine by photolysis of silylated iron carbonyl complexes in the presence of nitriles.¹ We report herein the use of a readily available iron carbonyl complex to effect this new chemical transformation and some of its possible uses in organic synthesis.

Complex 1, originally prepared by Fink,³ was easily obtained from 1,2-bis(dimethylsilyl)benzene⁴ and iron pentacarbonyl (eq 1).



Exposing hexane solutions of equimolecular amounts of nitrile and complex 1 to UV light for several hours afforded the disilylated enamines 2 in good yields (eq 2).⁵



These enamines are very stable and did not hydrolyze under neutral conditions. However, hydrolysis with dilute HCl led to the corresponding aldehydes in good yields.

As illustrated in Table I, a wide range of nitriles were converted into aldehyde-enamines. Alkyl and benzyl

(1) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* 1980, 278.

(2) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1979, 101, 6433.

(3) We found dozen-gram quantities of complex 1 were best obtained by using the photochemical reaction with $\text{Fe}(\text{CO})_5$ rather than using the reaction with $\text{Fe}_2(\text{CO})_9$ (Fink, W. *Helv. Chim. Acta* 1976, 59, 606). In a typical preparation, 6 mL (45×10^{-3} mol) of iron pentacarbonyl and 8.8 g (45×10^{-3} mol) of 1,2-bis(dimethylsilyl)benzene were dissolved in 600 mL of dry degassed hexane. The solution was irradiated at room temperature for 15 h, using an immersed 450-W high-pressure mercury lamp in a quartz reaction vessel. The solvent was evaporated under reduced pressure, and the brown residue was dissolved in 30 mL of degassed *n*-pentane; crystallization at -78°C afforded 11.0 g of complex 1 (68%) as off-white air-stable crystals.

(4) Fink, W. *Helv. Chim. Acta* 1974, 57, 1010; Bourgeois, P.; Calas, R. *J. Organomet. Chem.* 1975, 84, 165.

(5) The reaction of acetonitrile with complex 1 illustrates the standard procedure: complex 1 (3.09 g, 8.6×10^{-3} mol) and acetonitrile (0.35 g, 8.6×10^{-3} mol) were dissolved in 200 mL of dry degassed hexane. The solution was irradiated at room temperature for 30 h, using an immersed high-pressure 450-W mercury lamp in a quartz reaction vessel. The reaction mixture was filtrated, and the solvent was removed under reduced pressure. Distillation of the residue afforded 1.4 g (70%) of the disilylated vinylamine [bp (18 mm) = 95°C].