overall yield from the cyclization product IX. Selective functionalization of IX at C-5 rather than C-8 was designed into the synthesis by providing the bulky *gem*-dicarbethoxy substituents on C-7.

Saponification (2.7 *M* KOH, 50% EtOH, reflux, 6 hr) and decarboxylation (neat, 200°) converted ketodiester XI into the ketoacid XII in 95% yield. Treatment of this ketoacid with 37% aqueous formaldehyde (0.4 *M* KOH, H_2O, 25°, 1 hr)[11] gave in 77% yield a single crystalline lactone, mp 229–230°, identical by mass spectrum, uv, 100-MHz NMR,[12] and careful chromatographic comparison by HPLC and TLC in eight solvent systems with an authentic sample of natural steganone IV.[13]

Further proof of identity of our synthetic ketone was available from its reduction with $NaBH_4$ (CH_2Cl_2–methanol, 25°, 2 min) to give two major products, (±)-steganol (III), mp 155–158° (loss of methanol of crystallization) and (±)-episteganol (V), mp 215.5–217.5°, in the ratio 45:55, respectively, separable by silica gel chromatography (20% cyclohexane in ether). Finally, acetylation of steganol (Ac_2O, pyridine, 50°, 2 hr) gave (±)-steganacin, mp 212.5–214.5°, ir ($CHCl_3$) 1767, 1729 cm^{-1}, identical by uv, NMR, MS, and both TLC and HPLC chromatography with natural steganacin.[13]

The new availability of these unusual dibenzocyclooctadiene lactones in 10% overall yield from homopiperonyl alcohol permits for the first time a complete stereochemical correlation in this series and examination of the relative stabilities of the cis- and trans-fused 8-5 lactone systems. These and related studies will be reported in a separate communication.

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(2) Attempted oxidative closures of C-5 oxygenated systems (ketone, ketal, alcohol, protected alcohol) give no 8-membered ring products.

(3) Cf. R. G. Niak and R. S. Wheeler, *J. Chem. Soc.*, 1780 (1938). Modifications: (a) $NaBH_4$ reduction of piperonal, (b) HBr gas on a chloroform solution of piperonyl alcohol, (c) phase-transfer catalyzed reaction of the resulting benzyl bromide with NaCN,[4] (d) hydrolysis (6 *M* NaOH, 40% EtOH, reflux, 18 hr) of the nitrile, and (e) $LiAlH_4$ reduction of the resulting 3,4-methylenedioxyphenylacetic acid.

(4) C. M. Starks, *J. Am. Chem. Soc.*, **93**, 195 (1971).

(5) Prepared in >95% yield by $NaBH_4$ reduction of 3,4,5-trimethoxybenzaldehyde followed by bubbling HBr gas through a chloroform solution of the resulting alcohol.

(6) All new compounds gave satisfactory mass spectra, analytical, and spectroscopic data.

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(9) The monobromo compound shows NMR (100 MHz, $CDCl_3$) δ 5.15 doublet of doublets, $J = 11$ Hz, $J < 1$ Hz, indicative of benzylic bromination at C-5; ir ($CHCl_3$) 1725 cm^{-1}; mass spectrum *m/e* 565 (M$^+$).

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(11) Cf. D. Becker, L. R. Hughes, and R. A. Raphael, *J. Chem. Soc., Chem. Commun.*, 431 (1974). Our yield was obtained by quenching the reaction after 1 hr (10% H_2SO_4), partitioning between neutrals (steganone) and unreacted starting material, and resubjecting the recovered starting material to the reaction conditions. After three successive cycles the reported yield was obtained. Reaction times of longer than 1 hr led to substantial amounts of ketone reduction by a cross-Cannizzaro reaction.

(12) NMR (JEOL PFT 100 MHz and JEOL CW 100 MHz, $CDCl_3$, δ) 7.53, 6.63, 6.53 (all singlet, all 1 H); 6.10 (s, 2 H); ~4.35 (mult, 2 H); 3.89 (s, 6 H); 3.60 (s, 3 H). These values are reproducibly 0.04–0.08 ppm higher than those previously reported for steganone[1] but they are identical with those obtained from an authentic sample[13] measured on our instruments.

(13) We thank Professor Kupchan for supplying authentic samples of steganacin and steganone. Chromatographic comparison of authentic and synthetic compounds were performed on silica gel using the following solvent systems: chloroform; benzene; 20% ethyl acetate, chloroform; 20% ethyl acetate, benzene; 20% ether, benzene; 40% acetone, hexane; 20% cyclohexane, ether; 50% cyclohexane, ether. HPLC comparison was made on 3 × 2 ft × ⅛ in. Corasil columns with chloroform as solvent at 0.6 ml/min.

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Formation of Radical Anion from Tetracyanoethylene in Dimethyl Sulfoxide

Sir:

Tetracyanoethylene (TCNE) is one of the strongest electron acceptors and has been used in the studies of electron donor–acceptor (EDA) complexes.[1,2] It has been disclosed that, when TCNE is dissolved in a polar solvent of electron donating nature, a radical anion of TCNE is readily formed through ionic dissociation of the EDA complex between a TCNE molecule and a solvent one either spontaneously or upon photoillumination. Photoinduced formation of the TCNE radical anion in tetrahydrofuran was first reported by Ward,[3] and later studied in detail by Ilten and Calvin.[4] Stewart et al. found that the radical anion was formed spontaneously upon mixing TCNE into either dimethyl sulfoxide (DMSO) or *N,N*-dimethylacetamide.[5,6] They observed that the formation of the radical anion was so prompt that its concentration reached a maximum before starting the measurements of the radical anion by the electron spin resonance (ESR) method. This enabled them to observe only the decay process but not the formation process of the radical anion. The prompt formation was attributed to the efficient formation of the ground state EDA complex between a TCNE molecule and a solvent molecule and to the high enthalpy of complex formation, which caused the ionic dissociation through the appreciably populated triplet state of the complex. However, we recently found that the spontaneous formation of the TCNE radical anion in DMSO solution showed kinetic features much different from those reported by Stewart et al.[5,6] The difference is that the formation process was slow enough to be measured by a conventional ESR method, and that the radical anion is so stable that its decay was not observed in the present investigation.

DMSO was distilled under a reduced pressure, degassed by the freeze–pump–thaw method and stored under vacuum over molecular sieves which were baked beforehand. TCNE was recrystallized from dichloromethane and sublimed twice. It was mixed into DMSO under vacuum by breaking a break seal immediately before starting quantitative measurements of the radical anion from the intensity of its well-known ESR spectrum.[7] The samples were treated in complete darkness to avoid the effect of light on the formation of the radical anion.

The observed concentration of the TCNE radical anion is shown in Figure 1 as a function of time after the mixing. It increases gradually and then reaches a plateau value, which agrees with the concentration of TCNE fed. The formation of the radical anion is evidently much slower than that reported previously.[5,6] The formation was found to be enhanced by light from an incandescent lamp (100 W) as shown by a dashed curve in Figure 1. Even the room light was found to increase the rate of formation. The prompt formation of the radical anion observed previously seems to have resulted from this effect of light. Also the present re-

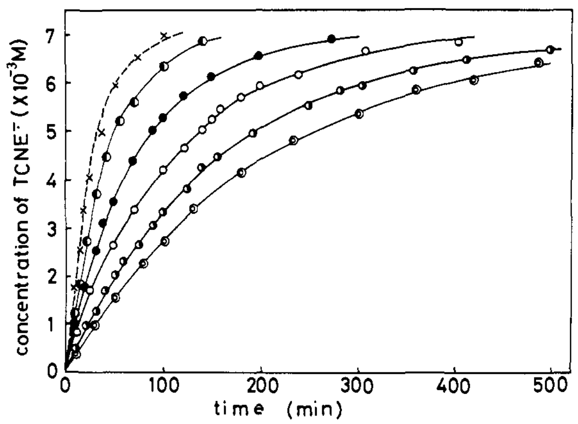

Figure 1. Concentration of TCNE radical anion formed in DMSO solution of TCNE (7×10^{-3} *M*) as a function of time after mixing TCNE into DMSO observed at (◎) 25°, (◑) 30°, (○) 35°, (●) 40°, and (◐) 45°C in the dark and (×) at 30°C under photoillumination.

sults do not agree with the previous ones in that the radical anion is so stable that its concentration remains unchanged after reaching the plateau value in the present investigation. The radical anion was found to be stable, even if the solution was exposed to air by breaking the sealed sample tube. The reason for this difference in the observed stability of the radical anion is not known at this moment, but we are wondering if some impurities in the reaction system might have reacted with the radical anion in the previous study.

The growth of the concentration of the radical anion agreed well with a first-order kinetics, which suggests that the radical anion results from a unimolecular dissociation of the EDA complex. Almost all TCNE is thought to be in complex with DMSO under the experimental conditions used.[5] The rate constant for the formation of radical anion was observed to be 1.1×10^{-4} sec^{-1} at 30°C and its temperature dependence agreed well with an Arrhenius relation, which gives an activation energy of 14 kcal/mol and a frequency factor of 2×10^{6} sec^{-1} in the temperature range examined (between 25 and 45°C). The temperature range was limited by the freezing point of DMSO (18.5°C) and its dissociation above 50°C.[5]

The slow formation of the radical anion observed in the present investigation is largely due to the small frequency factor for the formation process. As far as we know, this is the first success in determining the rate constant for the thermal ionic dissociation of an EDA complex. The observed slow ionic dissociation of the complex agrees with Mulliken's suggestion that in polar solvents dissociation of the complex into ions is governed by a slow, stabilizing solvation process.[8,9] Recently, Farrell and Ngô studied the spontaneous formation of TCNE radical anions in a TCNE-dimethylaniline system and found it to be apparently slow.[10] They interpreted this slow formation by the competition between the essentially fast formation process and the fast disappearance of the radical anion once formed. The present investigation indicates, however, that the ionic dissociation of the EDA complex occurs much more slowly than the complex formation does, at least in the TCNE-DMSO system.

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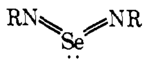
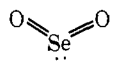
Allylic Amination of Olefins and Acetylenes by Imido Selenium Compounds

Sir:

In our recent report[1] on the vicinal oxyamination of olefins by imido osmium compounds we suggested that it might be the first example of a new class of reactions involving nitrogen and carbon analogues of known oxygen insertion processes. By finding that aza analogues (**1**) of selenium dioxide (**2**)[2] effect allylic amination of olefins, we have now extended this concept to a main group oxidant.



1a, R = *t*-Bu
1b, R = Ts



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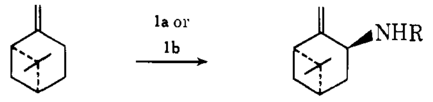
Imido selenium compounds such as **1** have not been described previously. Reaction of selenium tetrachloride with 2 equiv of *tert*-butylamine or of *p*-toluenesulfonamide[3] in methylene chloride in the presence of 4 equiv of an amine base produces solutions thought to contain **1a** and **1b**, respectively. Both **1a** and **1b** reacted with *β*-pinene (**3**) to afford the desired allylic amination products **4a** and **4b**. With less reactive olefins than *β*-pinene the alkyl imido reagent **1a** gave much poorer yields than the sulfonimido reagent **1b**. It was then found by one of us (T.H.) that an even more reactive aminating species was formed when 2 equiv of anhydrous Chloramine-T (TsNClNa) were stirred with selenium metal in methylene chloride (this reagent will be designated **1b′**). Due to its ease of preparation and superior reactivity this Chloramine-T derived reagent was used for most of the aminations described here.



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4a, R = *t*-Bu, 62%
4b, R = Ts, 82%

Examination of the examples in Table I reveals that this new nitrogen insertion reaction has much in common with the allylic insertion of oxygen into olefins by selenium dioxide. These aminations very likely occur via the same sequence of ene and [2,3]-sigmatropic reactions which we have established as the mechanism of the analogous oxoprocess.[4] Detailed comparison of these new allylic oxidants with selenium dioxide must be postponed, but several important points can be made now. Most olefins react readily with the imido reagent **1b′** at or below room temperature; thus it is much more reactive than SeO_2[5] and gives better yields with less reactive olefins, e.g., cases 1-7 Table I, but an even more striking feature of these allylic aminations is the almost complete absence of allylic rearrangement[6] products in situations where SeO_2 gives principally the abnormal, rearranged products (cases 1 and 2) or diene (case 25). The usual side reactions of SeO_2 oxidations appear to be suppressed by the milder conditions. The positional se-