the more stable hydrochloride derived from the amine of higher basicity being less reactive to electrophilic attack.

The reactions of amino acids or amino alcohols with phosgene are interesting since they provide in one step molecules with two different functional groups, namely isocyanato acid chlorides or isocyanato chloroformates. The synthesis of 6-isocyanatohexanoyl chloride by the action of phosgene on the amino acid was reported to be attained only by using an additional reagent such as hydrogen chloride, thionyl chloride, or phosphorus pentachloride besides phosgene.[5] When TCF was used in this preparation, however, 6-isocyanatohexanoyl chloride was obtained in 73% yield without an additional reagent. TCF also reacted smoothly with 3-aminopropanoic acid, and in contrast to phosgene, 3-isocyanatopropanoyl chloride was obtained quantitatively (97%).

In contrast to the preparation of alkyl isocyanato acid chlorides, the TCF method with aromatic amino acids gave results similar to those with phosgene.[5] Treatment of *o*-aminobenzoic acid with TCF resulted in the formation of isatoic anhydride in a quantitative yield, as observed with phosgene. The reaction between *m*-aminobenzoic acid and TCF failed to give the corresponding isocyanato acid chloride, and only an unidentified white solid was obtained. It was confirmed that an additional reagent such as phosphorus pentachloride was necessary to prepare *o*-isocyanatobenzoyl chloride (85% yield) as in the phosgene method.[5]

Reactions of amino alcohols with TCF proceeded similarly to those with phosgene.[6] 3-Aminopropanol and 2-aminoethanol gave 3-isocyanatopropyl chloroformate and 2-isocyanatoethyl chloroformate, respectively, in 53 and 21% yields.

Thus it was found that TCF is far superior to phosgene in the alkyl isocyanato acid chlorides syntheses, but was comparable to phosgene in the preparations of phenyl isocyanate, aromatic isocyanato acid chlorides, and alkyl isocyanato chloroformates.

Experimental Section[7]

Phenyl Isocyanate. To a mixture of 12.95 g (0.1 mol) of aniline hydrochloride and 100 ml of dry dioxane was added 6.3 ml (10.4 g, 0.05 mol) of TCF. The mixture was heated at 60 °C; after 1.5 h of stirring, it became a clear solution. Heating was discontinued after 3.5 h and the solvent was removed under reduced pressure. The residue was distilled at 70–73.5 °C (36 mm) to give 10.6 g (89%) of phenyl isocyanate. It was redistilled almost quantitatively, bp 75–77 °C (39 mm) [lit.[8] 55–57 °C (16 mm)].

***p*-Phenylene Diisocyanate. A. From the Hydrochloride.** To 100 ml of dry dioxane were added 14.48 g (0.08 mol) of *p*-phenylenediamine hydrochloride and 51 ml (84.2 g, 0.4 mol) of TCF. The mixture was heated at reflux for 20 h. The unreacted hydrochloride was filtered off and the filtrate was evaporated under reduced pressure. The residual white, crystalline solid was sublimed under vacuum to give 3.0 g (23%) of *p*-phenylene diisocyanate. It was sublimed again at 85 °C (7 mm) to give colorless crystals, mp 92–94 °C (lit.[8] 94–96 °C).

B. From the Free Base. To a solution of 8.64 g (0.08 mol) of *p*-phenylenediamine in 100 ml of dry dioxane was added 20.5 ml (34.8 g, 0.16 mol) of TCF with stirring. Precipitation took place instantaneously. After refluxing the mixture for 20 h, the undissolved white solid was filtered off and the filtrate was evaporated. The residual solid gave 6.0 g (47%) of *p*-phenylene diisocyanate on sublimation.

3-Isocyanatopropanoyl Chloride. To 250 ml of dry dioxane were added 12.6 g (0.1 mol) of powdered 3-aminopropanoic acid hydrochloride and then 37.9 ml (62.6 g, 0.3 mol) of TCF with stirring. The mixture became a clear solution after heating at 55 °C for 4.5 h. The heating was continued for an additional 6.5 h and then the solvent was removed under reduced pressure. The residual oil was distilled to give 13.0 g (97%) of 3-isocyanatopropanoyl chloride, bp 77–80 °C (10 mm) [lit.[5] 91–91.5 °C (24.5 mm)].

6-Isocyanatohexanoyl chloride was synthesized by virtually the same procedure, bp 112–113 °C (5 mm) [lit.[5] 114 °C (6 mm)].

Reaction of *o*-Aminobenzoic Acid with TCF. A. Without PCl_5. A mixture of 10.0 g (0.073 mol) of *o*-aminobenzoic acid and 36.8 ml (60.7 g, 0.3 mol) of TCF in 150 ml of dry dioxane was refluxed for 6 h. The resulting clear solution was evaporated to give a white solid. It was recrystallized from tetrahydrofuran to give 10.0 g (92%) of isatoic anhydride, mp 241–243 °C dec (lit.[5] 242–243 °C dec).

B. With PCl_5. To a mixture of 10.0 g of *o*-aminobenzoic acid and 36.8 ml of TCF in 150 ml of dry dioxane was added 15.2 g (0.073 mol) of phosphorus pentachloride with stirring. Phosphorus pentachloride went into solution in 1 h. The solution was allowed to stand at room temperature overnight and then the solvent was removed under reduced pressure. The residue was distilled two times to give 11.2 g (85%) of *o*-isocyanatobenzoyl chloride, bp 108–109.5 °C (2 mm), mp 30–32 °C (lit.[5] 32 °C).

3-Isocyanatopropyl Chloroformate. To a solution of 48.4 ml (79.8 g, 0.4 mol) of TCF in 250 ml of dry dioxane was added 7.5 g (0.1 mol) of 3-aminopropanol dropwise over a period of 1 h with cooling in an ice bath. The mixture was stirred with cooling for 30 min and then left standing at room temperature overnight. The solution was evaporated under reduced pressure and the residue was distilled to give 10.2 g of distillate boiling at 65–105 °C (7 mm). Fractional redistillation afforded 0.5 g of a forerun boiling at 23–60 °C (1 mm) and 8.7 g (53%) of 3-isocyanatopropyl chloroformate boiling at 70–74.5 °C (1 mm) [lit.[6] 82 °C (1.5 mm)]. The forerun was considered to consist of mostly 3-chloropropyl isocyanate from its boiling range [lit.[6] 34 °C (1.5 mm)] and ir spectrum.

2-Isocyanatoethyl Chloroformate. 2-Aminoethanol (6.1 g, 0.1 mol) was treated with 24.2 ml (40 g, 0.2 mol) of TCF in 250 ml of dry dioxane at 55–60 °C for 6 h. Fractional distillation gave 0.7 g (3%) of 2-chloroethyl isocyanate boiling at 41.5–45 °C (13 mm) [lit.[6] 35–36 °C (13 mm)], 3.2 g (21%) of 2-isocyanatoethyl chloroformate boiling at 89.5–90 °C (14 mm) [lit.[6] 86–87 °C (13 mm)], and 1 g (6%) of 2-oxazolidone boiling at 160–165 °C (2 mm), mp 86–88 °C (lit.[6] 89 °C).

Acknowledgment. The authors wish to express their appreciation to Hodogaya Kagaku Kogyo Co. for a gift of TCF.

Registry No.—Phenyl isocyanate, 103-71-9; aniline hydrochloride, 142-04-1; *p*-phenylene diisocyanate, 104-49-4; *p*-phenylenediamine hydrochloride, 624-18-0; *p*-phenylenediamine, 106-50-3; 3-isocyanatopropanoyl chloride, 3729-19-9; 3-aminopropanoic acid hydrochloride, 6057-90-5; 6-isocyanatohexanoyl chloride, 3729-18-8; *o*-aminobenzoic acid, 118-92-3; isatoic anhydride, 118-48-9; *o*-isocyanatobenzoyl chloride, 5100-23-2; 3-aminopropanol, 156-87-6; 3-isocyanatopropyl chloroformate, 13107-90-9; 3-chloropropyl isocyanate, 13010-19-0; 2-aminoethanol, 141-43-5; 2-chloroethyl isocyanate, 1943-83-5; 2-isocyanatoethyl chloroformate, 13107-89-6; 2-oxazolidone, 497-25-6; TCF, 23213-83-4; PCl_5, 10026-13-8.

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An Electron Spin Resonance Study of the Radical Anion of 7,8-Dimethylene-1,3,5-cyclooctatriene

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Several examples of pericyclic reactions in radical anions are known where the stereochemistry is the same as that of the excited state of the neutral molecule.[1] If these reactions are concerted, the parallel mode of reaction of the radical anions with the excited states is predicted by the highest occupied molecular orbital (HOMO) method.[2] Bauld and Cessac[3] have recently noted that the butadiene–cyclobutene

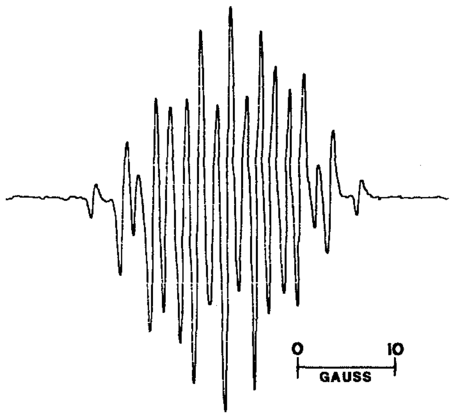
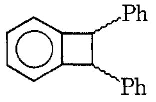
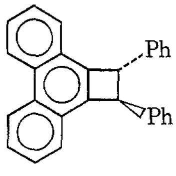


Figure 1. ESR spectrum of **3a**$\cdot^-$ in DMF at −60 °C.

radical anion transformation is allowed in the disrotatory mode by the HOMO method but is not allowed in either the disrotatory or conrotatory mode by the orbital correlation diagram (OCD) method.[4] INDO/MO calculations were carried out on this transformation giving a considerably lower barrier for the conrotatory mode. Interestingly, the radical anions of *cis*- and *trans*-**1**[5] and **2**[3] were found to undergo the cyclobutene to butadiene radical anion type transformation primarily in the conrotatory mode. We wish to report our preparation of the radical anion of 7,8-dimethylene-1,3,5-cyclooctatriene (**3a**) and our observation that this type of transformation does not take place between **3a**$\cdot^-$ and **4**$\cdot^-$ in either direction.



1



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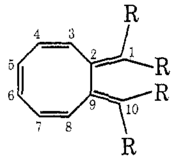
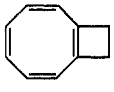


3a, R = H
b, R = D



4

Using special precautions to prevent exposure to oxygen,[6] a solution of **3a**[7] in deoxygenated DMF containing n-Bu$_4$NClO$_4$ was introduced into a standard variable temperature electrolytic cell. Reduction of this solution at −60 °C in an ESR cavity produced the spectrum shown in Figure 1 which could be satisfactorily simulated with $a^H = 4.31$ (2 H) and 3.10 G (6 H). Although the signal intensity decreased considerably upon warming to 0 °C, no evidence for a second radical could be found. Electroreduction of **3b** at −60 °C gave an ESR spectrum with $a^H = 4.31$ (2 H) and 3.43 G (2 H) and a small hyperfine splitting (hfs) of 0.44 G presumably for four deuteriums. An excellent simulation of the spectrum in Figure 1 was then obtained using $a^H = 4.31$ (2 H), 3.43 (2 H), and 2.96 G (4 H) with a line width of 0.50 G.

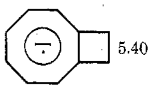
The above results support our assignment of structure **3a**$\cdot^-$ to the radical anion obtained from electroreduction of **3a** where the methylene hydrogens have a hfs of 2.96 G. Further support for this assignment comes from HMO and McLachlan[8] calculations carried out on **3a**$\cdot^-$ assuming a planar geometry. In Table I are given Hückel and McLachlan spin densities (p_c) along with those calculated from hfs's using the McConnell equation,[9] $a^H = -24p_c$. Excellent agreement is obtained suggesting that **3a**$\cdot^-$ is planar or very nearly so. The very small McLachlan spin densities at C-4 and C-7 nicely explain why only eight of the ten hydrogens in **3a**$\cdot^-$ give observable hfs's.

Table I. Spin Densities for 3a$\cdot^-$

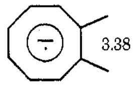
Position	Hückel	McLachlan	Exptl
1,10	0.1236	0.1767	0.1233
2,9	0.0120	−0.0353	
3,8	0.1822	0.2361	0.1796[a]
4,7	0.0586	0.0037	
5,6	0.1236	0.1188	0.1429[a]

[a] Assignment made based on the MO calculations.

Bauld and co-workers have reduced **4** electrochemically (presumably at room temperature) and have obtained an ESR spectrum with $a^H = 5.40$ (4 H) and 3.25 G (6 H).[10] Although assignment of this radical anion to structure **4**$\cdot^-$ is reasonable in view of the hfs of 3.21 G for the hydrogens in the cyclooctatetraene radical anion, we decided to prepare the radical anion of 1,2-dimethylcyclooctatetraene (**5**) for comparison. Reduction of **5** with a solution of Na in HMPA gave an ESR spectrum with hfs's of 3.38 (6 H) and 2.75 G (6 H) while reduction electrolytically in DMF (n-Bu$_4$NClO$_4$ as supporting electrolyte) at −65 °C gave $a^H = 3.49$ (6 H), 2.95 (4 H), and 2.62 G (2 H). The similarity in hfs's between **4**$\cdot^-$ and **5**$\cdot^-$ certainly confirms their assignment. The methylene splitting of 5.40 G in **4**$\cdot^-$ is 60% greater than the methyl splitting of 3.38 G in **5**$\cdot^-$ (HMPA) largely as a result of a conformational effect.[10]



4$\cdot^-$



5$\cdot^-$

A state correlation diagram for **3a**$\cdot^-$ (using Hückel energy levels) and **4**$\cdot^-$ reveals that transformation between ground states is allowed in the conrotatory mode if the degeneracy of ψ_4 and ψ_5 in **4**$\cdot^-$ is removed by placing the symmetric (C_2 axis) orbital higher in energy. Our results clearly show that the transformation of **3a**$\cdot^-$ to **4**$\cdot^-$ does not take place thermally under the conditions given. Since the width of the ESR spectrum for **4**$\cdot^-$ (41.1 G) is considerably greater than that for **3a**$\cdot^-$ (27.3 G), even a trace of **4**$\cdot^-$ would have been detected. The reverse reaction can also be ruled out based on earlier work.[10] We are presently investigating whether phenyl substituents at the methylene positions of **4**$\cdot^-$ will significantly reduce the energy barrier between **4**$\cdot^-$ and **3a**$\cdot^-$

Experimental Section

General. The ESR spectra were recorded on a Varian Associates V-4502 spectrometer. Electroreductions were carried out at a mercury surface using DMF which was previously distilled from CaH$_2$. HMPA was distilled from sodium prior to use as a solvent for sodium reductions.

Electroreduction of 3a. 7,8-Dimethylene-1,3,5-cyclooctatriene (**3a**) was prepared by the literature method[7] and immediately purified before use by chromatography on silica gel and elution with deoxygenated pentane under N$_2$. The bulk of the pentane was removed below room temperature by passing a stream of N$_2$ through the solution. Deoxygenated DMF was then added before the remainder of the pentane was removed by the same procedure. Addition of the electrolyte, tetra-n-butylammonium perchlorate, and transfer to the electrolytic cell was also carried out under N$_2$.

Preparation of 3b. Using the literature methods for preparing **3a**,[7,11,12] **3b** was synthesized from 1,2-dicarbomethoxycyclooctatetraene and aluminum deuteride: NMR (CCl$_4$) δ 5.67–6.00 (m, 4) and 6.16–6.42 (m, 2).

1,2-Dimethylcyclooctatetraene was prepared by the literature method.[13]

Acknowledgment. The authors are grateful to the Research Corporation for financial support. We wish to thank Professor Glen A. Russell for carrying out the MO calculation on **3a**·⁻.

Registry No.—**3a**, 10474-58-4; **3a**·⁻, 58873-29-3.

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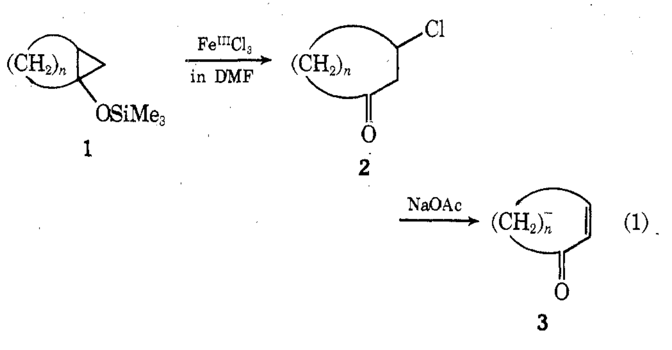
Communications

Reaction of 1-Silyloxybicyclo[*n*.1.0]alkanes with $Fe^{III}Cl_3$. A Facile Synthesis of 2-Cycloalkenones via Ring Enlargement of Cyclic Ketones

Summary: Reactions of 1-trimethylsilyloxybicyclo[*n*.1.0]-alkanes (**1**) with $Fe^{III}Cl_3$, followed by treatment with sodium acetate in methanol, furnish 2-cycloalkenones (**3**) in high yields; similar reactions with bis(trimethylsilyloxy)bicyclo[*n*.1.0]alkanes (**4**) afford cycloalkane-1,3-dione (**5**) in moderate yields.

Sir: Much attention has been directed to the utilization of silyl groups in organic synthesis in the past several years.[1] In our previous paper,[2] we described a regiospecific formation of 1,4 diketones by the oxidative coupling of silyl enol ethers with Ag_2O, in which we assumed Ag^I enolate intermediate regiospecifically formed through the reaction of silyl enol ether with Ag_2O. Herein, we wish to report an oxidation reaction of 1-silyloxybicyclo[*n*.1.0]alkanes (**1**) with $Fe^{III}Cl_3$, leading to the formation of the corresponding 2-cycloalkenone (**3**) via 3-chlorocycloalkanone (**2**) in moderate to excellent yields according to the eq 1. This reaction presents a new method for one-carbon ring homologation of cycloalkanones. It is of practical use since 1-silyloxybicyclo[*n*.1.0]alkanes are readily prepared by the Simmons–Smith reaction of silyl enol ethers of cycloalkanones.[3] Recently, Stork has reported a comparable ring homologation of cycloalkanones by the dichlorocyclopropanation of silyl enol ether followed by hydrolysis.[4]



A typical experimental procedure is illustrated by the reaction of 1-trimethylsilyloxybicyclo[4.1.0]heptane (**1b**) with $Fe^{III}Cl_3$. To a stirred solution of anhydrous $Fe^{III}Cl_3$ (973 mg, 6 mmol) in dimethylformamide (4 ml), a solution of **1b** (368 mg, 2 mmol) and pyridine (158 mg, 2 mmol) in dimethylformamide (4 ml) was added dropwise over 2 h at 0 ~ 10 °C under nitrogen. The resultant brown solution was stirred at room temperature for 1 h, and then poured into cold 1 N HCl aqueous solution and extracted repeatedly with chloroform. The chloroform extract was successively washed with 1 N HCl aqueous solution and with brine, dried over $MgSO_4$ and concentrated in vacuo. The concentrate was subjected to preparative GLC to afford 3-chlorocycloheptanone (**2b**) in 93% yield: ir 1705 cm^{-1}; NMR (CCl_4 with TMS) δ 1.4 ~ 2.3 (m, 6 H), 2.3 ~ 2.6 (m, 4 H), 4.1 ~ 4.4 (m, 1 H); mass M^+ 146 and 148 (3:1). After the concentrate was refluxed with sodium acetate in methanol for 2 h, 2-cycloheptenone (**3b**) was isolated in 84% yield by preparative GLC, which was identical in all respects with an authentic sample. No C_7 cyclic ketones other than **3b** were detected in the reaction mixture by GLC. Some results of 2-cycloalkenone synthesis are summarized in Table I.

Some remarks are to be added to Table I. The reaction of 1-trimethylsilyloxybicyclo[3.1.0]hexane (**1a**) with $Fe^{III}Cl_3$ at 0 ~ 10 °C produced 2-cyclohexenone (**3a**)[5] in almost quantitative yield prior to the treatment with sodium acetate in methanol. In this case, 3-chlorocyclohexanone (**2a**) initially formed underwent readily dehydrochlorination under the reaction conditions. The reaction with 1-trimethylsilyloxy-6-methylbicyclo[4.1.0]heptane (**1e**) afforded 3-methyl-2-cycloheptenone (62% isolated yield), after the treatment with sodium acetate, which was not contaminated with any isomeric methylcycloheptenones. This reaction represents a transformation of unsymmetrical cycloalkanone into regiospecifically homologated 2-cycloalkenone. The reaction of 1-trimethylsilyloxybicyclo[10.1.0]tridecane (**1g**) with $Fe^{III}Cl_3$, which was very sluggish at 0 ~ 10 °C, was carried out by heating at 80 °C for 3 h. Oxidative cleavage of the carbon–carbon bond of **1g** and dehydrochlorination of the resulting 3-chlorotridecanone (**2g**) took place successively in one flask at a temperature of 80 °C.[6] The product of *trans*-2-cyclotridecenone (**3g**) was isolated in 81% yield by preparative TLC on silica gel: ir 1690, 1662, 1625 cm^{-1}; NMR (CCl_4 with TMS) δ 1.15 ~ 1.85 (m, 16 H), 2.10 ~ 2.50 (m, 4 H), 6.05 (d, 1 H, J = 15.6 Hz), 6.61 (td, 1 H, J = 15.6 and 7.0 Hz); mass M^+ 194. Use of diethyl ether solvent[7] in the ring enlargement reaction resulted in a remarkable reduction in the yield of the corresponding 2-cycloalkenone [e.g., 5-methyl-2-cycloheptenone (47%), *trans*-2-cyclotridecenone (56%)]. $CuCl_2$ can also be used in place of $Fe^{III}Cl_3$ in the present reaction, but was less effective [e.g., 2-cyclohexenone (60% yield)] than $Fe^{III}Cl_3$.