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# BRIDGED FERROCENES

## XII*. THE SYNTHESIS OF [3]FERROCENOPHAN-1-ONE FROM FERROCENE BY A NOVEL ONE-STEP ANNELATION REACTION

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## SUMMARY

The reaction of ferrocene with acryloyl chloride in methylene chloride at −78° in the presence of aluminium chloride affords [3]ferrocenophan-1-one in good yield. At higher temperatures, propanoylferrocene is also formed in addition to the bridged ketone.

## INTRODUCTION

Heteroannularly bridged ferrocenes, the [*m*]ferrocenophanes, have played an important role in the investigation of the physical and chemical properties of the ferrocene molecule. In particular, compounds of the [3]ferrocenophane type have been used as substrates to study the mechanism of electrophilic substitution[2], the capacity to stabilize neighbouring electron-deficient centres[3], inter- and intra-molecular electron-transfer processes[4], and the conformational properties[5] of ferrocene and its derivatives.

Introduction of a three-carbon interannular bridge into the ferrocene molecule is usually achieved by cyclization of 3-ferrocenylpropanoic acid ($FcCH_2CH_2CO_2H$) to [3]ferrocenophan-1-one (I), most conveniently effected in trifluoroacetic anhydride solution although other methods have been used[6]. Three different synthetic routes to this acid precursor from readily accessible derivatives (*viz.* FcCHO; FcCOMe; $FcCH_2NMe_2$) have been described[7]. Each of these routes involves several separate steps, however, and the preparation of the bridged ketone (I) in moderately large quantities becomes a time-consuming and somewhat laborious process. Introduction of additional interannular bridges can be accomplished by repetition of the sequence of reactions[8] with a corresponding increase in the experimental labour involved *e.g.* Rinehart's synthesis[8b] of triply bridged ferrocenes, the [3][3][3]ferrocenophanes, from ferrocene requires a sequence of eighteen separate steps.

In this paper, we describe an experimentally convenient annelation reaction whereby an interannular three-carbon bridge can be introduced in one step into the ferrocene molecule.

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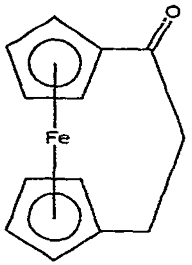
* For Part XI, see ref. 1.

## DISCUSSION

We have found that [3]ferrocenophan-1-one (I) is formed in reproducibly good yield (40–60%) in the reaction of ferrocene with acryloyl chloride in methylene chloride solution in the presence of aluminium chloride as Lewis acid catalyst. When the reaction is conducted at low temperature (−78°), this bridged ketone is the only product formed in significant proportions. At higher temperatures (> −40°) however, the same reaction also affords propanoylferrocene (II). At 0°, the bridged and unbridged ketones [(I) and (II)] are formed in approximately equal amounts.



(I)

$FcCOCH_2CH_3$

(II)

$FcCOCH{=}CH_2$

(III)

($Fc = C_5H_5FeC_5H_4$)

The absence of acryloylferrocene (III) in the products from these reactions was surprising since analogous Friedel–Crafts acylations of ferrocene using other α,β-unsaturated acid chlorides such as crotonoyl and cinnamoyl chloride behave unexceptionally[9,*] and give the expected α,β-unsaturated ketones (FcCOCH=CHMe and FcCOCH=CHPh respectively). Furthermore, we have shown in separate experiments that acryloylferrocene, prepared by a different method[11], does not undergo cyclization to the ketone (I) on treatment in methylene chloride solution either with aluminium chloride or with aluminium chloride/hydrogen chloride. In the latter reaction, addition of HCl across the carbon–carbon double bond occurred giving (3-chloropropanoyl)ferrocene ($FcCOCH_2CH_2Cl$) as the sole product. A similar lack of success attended efforts to induce cyclization of crotonoyl- and cinnamoylferrocene by the action of Lewis acid.

The formation of the saturated ketone (II) in the aforementioned reaction was also unexpected. We reasoned that this compound could be formed from acryloylferrocene produced in the reaction and, indeed, we have shown separately that acryloylferrocene is converted to propanoylferrocene when allowed to react with aluminium chloride and ferrocene in methylene chloride solution. In this reaction, ferrocene serves as a one-electron reducing agent and an equimolar amount of ferricenium cation is produced in the process. Similar results have recently been described[12] by Japanese workers who concluded, however, that only enedione groups can be reduced by ferrocene/aluminium chloride mixtures (*i.e.* $-COCH{=}CHCO- \longrightarrow -COCH_2CH_2CO-$). In our reduction reaction, it may be speculated (Scheme 1) that one-electron reduction of the aluminium chloride complex of acryloylferrocene, which we formulate

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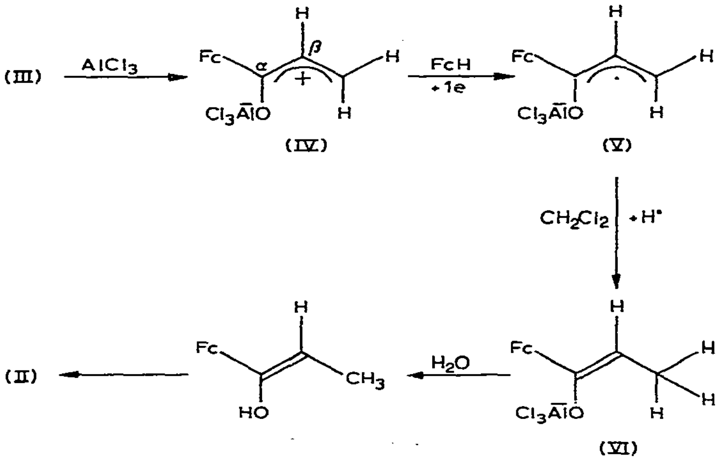
[*] The attempted preparation of 1,1′-dicrotonoylferrocene by this reaction, however, leads to the formation of [5]ferrocenophane-1,5-diones[10].

SCHEME 1



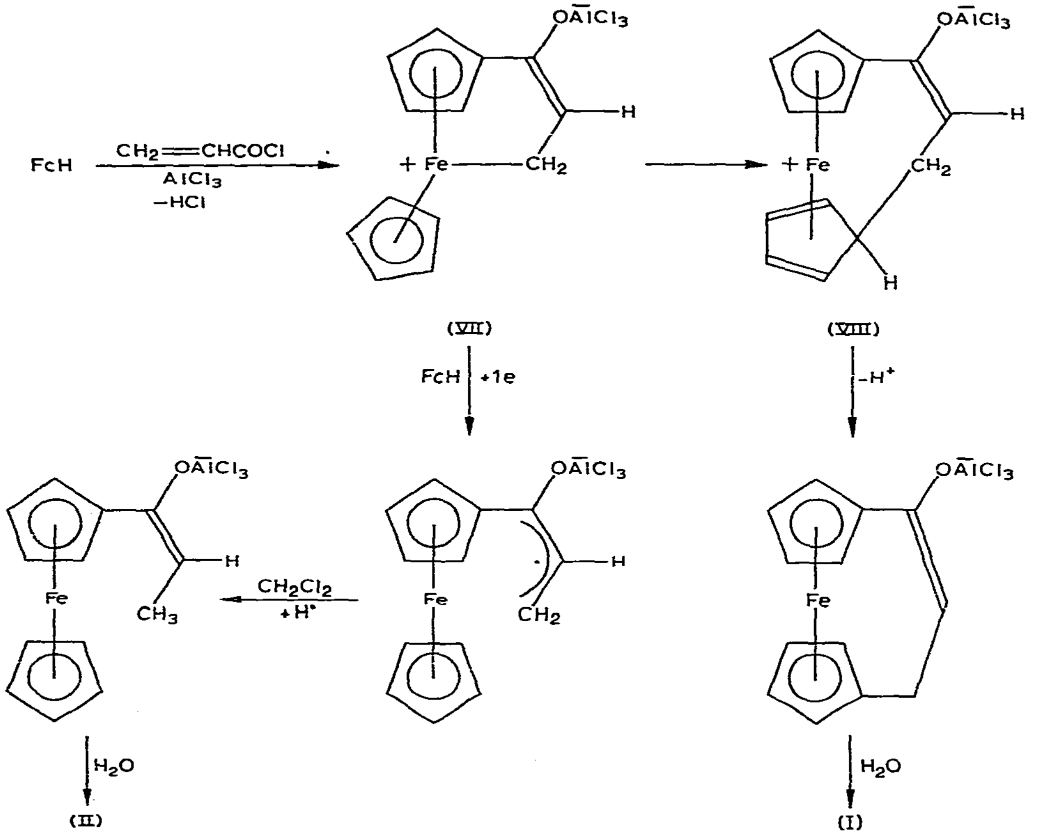
as a ferrocenylallyl cation (IV) (*cf.* ref. 13), generates an unstable allylic radical (V) which abstracts a hydrogen atom from a solvent molecule. Hydrolysis of the aluminium enolate (VI) thereby formed leads directly to the enol tautomer of the product (II).

Neither crotonoyl- nor cinnamoylferrocene undergoes reduction by ferrocene under similar reaction conditions. This may be due to adverse steric factors which hinder electron transfer from ferrocene to the terminal allylic carbon atom of the complexes corresponding to (IV). Alternatively, the presence of an electron-donating methyl or phenyl group attached to this carbon atom may stabilize the aluminium chloride complexes of these ketones such that they are resistant to one-electron reduction.

The results of the experiments so far described establish that neither acryloylferrocene (III) nor its aluminium chloride complex (IV) is an intermediate in the formation of the bridged ketone (I). Further, although we have demonstrated (*vide supra*) that acryloylferrocene undergoes reduction under the conditions of the original Friedel–Crafts reaction, this does not necessarily require that this unsaturated ketone is an intermediate in the production of propanoylferrocene (II) from ferrocene and acryloyl chloride. We tentatively suggest the mechanism outlined in Scheme 2 for the overall reaction. In view of the established Lewis basicity of the iron atom in ferrocene[14], formation of a metal $\sigma$-alkenyl intermediate such as (VII) from ferrocene, acryloyl chloride, and aluminium chloride appears reasonable. Migration of the methylene group in this structure from the iron atom to the unsubstituted cyclopentadienyl ring followed by proton loss generates an aluminium enolate of the eventual product (I).

If the rearrangement step [(VII)→(VIII)] is relatively slow, however, and if the iron–methylene bond in (VII) is relatively weak, it appears possible that the alternative reaction pathway leading to propanoylferrocene (II) (*cf.* Scheme 1) could compete with interannular cyclization particularly at higher temperatures, in harmony with the experimental findings. It is significant that formation of reduced ketone (II) in this reaction is always accompanied by production of an equimolar amount of

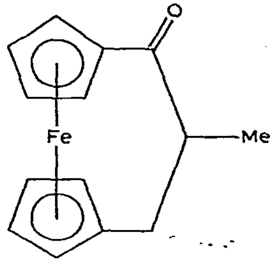
SCHEME 2



ferricenium ion. The absence of cyclized products in the analogous reactions of ferrocene with crotonoyl and cinnamoyl chloride can also be accommodated. In these cases, intermediates corresponding to the $\sigma$-alkenyl complex (VII) would be destabilized by the operation of both steric and electronic effects of the additional groups (Me, Ph) attached to the metal-bonded carbon atom.

Finally, it is necessary to account for the failure of acryloylferrocene to undergo cyclization on treatment with aluminium chloride. At first sight, there appears no compelling reason why the proposed cyclization intermediate (VII) should not be capable of formation by such a reaction. However, it is conceivable that the deep blue complex formed between acryloylferrocene and aluminium chloride would be generated with the stereochemistry depicted in (IV). If partial double-bond character between $C_\alpha$ and $C_\beta$ in this allylic cation prevents rotation of the groups around this bond, as found for other ferrocenylallyl cations[15], approach of the terminal methylene group within bonding distance of the iron atom is prevented and formation of the intermediate (VII) cannot occur.

We have also found that this annelation reaction can be adapted to the synthesis of [3]ferrocenophan-1-ones bearing a substituent on the central bridge atom. Thus, the reaction of ferrocene with methacryloyl chloride ($CH_2$=CMeCOCl) and aluminium chloride in methylene chloride at −78° affords the bridged ketone (IX).



(IX)

At higher reaction temperatures, (2-methylpropanoyl)ferrocene ($FcCOCHMe_2$) is also formed. Preliminary experiments have demonstrated that the reaction is also applicable to the synthesis of multibridged ferrocenes and we plan to explore the utility of the method in this connection (*cf.* ref. 16).

## EXPERIMENTAL

PMR spectra were recorded for $CDCl_3$ solns. on a Perkin–Elmer R12A spectrometer at 60 MHz using TMS as internal reference. Melting points were determined in sealed evacuated capillaries and are uncorrected. Ligroin refers to petrol b.p. 40–60°. Chromatographies were carried out using Spence Grade H alumina which had been partially deactivated by exposure to the atmosphere for 6 h. Cinnamoyl chloride and 3-chloropropanoyl chloride were used as supplied commercially. Yields of product are based upon unrecovered starting material.

### *Acryloyl chloride*

Acrylic acid (36.0 g; 0.5 mol) was added dropwise over 45 min to freshly distilled thionyl chloride (60.0 g; 0.5 mol) stirred at 60° in a flask protected by a $CaCl_2$ drying tube. When addition was complete, the solution was refluxed for 1 h and then distilled through a Vigreux column. Acryloyl chloride (28.0 g; 62%) was collected as a colourless liquid, b.p. 75° (lit.[17] 75°); PMR $\tau$ 3.1–3.9 (ABC pattern).

### *Methacryloyl chloride*

The reaction between methacrylic acid (21.5 g; 0.25 mol) and thionyl chloride (29.0 g; 0.25 mol) was carried out as in the preceding experiment and afforded methacryloyl chloride (15.0 g; 58%) as a colourless liquid, b.p. 96° (lit.[17] 96°); PMR $\tau$ 3.4–3.5, 3.8–4.0 (2 m; vinyl protons), 7.9–8.0 (m; Me protons).

### *Crotonoyl chloride*

Crotonic acid (21.5 g; 0.25 mol) was added portionwise over 45 min to freshly distilled thionyl chloride (29.0 g; 0.25 mol) stirred at 60° and the solution was then refluxed for 1 h. The solution was then distilled through a Vigreux column under reduced pressure and crotonoyl chloride (15.0 g; 58%) was collected as a colourless liquid, b.p. 34°/18 mmHg (lit.[17] 35°/18 mmHg); PMR $\tau$ 2.4–3.1, 3.7–3.8, 3.8–4.1, 7.9–8.1 ($ABX_3$ pattern).

### *Acryloylferrocene (III)*

3-Chloropropanoyl chloride (4.2 g; 0.033 mol) was added dropwise to a stirred soln. of ferrocene (6.2 g; 0.033 mol) in $CH_2Cl_2$ (30 ml) containing finely ground $AlCl_3$ (4.4 g; 0.033 mol) cooled in an ice/salt bath. The mixture was stirred overnight and allowed to come to room temp., and then poured into water. The $CH_2Cl_2$ layer was separated and combined with $CH_2Cl_2$ extracts of the aqueous layer. The total extract was washed ($H_2O$), dried ($MgSO_4$), evaporated to low bulk, and chromatographed. Ligroin eluted unchanged ferrocene (3.2 g; 51 % recovery). Ligroin/ether (3/1) eluted acryloylferrocene (3.3 g; 85 %), formed by dehydrochlorination of (3-chloropropanoyl)ferrocene on $Al_2O_3$ (*cf.* ref. 11). The compound crystallised from ligroin/ether as a red solid, m.p. 71–72° (lit.[18] 73–74.5°); PMR $\tau$ 2.8–4.5 (ABX pattern; vinyl protons), 5.15, 5.44 (2t; $C_5H_4$ protons), 5.80 (s; $C_5H_5$ protons).

### *Crotonoylferrocene*

Crotonoylferrocene was prepared by the reaction between ferrocene, crotonoyl chloride, and $AlCl_3$ in $CH_2Cl_2$ carried out as described in the preceding experiment. Crotonoylferrocene was obtained as a red solid, m.p. 108–110° (lit.[9b] 110°); PMR $\tau$ 2.8–3.7 (m; vinyl protons), 5.17, 5.47 (2t; $C_5H_4$ protons), 5.80 (s; $C_5H_5$ protons), 8.04 (bd; Me protons).

### *Cinnamoylferrocene*

Cinnamoylferrocene was prepared by the reaction between ferrocene, cinnamoyl chloride, and $AlCl_3$ in $CH_2Cl_2$ carried out as described for a previous experiment. Cinnamoylferrocene was obtained as a dark red solid, m.p. 139–140° (lit.[9a] 139.5–139.7°); PMR $\tau$ 2.13, 2.91 (2d; vinyl protons), 2.4–2.6 (m; Ph protons), 5.06, 5.43 (2t; $C_5H_4$ protons), 5.80 (s; $C_5H_5$ protons).

### *Friedel–Crafts reactions of ferrocene with acryloyl chloride*

#### (*a*). *Reactions at* −78°

A solution of freshly distilled acryloyl chloride (0.91 g; 0.01 mol) in $CH_2Cl_2$ (3 ml) was added dropwise over 15 min to a stirred suspension of finely ground $AlCl_3$ (1.33 g; 0.01 mol) in $CH_2Cl_2$ (20 ml) containing ferrocene (1.86 g; 0.01 mol) at −78° in an $Me_2CO$/solid $CO_2$ bath. The mixture was stirred for 6 h at −78° and then poured directly into water (100 ml). The aqueous and organic layers were separated and treated as described below.

*Aqueous layer.* This was washed with $CH_2Cl_2$ and then sufficient $TiCl_3 \cdot aq$ added to reduce ferricenium ions present. The solution was extracted with $CH_2Cl_2$ and the extract washed ($H_2O$), dried ($MgSO_4$), and evaporated affording only a trace of ferrocene (40 mg).

*Organic layer.* This was washed ($H_2O$), dried ($MgSO_4$), evaporated to low bulk, and chromatographed. Ligroin eluted unchanged ferrocene (1.00 g; 54 % recovery). Ligroin/ether (3/1) eluted [3]ferrocenophan-1-one (I) (0.62 g; 55 % yield; 25 % conversion of ferrocene) which crystallized from $CH_2Cl_2$/hexane as an orange-yellow solid, m.p. 147–148° (lit.[19] 145.5–146.5°); PMR $\tau$ 5.13, 5.37, 5.61, 5.96 (4t; cyclopentadienyl protons), 7.05 (s; methylene protons). Minor amounts of coloured compounds, very strongly adsorbed at the top of the $Al_2O_3$ column, were not investigated.

Repetition of the reaction at −78° on a larger scale using tenth-molar amounts of ferrocene (18.6 g), acryloyl chloride (9.1 g), and $AlCl_3$ (13.3 g) in $CH_2Cl_2$ (200 ml) for 6 h afforded [3]ferrocenophan-1-one (5.1 g; 46% yield; 21% conversion of ferrocene) with recovered ferrocene (10 g).

When the small-scale reaction was carried out using 2/1/1 and 1/3/3 molar ratios of ferrocene, acryloyl chloride, and $AlCl_3$ respectively, the yields of ketone (I) were not improved over that obtained using a 1/1/1 ratio.

### (*b*). *Reaction at* 0°

The reaction described under (*a*) was repeated using identical quantities of reactants but keeping the temperature at 0° using an ice bath. Work-up of the water-soluble products as before gave ferrocene (0.19 g; 21%) from reduction of ferricenium ions formed. Chromatography of the $CH_2Cl_2$-soluble products afforded, in order of elution: unchanged ferrocene (0.98 g; 53% recovery); propanoylferrocene (II) (0.22 g; 19%), an orange solid, m.p. 35–37° (lit.[9a] 38°), PMR $\tau$ 5.20, 5.50 (2t; $C_5H_4$ protons), 5.80 (s; $C_5H_5$ protons), 7.25 (q; methylene protons), 8.79 (t; Me protons); bridged ketone (I) (0.38 g; 33%).

### (*c*). *Reaction at* −30° *to* −40°

Repetition of the small-scale reaction described under (*a*) keeping the temp between −30° and −40° afforded propanoylferrocene (10%) and bridged ketone (I) (32%) with unchanged ferrocene (43% recovery).

### 2-*Methyl*[3]*ferrocenophan*-1-*one* (*IX*)

A soln. of freshly distilled methacryloyl chloride (1.05 g; 0.01 mol) in $CH_2Cl_2$ (3 ml) was added dropwise during 15 min to a stirred suspension of $AlCl_3$ (1.33 g; 0.01 mol) in $CH_2Cl_2$ (20 ml) containing ferrocene (1.86 g; 0.01 mol) at −78°. The mixture was stirred for 6 h at this temp and then poured directly into water. The organic layer was separated, washed ($H_2O$), dried ($MgSO_4$), evaporated to low bulk, and chromatographed. Ligroin eluted unchanged ferrocene (1.05 g; 56% recovery). Ligroin/ether (3/1) eluted the ketone (IX) (0.62 g; 54% yield; 24% conversion of ferrocene) which crystallized from $CH_2Cl_2$/hexane as an orange solid, m.p. 100–102° (lit.[20] 102°); PMR $\tau$ 4.9–6.1 (m; cyclopentadienyl protons), 6.2–6.4 (m; methine proton), 7.15–7.3 (m; methylene protons), 8.95 (d; Me protons).

Repetition of this reaction at 0° and work-up as before afforded, in order of elution: unchanged ferrocene (50% recovery); (2-methylpropanoyl)ferrocene (FcCO-$CHMe_2$) (33%), an orange liquid (lit.[21] liquid); PMR $\tau$ 5.17, 5.47 (2t; $C_5H_4$ protons), 5.78 (s, $C_5H_5$ protons), 6.93 (sp; methine proton), 8.80 (d; Me protons); 2-methyl[3]-ferrocenophan-1-one (14%). In addition, ferrocene (39%) was obtained by $TiCl_3$ reduction of ferricenium ions formed in the reaction.

### *Attempted cyclization of acryloylferrocene*

(*a*). $AlCl_3$ (0.27 g; 2 mmol) was added to a solution of acryloylferrocene (0.24 g; 1 mmol) in $CH_2Cl_2$ (20 ml). The mixture was stirred overnight at room temperature and then poured into water. The organic layer was separated, washed ($H_2O$), dried ($MgSO_4$), evaporated to low bulk and chromatographed. Only unchanged acryloylferrocene was recovered (94%).

(*b*). Dry HCl gas was bubbled through a stirred suspension of $AlCl_3$ (0.13 g; 1.0 mmol) in a soln. of acryloylferrocene (0.12 g; 0.5 mmol) in $CH_2Cl_2$ (20 ml) for 10 min. The mixture was then stirred for 5 h and worked up as described under (*a*). The product was chromatographed on preparative thin-layer $SiO_2$ plates. Ligroin/ether (3/1) eluted (3-chloropropanoyl)ferrocene ($FcCOCH_2CH_2Cl$) (0.125 g; 90%) which was obtained as an orange solid, m.p. 62–63° (lit.[22] 62.5–63.5°), PMR $\tau$ 5.20, 5.45 (2t; $C_5H_4$ protons), 5.77 (s; $C_5H_5$ protons), 6.09, 6.83 (2t; methylene protons).

Similarly, attempts to induce cyclization of crotonoyl- and cinnamoylferrocene by treatment with $AlCl_3$ were unsuccessful and the ketones were recovered unchanged.

### *Reduction of acryloylferrocene*

Ferrocene (0.37 g; 2.0 mmol) and finely ground $AlCl_3$ (0.27 g; 2.0 mmol) were added to a stirred solution of acryloylferrocene (0.24 g; 1.0 mmol) in $CH_2Cl_2$ (20 ml). The mixture was stirred at room temperature for 1 h and then poured into water. The aqueous and organic layers were separated and treated as described below.

*Aqueous layer*. This was washed with $CH_2Cl_2$ and then treated with sufficient $TiCl_3 \cdot aq$ to reduce ferricenium ions present. The solution was extracted with $CH_2Cl_2$ and the extract washed ($H_2O$), dried ($MgSO_4$), and evaporated giving ferrocene (0.18 g; 86%).

*Organic layer*. This was washed ($H_2O$), dried ($MgSO_4$), evaporated to low bulk, and chromatographed. Ligroin eluted unchanged ferrocene (0.16 g; 43% recovery). Ligroin/ether (3/1) eluted propanoylferrocene (0.20 g; 73%), identical with the compound described in a previous experiment.

Attempts to effect a similar reduction of crotonoyl- and cinnamoylferrocene by ferrocene/$AlCl_3$ were unsuccessful and the ketones were recovered unchanged from these reactions.

## ACKNOWLEDGEMENTS

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