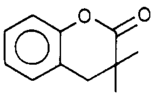
reaction vs. the classical Fries is the ability of the former to accommodate hindered acyl groups.

Cross-over reactions were utilized to determine the nature of this acyl migration. Thus, reaction of a mixture of **3c** and **3h** (1 equiv each) with *sec*-butyllithium (2 equiv) under the standard conditions yielded only **4c** and **4h**, with none of the corresponding intermolecular reaction products **4f** and **4g** present by GC analysis. Likewise, the similar reaction of a mixture of **3f** and **3g** with *sec*-butyllithium afforded only **4f** and **4g**. It may, therefore, be concluded on the basis of these experiments that the acyl migration step in this reaction is an *intramolecular* process. Paralleling these results is the fact that the reaction of *p*-bromophenyl pivaloate with *sec*-butyllithium under identical conditions provided only 3% of the acylation product *p*-hydroxypivalophenone, further demonstrating that intermolecular acylation is not a facile occurrence.

Interestingly, the reaction of *o*-bromophenyl 3-chloro-2,2-dimethylpropionate (**3i**) with *sec*-butyllithium furnished the corresponding acyl migration product **4i** without any trace of the dimethylcoumarin derivative **5**[11] thereby illustrating the inability of Parham-type cyclization[12] to favorably compete with the metal-promoted Fries rearrangement. Treatment of **4i** with sodium hydride (1.5 equiv, THF, 60 °C, 1 h) afforded the 3,3-dimethyl-4-chromanone (**6**) in essentially quantitative yield, while sequential reaction of **4i** with borane (2.1 equiv, THF, 0 °C, 30 min) and aluminum chloride (2.1 equiv, $ClCH_2CH_2Cl$, 0 °C, 30 min) cleanly produced the 4-hydroxy-2,3-dimethylindene (**7**) (79%);[13] this establishes efficient, new synthetic entries into these bicyclic systems.



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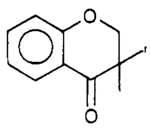

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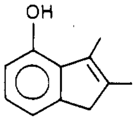

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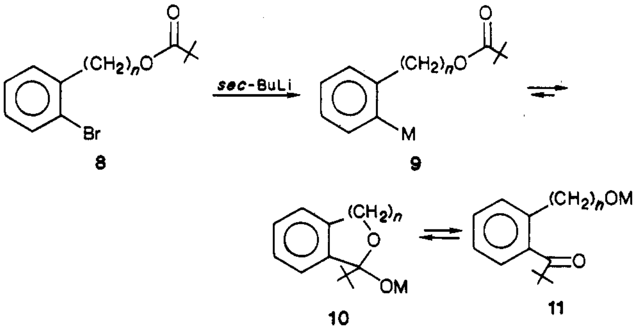

We have also examined the propensity for the series of pivaloates **8**, having the ester functionality separated from the aromatic nucleus by a carbon chain, to participate in this acyl migration reaction. Baldwin's rules[14] predict that exo-trig cyclizations such as **9** → **10** should be favored when n = 0–3. Accordingly, we have found that this novel rearrangement does indeed occur readily for these substrates. Interestingly, however, utilization of the pivaloate **8** (where n = 1) in the reaction depicted above (carried out identically to the transformation **3** → **4** detailed earlier) furnished only **10** (M = H) upon hydrolysis (86% yield); no trace of **11** (M = H) was detected.[15] Conversely, the same process with n = 2 provided the acyl migration adduct as an approximately equal mixture of tautomers **10** and **11** (M = H, 77% yield),[16] whereas the pivaloate **8** with n = 3 afforded only the hydroxy ketone **11** (M = H, 58% yield). As expected, the reaction of **8** (n = 4) with *sec*-butyllithium afforded the respective migration product **11** in low yield (M = H, 16%).[17]

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Supplementary Material Available: Experimental findings for **4e**, **4f**, **4h**, **4i**, **4k**, **5**, **6**, **7**, **9** (n = 0, M = $SiMe_3$), **10** (n = 1 and 2, M = Me), and **11** (n = 3 and 4, M = H) (3 pages). Ordering information is given on any current masthead page.

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[11] Prepared from dihydrocoumarin via two successive deprotonation/alkylation reactions using LDA and MeI.

[12] Parham, W. E.; Bradsher, C. K. *Acc. Chem. Res.* **1982**, *15*, 300.

[13] The regiochemistry of **7** was confirmed by ^{1}H and ^{13}C NMR (500 MHz) decoupling experiments.

[14] Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734, 738.

[15] The formation of the essentially pure hemiketal **10** (n = 1, M = H) is in contrast to the tautomeric equilibrium mixtures of other substituted 1-hydroxyphthalans and hydroxy ketones previously reported: Berner, E. *Acta Chem. Scand., Ser. B* **1982**, *36*, 729. Smith, J. G.; Dibble, P. W. *Tetrahedron* **1984**, 1667.

[16] Both the hemiketal **10** (n = 1, M = H) and the mixture of **10** and **11** (n = 2, M = H) were transformed into the pure corresponding ketals **10** (M = Me, n = 1: 93% and n = 2: 95% isolated yields) by treatment with methanol/cat. TsOH (25 °C, 1 h).

[17] We attempted to elucidate the nature of the intermediate for the transformation **8** → **11** where n = 0 by carrying out the reaction between *o*-bromophenyl pivaloate and *sec*-butyllithium in the presence of chlorotrimethylsilane (5.0 equiv, −95 °C).[18] Examination of the reaction solution revealed none of the "trapped intermediate" **10** (n = 0, M = $SiMe_3$) or even the O-silylated acyl migration derivative **11** (n = 0, M = $SiMe_3$). Instead, the sole product formed in the reaction was **9** (n = 0, M = $SiMe_3$, 92% yield by GC), derived from silylation of the initially produced aryllithium species.[19] Hence, while the metal-promoted Fries rearrangement appears to be a facile process (vide supra), the intermediate aryllithium **9** (n = 0, M = Li) obtained from metal-halogen exchange evidently has a finite lifetime which enables it to be trapped with a reactive electrophile such as chlorotrimethylsilane before acyl migration can occur.

[18] The reaction between esters and alkyllithiums in the presence of chlorotrimethylsilane has been found to produce high yields of the corresponding "Me_3Si-trapped" ketals: Cooke, M. P., Jr. *J. Org. Chem.* **1986**, *51*, 951.

[19] An in situ trapping of aryllithium derivatives with chlorotrimethylsilane has previously been reported: Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155.

Joseph A. Miller
The Procter & Gamble Co.
Miami Valley Laboratories
Cincinnati, Ohio 45247

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Catalysis of Olefin Isomerization by Tight Ion Pairs

Summary: Tight ion pairs of 3-bromo-3-phenyldiazirine and triphenylmethyl bromide catalyze the isomerization of diethyl maleate to diethyl fumarate.

Sir: The conversion of the maleate esters to fumarate esters is a classic isomerization transformation[1] whose reaction characteristics have been thoroughly investigated under thermal,[2] free radical,[3] and both acid- and base-catalyzed conditions.[4,5] However, maleic acid and its esters

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[1] Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill, New York, 1962; pp 341–346.

[2] Kwie, W. W.; Gardiner, W. C., Jr. *Tetrahedron Lett.* **1963**, 405.

[3] Brown, W. G.; Jankowski, S. *J. Am. Chem. Soc.* **1966**, *88*, 233.

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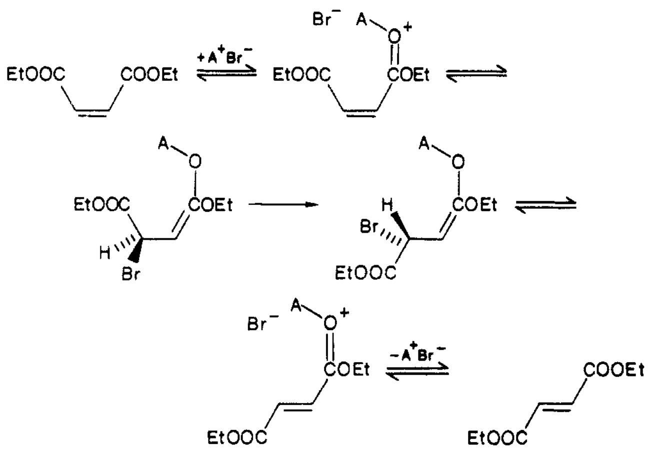
Scheme I



are stable to isomerization in neutral media and in the presence of covalent substrates. We were therefore surprised to find, during investigations of the cyclopropanation of diethyl maleate (DEM) and diethyl fumarate (DEF) by thermal and photochemical decomposition of 3-bromo-3-phenyldiazirine (1), that complete conversion of DEM to DEF was attained with catalytic amounts of 1.

Diazirine 1 was prepared by Graham's procedure[6] and treated with bisulfite solution to ensure the absence of molecular bromine. Addition of 1 to DEM in anhydrous carbon tetrachloride (1/DEM = 4:3 to 1:10) at room temperature caused its complete conversion to DEF. That the structural integrity of 1 was maintained during the course of the DEM to DEF conversion was demonstrated by the absence of any change in the characteristic electronic spectrum of 1 in the reaction solution.

The conversion of DEM to DEF was followed by both ^{1}H NMR spectroscopy and by capillary GC. Integrated peak areas provided the fraction of DEM to the reaction mixture at a given time. Plots of log (DEM/DEF + DEM) vs. time gave excellent straight lines (correlation coefficient > 0.98), demonstrating first-order dependence on the concentration of DEM. First-order rate dependence on the concentration of 1, which remained unchanged during the course of reaction, was determined from the increase in the reaction rate constant with the correponding increase in the initial diazirine concentration. The calculated rate constant for isomerization of diethyl maleate by 1 was 8.0×10^{-6} M^{-1} s^{-1} at 30 °C in anhydrous carbon tetrachloride. Isomerization of DEM by 1 was significantly slower in dipolar aprotic solvents such as dimethyl sulfoxide. Neither 3-chloro-3-phenyldiazirine (2) nor 3-bromo-3-benzyldiazirine (3) were effective in catalyzing the isomerization of diethyl maleate, even after heating the reaction solution in carbon tetrachloride at 50 °C for 2 h.

The relative inertness of DEM to isomerization in the presence of covalent substrates that now include 2 and 3 prompted us to consider 1 as a source of bromide ion and the corresponding 3-phenyldiazirinium cation (eq 1), either

1 4 (1)

of which could be the actual catalyst. The pioneering work of Moss and co-workers has demonstrated the existence of tight ion pairs such as 4 from exchange reactions of 3-halo-3-aryldiazirines.[7] Since the 3-phenyldiazirinium ion has not yet been isolated as a stable salt, triphenylmethyl tetrafluoroborate was used as its substitute but without detectable isomerization of DEM in carbon tetrachloride solution. Similarly, tetra-*n*-butylammonium bromide was ineffective in causing the conversion of maleate to fumarate. However, triphenylmethyl bromide (5) was more effective than 1 in catalyzing this reaction ($k^{30\,°\mathrm{C}} = 8.5 \times 10^{-4}$ M^{-1} s^{-1}). Like 2, triphenylmethyl chloride (6) did not cause isomerization of DEM even at 77 °C.

The most plausible explanation for these results is that isomerization of DEM to DEF is catalyzed by the tight ion pair of either 1 or 5 (A$^+$Br$^-$, Scheme I). Substrates such as 2, 3, or 6 are not sufficiently ionized in carbon tetrachloride to cause isomerization. Basic solvents such as Me$_2$SO compete with DEM for association with the carbocation. In addition, consistent with ion pair involvement, both the trityl cation (Ph$_3$C$^+$BF$_4^-$) and bromide ion (Bu$_4$N$^+$Br$^-$), separately employed as common ions, inhibit isomerization of DEM by 5. The equilibrium constants for 3-bromo-3-phenyldiazirine, triphenylmethyl bromide and triphenylmethyl chloride have been measured at 25 °C, and the values are 5×10^{-5}, 2×10^{-3}, and 5×10^{-4}, respectively.[8] Obviously, the nucleophilicities of the halides play a major role in determining the rate of isomerization.

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Michael T. H. Liu,[*9] **Michael P. Doyle**[*10]
Kuo-Liang Loh,[10] **Surinder M. Anand**[9]
Department of Chemistry
University of Prince Edward Island
Charlottetown, P.E.I. C1A 4P3, Canada, and
Department of Chemistry
Trinity University
San Antonio, Texas 78284
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(5) Gilbert, W. I.; Turkevich, J.; Wallis, E. S. *J. Org. Chem.* **1939**, *3*, 611.

(6) Graham, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 4396.

(7) Moss, R. A.; Terpinski, J.; Cox, D. P.; Denney, D. Z.; Krogh-Jesperson, K. *J. Am. Chem. Soc.* **1985**, *107*, 2743.

(8) Liu, M. T. H.; and Paike, N., to be published. The ion-pairing equilibrium constants (eq 1) in CH$_3$CN have been measured by conductance method.

(9) University of Prince Edward Island.

(10) Trinity University.