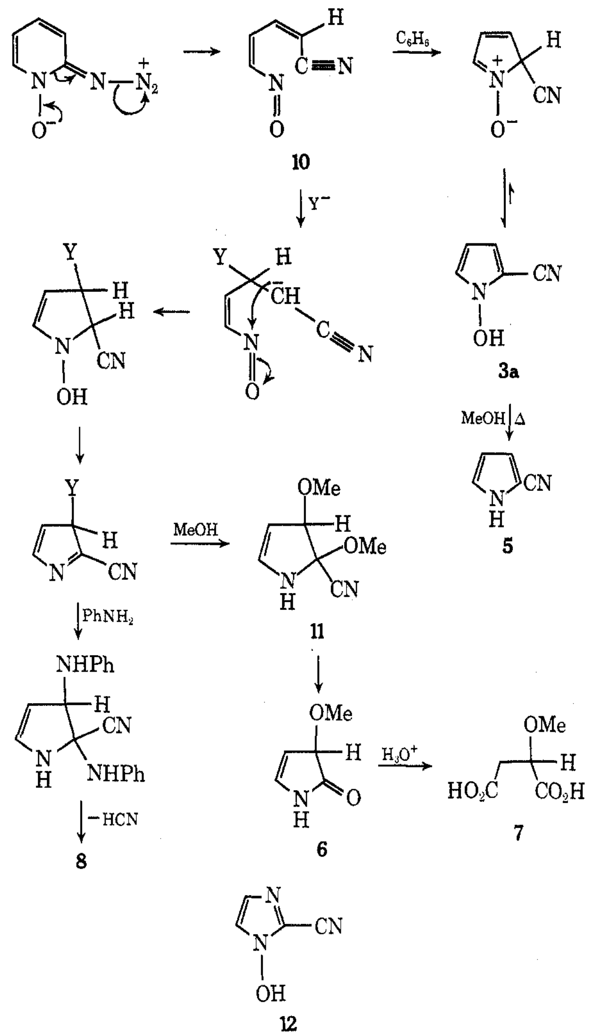
azides **1b–e** gave similar products on thermolysis in nucleophilic solvents.

A plausible mechanism which would account for the formation of products **3**, **6**, and **8** involves a nitrogen elimination concerted with ring opening to give the unsaturated nitrile (**10**). This can either undergo electrocyclic ring closure and tautomerization to give **3** or a Michael addition of solvent followed by cyclization and dehydration to **6** or **8**. Mechanistic analogy for **11** → **6** exists.[10]



The potential generality of this ring contraction is indicated by the production of 2-cyano-*N*-hydroxyimidazole (**12**) [83%; mp 169–170° dec; ir (KBr) 2400 (NOH), 2225 cm^{-1} (C≡N); mass spectrum *m/e* 109 (M$^+$), 92 (M$^+$ − OH)] by the thermolysis of **4** in benzene.

Extensions to fused systems and to the azidopyrimidine 1-oxides are now under investigation.

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[10] S. M. McElvain and R. L. Clarke, *J. Amer. Chem. Soc.*, **69**, 2657, 2661 (1947); S. M. McElvain and C. L. Stevens, *ibid.*, **69**, 2663 (1947); R. Roger and D. Neilson, *Chem. Rev.*, **61**, 192 (1961).

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Stearoyl Methanesulfonate. A Mixed Anhydride from an Isopropenyl Ester

Summary: Isopropenyl stearate and methanesulfonic acid react at ambient temperatures in methylene chloride to give the mixed anhydride stearoyl methanesulfonate, a powerful stearoylating agent.

Sir: Mixed carboxylic-oxy acid anhydrides have been regarded as highly effective acylating agents. They have been prepared by the reaction of a silver sulfonate with an acid chloride,[1] a sulfonic acid with a ketene,[2] a sulfonic acid with an acid chloride,[3] or a sulfonic acid with a carboxylic anhydride[3] or from a lithium carboxylate and the sulfur trioxide-*N*,*N*-dimethylformamide complex.[4]

Nevertheless, little attention has been given to the facile synthesis of these acylating agents from sulfonic acids and isopropenyl esters. An early report[5] on the reactions of isopropenyl acetate (IPA) acknowledged that IPA reacts with carboxylic acids in the presence of a catalytic amount of sulfuric acid to give mixed carboxylic anhydrides. Another group studied the kinetics of various acid-catalyzed IPA reactions and concluded that the active intermediates are mixed acetic–sulfonic or acetic–sulfuric anhydrides.[6] Isopropenyl esters now may be prepared easily by reaction of a carboxylic acid with propyne in the presence of zinc oxide or the zinc carboxylate,[7] and this opens a new synthetic pathway to the once difficult to obtain mixed anhydrides.

We have isolated the mixed anhydride stearoyl methanesulfonate from the reaction mixture of equimolar amounts of isopropenyl stearate and anhydrous methanesulfonic acid in methylene chloride. Although attempts to recrystallize the white solid led to disproportionation, ir analysis and potentiometric titration demonstrated that the initial product was reasonably pure mixed anhydride. Ir absorptions (in a Nujol mull) occur at 1805 and 1185 cm^{-1} and are typical[1c] for mixed carboxylic–sulfonic anhydrides. Ir analysis also showed that the material was essentially free of stearic acid, stearic anhydride, and isopropenyl stearate. A weighed sample of product was hydrolyzed in a known amount of dilute aqueous sodium hydroxide, and the resulting solution was back-titrated with 0.1 *N* hydrochloric acid. Two potentiometric end points were observed, one corresponding to double the amount of sodium hydroxide of the other; one end point was in the pH 5 region (methanesulfonic acid) and the other at pH 9 (stearic acid). The equivalent weight of the mixed anhydride calculated from the titration was within 3% of the theoretical value. The stearic acid that resulted from the hydrolysis and subsequent acidification was isolated in 93% yield and identified by its melting point and its ir spectrum. Quenching of the

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[1] (a) F. Effenberger and G. Epple, *Angew. Chem., Int. Ed. Engl.*, **11**, 299 (1972). (b) A. Baroni, *Atti Acad. Lincei*, **17**, 1081 (1933). (c) C. G. Overberger and E. Sarlo, *J. Amer. Chem. Soc.*, **85**, 2446 (1963).

[2] G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, **27**, 2667 (1962).

[3] M. H. Karger and Y. Mazur, *J. Amer. Chem. Soc.*, **90**, 3878 (1968).

[4] W. L. Garbrecht, *J. Org. Chem.*, **24**, 368 (1959).

[5] H. J. Hagemeyer, Jr., and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

[6] E. A. Jeffery and D. P. N. Satchell, *J. Chem. Soc.*, 1876, 1887, 1906 (1962).

[7] E. S. Rothman and S. Serota, *J. Amer. Oil Chem. Soc.*, **48**, 373 (1971).

mixed anhydride in methanol produced methyl stearate; *tert*-butyl stearate resulted from quenching in *tert*-butyl alcohol.

Glpc evidence confirms that the isolated material that we have labeled "mixed anhydride" is not merely an IPS–methanesulfonic acid adduct $C_{17}H_{35}CO_2C(CH_3)_2OSO_2CH_3$. The glpc trace of a methylene chloride solution of *isolated* mixed anhydride previously quenched with methanol showed the absence of acetone, whereas repetition of the experiment with *in situ* generated mixed anhydride plus methanol revealed the presence of acetone.

Ir analysis of a mixture of equimolar amounts of isopropenyl acetate and methanesulfonic acid in methylene chloride also suggests the formation of mixed anhydride (ν_{max} 1800 cm^{-1} *vs.* 1825 cm^{-1} for acetic anhydride). No acetyl methanesulfonate was isolated, however.

This work is part of an extensive study of low temperature acylation procedures using isopropenyl esters in the presence of strong oxy acids. In these applications the mixed anhydride generally is formed *in situ*. Since (1) addition of a stoichiometric quantity of the strong acid is essential for complete acylation to occur, (2) neither the stearic acid–strong acid combination nor the stearic anhydride–strong acid combination is capable of acylation at such ambient temperatures, at reasonable rates, (3) the formation of a mixed anhydride is demonstrated, and (4) the mixed anhydride is shown to be a potent acylating agent, we are confident that the active materials in these ambient temperature acylation reactions are mixed anhydrides. The results of the application studies using the mixed anhydride acylating agents will be published separately.[8]

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[8] Detailed experimental data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to code number JOC-73-174. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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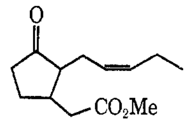
Dihydro-1,3-oxazines. XVI. A General Synthesis of 2-Alkylcyclopentenones and a Method for Adding CH_2CO_2Me to Electrophilic Olefins. Application to the Synthesis of Methyl Jasmonate[1]

Summary: Addition of Grignard reagents to elaborated oxazines **3** gives the keto aldehyde **5** which is readily cyclized to the 2-alkylcyclopentenone **6**; the latter then is transformed into methyl jasmonate by Michael addition of the ketene *N,O*-acetal, **7**.

Sir: We wish to further illustrate the utility of the dihydro-1,3-oxazine system **2** as a synthetic tool by describing a total synthesis of methyl jasmonate (**1**), an



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essential constituent for the characteristic odor of Jasmine.[2] The carboxylic acid of **1** has recently been reported to be a green plant growth inhibitor.[3] Although the synthesis of **1** has been accomplished,[4] we report a route which, in addition to culminating in (±)-**1**, provides a general method for (a) obtaining 2-alkylcyclopentenones, **6**,[5] and (b) Michael addition of CH_2CO_2Me to electrophilic olefins. Treatment of the 2-methyloxazine **2**[6,7] with 1.0 equiv of butyllithium followed by addition of 1.0 equiv of 2-iodomethyl-1,3-dioxolane afforded the alkylated oxazine **3** in 83% yield (Scheme I). The latter was transformed into its methiodide salt which was utilized with or without isolation[8] in the reaction with the Grignard reagent of *cis*-1-bromo-3-hexene[9] (THF) producing the alkylated oxazine, **4** (51%). Heating **4** in aqueous oxalic acid for 2 hr resulted in the cleavage of both masking groups and provided the keto aldehyde **5** in good yield. The cyclopentenone **6** was efficiently formed (72% yield from **4**) when the keto aldehyde was heated in 1% sodium hydroxide solution for 30 min.[10] This synthesis of 2-substituted cyclopentenones should find considerable utility when one considers the variation of Grignard reagents that could be added to the dioxolane-substituted oxazine, **3**.

The formation of **6** represented a key intermediate in the jasmonic ester synthesis in view of our observation that the ketene *N,O*-acetal **7**[1] behaves as a highly reactive nucleophile toward electrophilic olefins[11]

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[1] For the previous paper in this series, see A. I. Meyers and N. Nazarenko, *J. Amer. Chem. Soc.*, **94**, 3243 (1972).

[2] E. Demole, E. Lederer, and D. Mercier, *Helv. Chim. Acta*, **45**, 675 (1962).

[3] D. C. Aldridge, S. Galt, D. Giles, and W. B. Turner, *J. Chem. Soc. C*, 1623 (1971).

[4] E. Demole and M. Stall, *Helv. Chim. Acta*, **45**, 692 (1962); K. Sisido, S. Kurozumi, and K. Utimoto, *J. Org. Chem.*, **34**, 2661 (1969); G. Büchi and B. Egger, *ibid.*, **36**, 2021 (1971). The absolute configuration is also known [R. K. Hill and A. G. Edwards, *Tetrahedron*, **21**, 1501 (1965)].

[5] Various methods have recently been reported to lead to substituted cyclopentenones: W. D. Woessner and R. A. Ellison, *Tetrahedron Lett.*, 3735 (1972); *Chem. Commun.*, 529 (1972); P. A. Grieco, *J. Org. Chem.*, **37**, 2363 (1972); W. F. Berkowitz and A. A. Ozario, *ibid.*, **36**, 3787 (1971); G. Stork, G. L. Nelson, F. Rouessac, and O. Gringore, *J. Amer. Chem. Soc.*, **93**, 3091 (1971); J. E. McMurray and J. Melton, *ibid.*, **93**, 5309 (1971).

[6] Commercially available from Columbia Organic Chemical Co., Columbia, S. C.

[7] Complete experimental details on all compounds described in this communication will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JOC-73-175. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

[8] A. I. Meyers and E. M. Smith, *J. Amer. Chem. Soc.*, **92**, 1084 (1970). The full paper describing this ketone synthesis is currently in press (*J. Org. Chem.*).

[9] F. Sondheimer, *J. Chem. Soc.*, 877 (1950).

[10] In another experiment, *n*-hexylmagnesium bromide was added to the methiodide salt of **3** producing the corresponding *n*-hexyl keto aldehyde and ultimately the 2-*n*-hexylcyclopentenone in good yield.

[11] A variety of electrophilic olefins (esters, nitriles, ketones) have been examined and appear to behave in the fashion described in Scheme II. Certain limitations have been found, however, in highly substituted compounds (*e.g.*, $\Delta^{1,9}$-2-octalone) and unsaturated aldehydes (*e.g.*, Δ^1-cyclopentene carboxaldehyde). Studies are continuing to determine whether or not conditions could be found to implement these transformations successfully.