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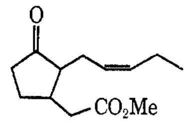
Dihydro-1,3-oxazines. XVI. A General Synthesis of 2-Alkylcyclopentenones and a Method for Adding CH_2CO_2Me to Electrophilic Olefins. Application to the Synthesis of Methyl Jasmonate[1]

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 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**.



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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.

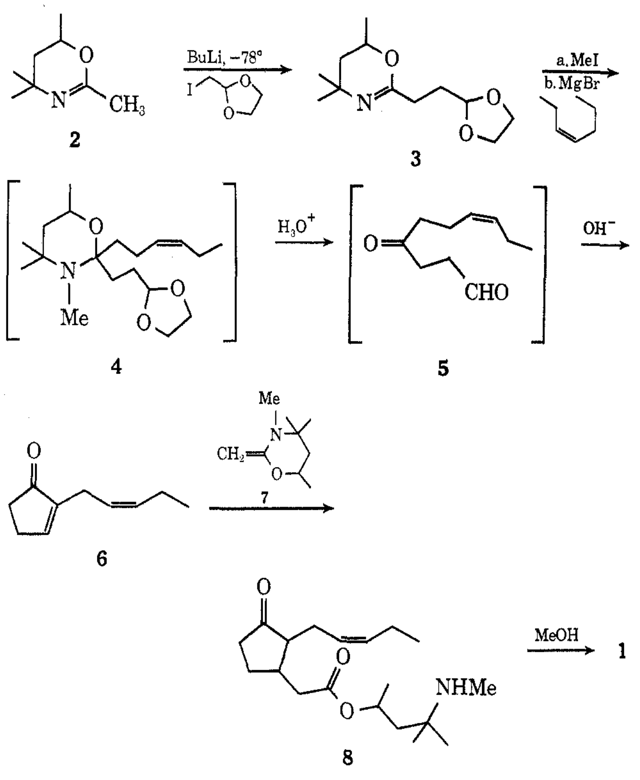
[8] A. I. Meyers and E. M. Smith, *J. Amer. Chem. Soc.*, **92**, 1084 (1970). The full paper describing this ketone synthesis is currently in press (*J. Org. Chem.*).

[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.

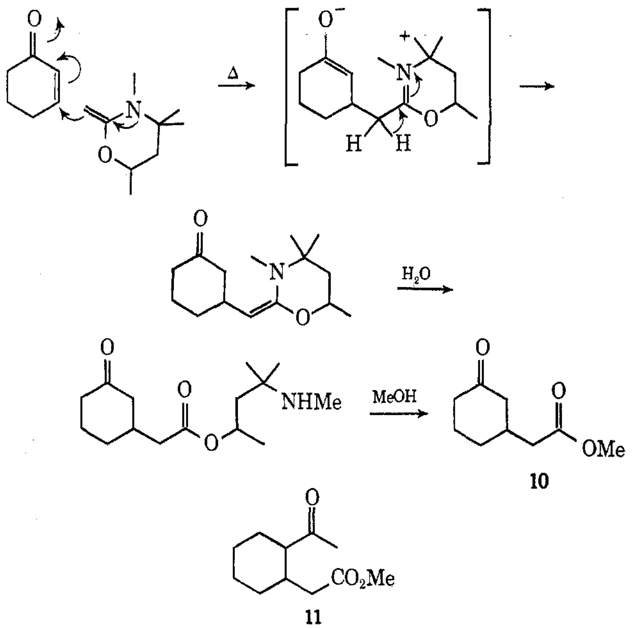
[11] A variety of electrophilic olefins (esters, nitriles, ketones) have been examined and appear to behave in the fashion described in Scheme II. Certain limitations have been found, however, in highly substituted compounds (*e.g.*, $\Delta^{1,9}$-2-octalone) and unsaturated aldehydes (*e.g.*, Δ^{1}-cyclopentene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

SCHEME I



(Scheme II). Thus, α,β-unsaturated carbonyl compounds are readily homologated to the acetic esters by treatment with **7** followed by hydrolysis and transesterification. In this manner, 2-cyclohexenone was converted to the keto ester (benzene, 80°, 3 hr) **10** in 55% yield and 2-acetylcyclohexene was transformed into the keto ester **11** (toluene, 110°, 3 hr) in 62% yield. Although these compounds could conceivably be prepared using sodio malonate, the absence of the hydrolysis–decarboxylation step in the present method is significant.

SCHEME II



Addition of the ketene *N,O*-acetal **7** to the cyclopentenone **6** (3 hr, 135°) afforded the keto ester **8** after quenching in water. Transesterification using methanol and a catalytic amount of *p*-toluenesulfonic acid led to (±)-methyl jasmonate (**1**) (40% based on **6** recovered) whose properties were identical with those reported.[4]

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The Photochemical Decomposition of Triphenyltriazafulvenes

Summary: Dehydrohalogenation of **1a**, **1b**, and **3** at −78° affords the triazafulvenes **2a**, **2b**, and **4**, photolysis of which affords a mixture of products; the intermediacy of the *exo*-methyleneazirine (triphenylazatriafulvene) **10** is strongly implicated.

Sir: An elegant approach to the synthesis of the theoretically interesting heterocyclic variant of cyclopropenone, azirinone, *via* decomposition at −30° of α-azidophenylketene gave only carbon monoxide and benzonitrile.[1] An analogous reaction an α-azidoallene or an isomeric triazafulvene might provide evidence for the presence of an equally interesting azatriafulvene. We now wish to report our observations on the photochemical decomposition of the triphenyltriazafulvenes, **2** and **4**.

The substituted 2-(1,3,4-triazolyl)diphenylcarbinol (**3**, X = OH) and 4-(1,2,3-triazolyl)diphenylcarbinols (**1a**, **1b**, X = OH)[2,3] were converted to the hydrochloride salts of the chlorides (**1a**, **1b**, **3**, X = Cl) by thionyl chloride in benzene at 30°. Dehydrohalogenation of these salts with triethylamine in THF at −78° gave intensely colored solutions of **2a** (λ_{max} 463 nm), **2b** (λ_{max} 454 nm), and **4** (λ_{max} 442 nm) which appeared to be quite stable for a long period of time at this temperature.[4] However, warming the THF solutions to 30° led to rapid dimerization to give the photochemically inert 4*H*,10*H*-ditriazo[1,2-*a*:1′,2′-*d*]pyrazines, **5**, mp 278–280°, and **6**, mp 291–293°, characterized by their acid-catalyzed hydrolysis to **1a** (X = OH) and **3** (X = OH).[3,5] The fulvenes

(1) A. Hassner, R. J. Isbister, R. B. Greenwald, J. T. Klug, and E. C. Taylor, *Tetrahedron*, **25**, 1637 (1969).

(2) These precursors resulted from the addition of excess phenyllithium to the corresponding carbomethoxytriazoles. Complete synthetic details and physical properties will appear in our full paper.

(3) All new compounds reported herein gave satisfactory elemental analyses and displayed structurally consistent ir, nmr, and mass spectra including an exact mass determination.

(4) A phenyl substituent at C-5 appears to be a requirement for stability in **2** based on the observation that when R = H the lifetime of this fulvene was <3 sec at −78°.

(5) Analogous (1,3) cycloadditions of 6,6-diphenyl-1,4-diazafulvene and 6,6-diphenyl-1,2,3,4-tetraazafulvene have been reported: W. Rohr, R. Swoboda, and H. A. Staab, *Ber.*, **101**, 3491 (1968); H. Behringer and M. Matner, *Tetrahedron Lett.*, 1663 (1966).