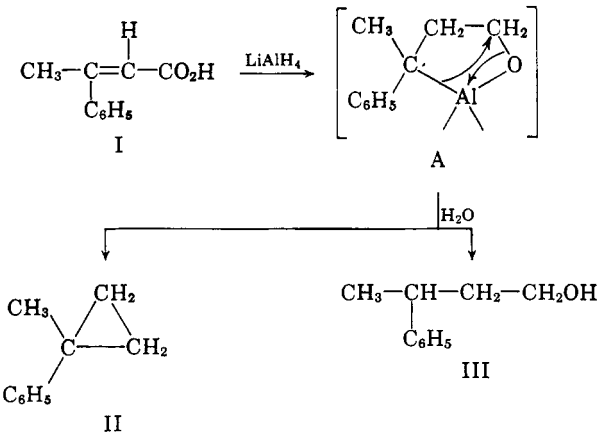
ditions that favor one or the other of these two products. The pattern of results indicates that the two products have a common precursor, and that the relative yields are controlled by the amount of time the reaction is allowed to go before the reaction mixture is quenched. This fact coupled with the structures of starting materials and products indicates that the intermediate in question has structure A.[2b]



I A II III

Numerous examples of reduction of α,β-unsaturated carbonyl compounds have appeared in the literature,[3] but the formation of cyclopropane derivatives has not been reported.

The over-all conversion of I to II resembles a number of known preparations of cyclopropane compounds.[4] Thus treatment of β-methylallyl chloride with diborane gave methylcyclopropane.[4a] Similarly, 1-chloro-3-methyl-1,2-butadiene and lithium aluminum hydride gave 1,1-dimethylcyclopropane.[4b] Finally, 2-methylallyl ethyl ether and diisobutylaluminum hydride gave methylcyclopropane.[4c] The critical ring-closing steps in all of these preparations resemble one another in the sense that they are intramolecular nucleophilic substitution reactions.

The scope and limitations of our reaction have not been examined, but, in principle, the reaction might be applicable to a broad range of α,β-unsaturated carbonyl compounds.

Experimental

1-Methyl-1-phenylcyclopropane (II).—Run 5 will be described. To a stirred suspension of 5.0 g. of lithium aluminum hydride in 35 ml. of tetrahydrofuran (distilled from lithium aluminum hydride) at −78° under an atmosphere of dry nitrogen was added 10 g. of *trans*-β-methylcinnamic acid[5] (m.p. 98°) in 40 ml. of tetrahydrofuran (distilled from lithium aluminum hydride). The reaction mixture was allowed to warm to 20°, and was stirred under reflux for 185 hr. The excess lithium aluminum hydride was decomposed with 10 ml. of cold water, then with 100 ml. of cold 12 *N* sulfuric acid. The resulting mixture was extracted four times with 50 ml. of ether, and the combined organic layers were in turn washed with 50 ml. of saturated sodium bicarbonate solution and twice with 50 ml. of water. The ether layer was dried, and the solvent was slowly evaporated through a Vigreux column. The residual oil was chromatographed on 250 g. of silica gel with pentane as the eluent for the hydrocarbon, then with methanol to strip the column. The pentane fraction was evaporated, and the residual oil was distilled at 85° (32 mm.) to give 5.4 g. (69%) of 1-methylphenylcyclopropane, $n^{25}D$ 1.5139 (lit.[6] $n^{20}D$ 1.5160). Analysis of this material by vapor phase chromatography (4-methyl-4-nitropimelonitrile column at 90°) demonstrated purity.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.88; H, 9.21.

The infrared spectrum was almost identical with that found in the literature[7] for 1-methylphenylcyclopropane with the characteristic absorption at 9.85 μ. The phenyl protons appeared in the nuclear magnetic resonance spectrum at τ 2.89, the methyl protons as a singlet at 8.78 and the methylene protons as a multiplet centered at 9.32. These absorptions integrated to give a ratio of 5:3:4.

The methanol fraction was evaporated, and the residual oil was flash distilled at 7 mm. to give 1 g. of material, which was analyzed by vapor phase chromatography (5% *m*-phenyl ether on Fluoropak at 170°) to be 80% of 3-phenyl-1-butanol and five other components totaling 20%. The major product had a retention time identical with authentic 3-phenyl-1-butanol.[8]

(3) For example: (a) M. J. Jorgenson, *Tetrahedron Letters*, 559 (1962); (b) L. Li and W. H. Elliott, *J. Am. Chem. Soc.*, **74**, 4089 (1952); (c) G. E. Benedict and R. R. Russell, *ibid.*, **73**, 5444 (1951); (d) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954); (e) J. S. Meek and R. D. Stacy, *J. Org. Chem.*, **26**, 300 (1961).

(4) (a) M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 1886 (1960); (b) T. L. Jacobs and R. D. Wilcox, *ibid.*, **86**, 2240 (1964); (c) L. I. Zakharkin and L. A. Savina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1693 (1963).

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(6) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *ibid.*, **65**, 1469 (1943).

(7) F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, *J. Chem. Soc.*, 2999 (1951).

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Furano Compounds. VI. The Synthesis of Linear Furanoxanthones[1]

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In general the fusion of the furan ring in the various naturally occurring furano compounds is of two types, *viz.*, angular or linear, the most typical examples being angelicin (angular furanocoumarin) and psoralen (linear furanocoumarin). The synthesis of a number of furanoxanthones of the angular type has been recorded from these laboratories.[2-4] It is common knowledge that, while the synthesis of these angular furano compounds is fairly simple, the synthesis of their linear isomers is more difficult. A convenient method which has been developed for the synthesis of linear furanocoumarins is the one due to Kaufman.[5] This involves the use of a blocking group, like an acetyl group (introduced by the Fries rearrangement), so that the Claisen rearrangement of an allyloxycoumarin produces an appropriate intermediate for the synthesis of a linear furano compound. This has been adopted for the synthesis of linear furanoxanthones for the first time.

Thus the furan ring has been built on two typical xanthones, *viz.*, on 3-hydroxyxanthone[3] (an analog of the naturally occurring 7-hydroxychromone) and on 3-hydroxy-7-methylxanthone[4] (an analog of the widely distributed 6-methylchromone derivatives). These

(1) This article forms part of the material for the Ph.D. thesis to be submitted by Y. S. Agasimundin to the Karnatak University.

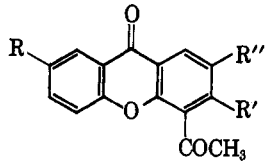
(2) G. S. Puarnik and S. Rajagopal, *Ber.*, **96**, 976 (1963).

(3) G. S. Puranik and S. Rajagopal, *J. Org. Chem.*, **29**, 1089 (1964).

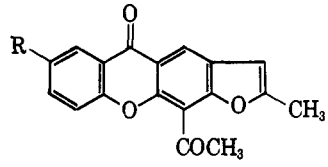
(4) Y. S. Agasimundin and S. Rajagopal, *Ber.*, in press.

(5) K. D. Kaufman and L. R. Worden, *J. Org. Chem.*, **26**, 4721 (1961).

phenols were acetylated and rearranged to obtain 4-acetyl-3-hydroxyxanthones (Ia and If) which were then allylated and subjected to Claisen rearrangement conditions. After acetylation and addition of bromine to the 2-allyl-3-hydroxy-4-acetylxanthones (Ic and Ih) treatment with ethanolic potassium hydroxide resulted in simultaneous dehalogenation and cyclization to yield 4-acetyl-2′-methylfurano[4′,5′:2,3]xanthone (IIa) and 4-acetyl-2′,7-dimethylfurano[4′,5′:2,3]xanthone (IIb). These compounds are expected to possess photodynamic activity.



Ia, R, R″ = H; R′ = OH
b, R, R″ = H; R′ = $OCH_2CH{=}CH_2$
c, R = H; R′ = OH; R″ = $CH_2CH{=}CH_2$
d, R = H; R′ = $OCOCH_3$; R″ = $CH_2CH{=}CH_2$
e, R = H; R′ = $OCOCH_3$; R″ = $CH_2CHBrCH_2Br$
f, R = CH_3; R′ = OH; R″ = H
g, R = CH_3; R′ = $OCH_2CH{=}CH_2$; R″ = H
h, R = CH_3; R′ = OH; R″ = $CH_2CH{=}CH_2$
i, R = CH_3; R′ = $OCOCH_3$; R″ = $CH_2CH{=}CH_2$
j, R = CH_3; R′ = $OCOCH_3$; R″ = $CH_2CHBrCH_2Br$



IIa, R = H
b, R = CH_3

The two compounds IIa and IIb, besides showing strong infrared bands in the regions indicated and correlated for isomeric furanoxanthones in an earlier paper,[3] exhibit strong absorption at 1695 and 1690 $cm.^{-1}$, respectively, characteristic of acyl carbonyl and simple monoaryl ketones.[6]

Experimental

2-Allyloxy-4-acetylxanthone (Ib).—3-Hydroxy-4-acetylxanthone[3] (Ia, 1.5 g.) in acetone (180 ml.) was treated with allyl bromide (5 ml.) and anhydrous potassium carbonate (6 g.), and the mixture was refluxed vigorously for 40 hr. The reaction product was filtered from the potassium salts and the solvent was removed from the filtrate. The residual allyloxy compound, when crystallized from alcohol, was obtained as colorless long rods, m.p. 152°, yield 1.0 g.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.48; H, 4.76. Found: C, 72.98; H, 4.87.

2-Allyl-3-hydroxy-4-acetylxanthone (Ic).—3-Allyloxy-4-acetylxanthone (1.2 g.) in freshly distilled diethylaniline (15 ml.) was refluxed for 90 min. The cooled reaction mixture was acidified with dilute hydrochloric acid and after 2 hr., the product was collected by filtration. It crystallized from alcohol as pale yellow rectangular plates, m.p. 189°, yield 0.5 g. An ethanolic solution of the substance gives a reddish brown coloration with aqueous ferric chloride.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.48; H, 4.76. Found: C, 73.80; H, 4.91.

2-Allyl-3-acetoxy-4-acetylxanthone (Id).—2-Allyl-3-hydroxy-4-acetylxanthone (0.5 g.) in acetic anhydride (10 ml.) and a drop of pyridine was refluxed for 3 hr., cooled, and poured into ice-water. The colorless acetoxy compound was filtered and washed with water. It crystallized from alcohol as colorless plates, m.p. 171°, yield 0.51 g.

Anal. Calcd. for $C_{26}H_{16}O_5$: C, 71.44; H, 4.76. Found: C, 71.67; H, 4.58.

2-(2′,3′-Dibromopropyl)-3-acetoxy-4-acetylxanthone (Ie).—To a solution of 2-allyl-3-acetoxy-4-acetylxanthone (0.56 g., 0.00175 mole) in chloroform (40 ml.), a solution of bromine (0.28 g., 0.00175 mole) in chloroform (15 ml.) was added dropwise with stirring. After stirring for a further period of 1 hr., the solvent was removed. The residual oily product, on crystallization from alcohol, gave the dibromo compound as colorless cubes, m.p. 136°, yield 0.5 g.

Anal. Calcd. for $C_{20}H_{16}Br_2O_5$: C, 48.39; H, 3.23. Found: C, 48.44; H, 3.55.

4-Acetyl-2′-methylfurano[4′,5′:2,3]xanthone (IIa).—2-(2′,3′-Dibromopropyl)-3-acetoxy-4-acetylxanthone (0.4 g., 0.0008 mole) in a solution of potassium hydroxide (0.448 g., 0.008 mole) in alcohol (12 ml.) was refluxed for 2 hr. After cooling, the reaction product was diluted with water, acidified with dilute hydrochloric acid, and left overnight. The precipitate thus obtained was filtered and washed with water. On crystallization from alcohol, 4-acetyl-2′-methylfurano[4′,5′:2,3]xanthone was obtained as pale yellow plates: m.p. 187°; yield 0.11 g.; main infrared bands (Nujol) at 1695 (s), 1470 (s), 1282 (s), 1244 (s), 1039 (w), 877 (w), and 818 (w) $cm.^{-1}$.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.98; H, 4.11. Found: C, 74.25; H, 4.27.

Its 2,4-dinitrophenylhydrazone was obtained as orange tiny needles (acetic acid) blackening at 318–319°.

3-Allyloxy-4-acetyl-7-methylxanthone (Ig).—Allylation of 3-hydroxy-4-acetyl-7-methylxanthone (If, 1.4 g.) under the conditions given for Ib, gave 1.3 g. of colorless needles, m.p. 153° after crystallization from alcohol.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.19. Found: C, 73.92; H, 5.37.

2-Allyl-3-hydroxy-4-acetyl-7-methylxanthone (Ih).—Claisen rearrangement of 1.2 g. of 3-allyloxy-4-acetyl-7-methylxanthone under the conditions described for the preparation of Ic gave a product which crystallized from alcohol as colorless needles, m.p. 169°, yield 0.45 g. An ethanolic solution of the substance gives a reddish brown coloration with aqueous ferric chloride.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.19. Found: C, 73.72; H, 5.35.

2-Allyl-3-acetoxy-4-acetyl-7-methylxanthone (Ii).—Acetylation of 0.4 g. of 2-allyl-3-hydroxy-4-acetyl-7-methylxanthone gave 0.4 g. of colorless needles, m.p. 170°, after crystallization from alcohol.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.14. Found: C, 71.79; H, 5.06.

2-(2′,3′-Dibromopropyl)-3-acetoxy-4-acetyl-8-methylxanthone (Ij).—Bromination of 0.35 g. of 2-allyl-3-acetoxy-4-acetyl-7-methylxanthone in chloroform gave 0.32 g. of the dibromide. This crystallized from alcohol as colorless tiny needles, m.p. 139°.

Anal. Calcd. for $C_{21}H_{18}Br_2O_5$: C, 49.41; H, 3.53. Found: C, 49.73; H, 3.71.

2′,7-Dimethyl-4-acetylfurano[4′,5′:2,3]xanthone (IIb).—The cyclization of 0.265 g. of 2-(2′,3′-dibromopropyl)-3-acetoxy-4-acetyl-7-methylxanthone was accomplished employing ethanolic potassium hydroxide as in the case of IIa. The product crystallized from alcohol as pale yellow needles: m.p. 241°; yield 0.05 g.; main infrared bands (Nujol) 1690 (s), 1470 (s), 1255 (m), 1042 (w), and 828 (s) $cm.^{-1}$.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.49; H, 4.58. Found: C, 74.91; H, 4.63.

Its 2,4-dinitrophenylhydrazone was obtained as orange tiny needles (acetic acid). It does not melt up to 320°.

Acknowledgment.—Our thanks are due to Professor S. Siddappa for his kind interest. We also record our thanks to the Council of Scientific and Industrial Research, New Delhi, for the award of a Junior Research Fellowship to Y. S. Agasimundin.

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