uv λ_{max} 229 (ϵ 37,000), 286 (ϵ 8300), and 294 mμ (ϵ 7700); nmr δ 3.85 (3 H, N_{Ind}-methyl) and 2.32 (3 H, N_B-methyl).

Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.88; H, 7.84; N, 9.08. Found: C, 77.91; H, 7.94; N, 9.18.

Wolff-Kishner Reduction of 8b.—A mixture of 1.0 g (0.00325 mol) of **8b**, 9.2 g of hydrazine hydrate, 1.0 g of sodium hydroxide, and 55 ml of ethylene glycol was refluxed under nitrogen for 1 hr and distilled at atmospheric pressure until the reflux temperature was a constant 194°. Additional ethylene glycol was added to replace that lost in the distillation and refluxing was continued for 2.5 hr. The reaction mixture was concentrated by distillation until crystals started to separate and was poured into 500 ml of ice–water. The precipitated solid was collected, washed well with water, and dissolved in dichloromethane. Evaporation of the dried solution gave 900 mg of a solid residue which showed a single spot (R_f 0.44) on thin layer chromatography. Recrystallization from acetonitrile gave 700 mg of **12b**, mp 127–128°, identified by mixture melting point, thin layer chromatography, and infrared spectrum.

Wolff-Kishner Reduction of 8a.—A Wolff-Kishner reduction was carried out with 3.2 g (0.01 mol) of **8a**, using *exactly* the same conditions described above. The precipitate which separated on pouring the reaction mixture into water was dissolved in dichloromethane. The solution was washed well with water, dried, and evaporated to an oily residue. This was chromatographed over 60 g of alumina, using dichloromethane as the eluent. Evaporation of the first 1000 ml of eluate gave 900 mg of a crystalline residue which could be shown by chromatography to consist of a mixture of the expected product together with some faster moving material. Recrystallization from Skellysolve B gave 400 mg of **12a**, mp 121–123°, which showed a single spot (R_f 0.28) on thin layer chromatography. Recrystallization gave material, mp 123–124°, which was identified as **12a** by mixture melting point, thin layer chromatography, and comparison of infrared spectra.

Registry No.—2, 16957-67-8; 3, 21369-44-8; **7a**, 21369-45-9; **7a** (phosphate salt), 21369-46-0; **7b**, 21369-47-1; **7b** (phosphate salt), 21369-48-2; **8a**, 21372-16-7; **8b**, 21372-17-8; **9a**, 21372-18-9; **9b**, 21372-19-0; **10a**, 21372-20-3; **10b**, 21372-21-4; **11a**, 21372-22-5; **11b**, 21372-23-6; **12a**, 21372-24-7; **12b**, 21372-25-8.

Acknowledgment.—The authors are indebted to the Chemical Development Department under the supervision of Dr. A. W. Ruddy and the Analytical and Physical Chemistry Department under the supervision of Mr. A. D. Lewis. In particular, we wish to thank Mr. G. Conrad and Mr. J. Genzer for large-scale preparation of intermediates, Mrs. U. Zeek for microanalyses, and Mr. R. Puchalski and Dr. R. C. Greenough for the determination of spectra.

Substituted γ-Pyrans[1]

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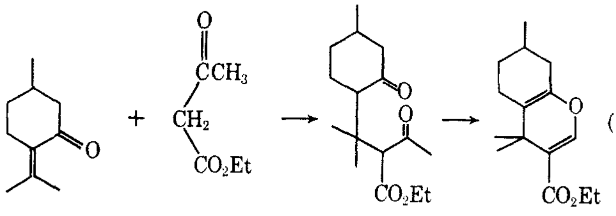
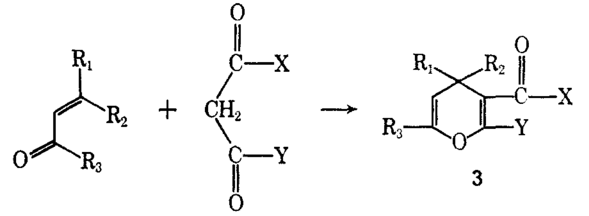
A general route to substituted γ-pyran derivatives involving the zinc chloride catalyzed condensation of β-dicarbonyl compounds with aldehydes or α,β-unsaturated ketones and aldehydes is described. For example, ethyl acetoacetate reacts with formaldehyde to give 3,5-dicarboethoxy-2,6-dimethyl-4H-pyran, and with mesityl oxide to give 3-carboethoxy-2,4,4,6-tetramethyl-4H-pyran. Chemical and spectral properties of these γ-pyran derivatives are described.

γ-Diketones are readily converted by acid into resonance stabilized furan derivatives,[2] while δ-diketones, when subjected to similar conditions, are generally assumed to undergo intramolecular aldol cyclization to cyclohexenone derivatives.[3] γ-Pyran derivatives have only been obtained in cases where structural features, such as the lack of an enolizable hydrogen[4] or improper geometric relationships,[5] prohibit the formation of cyclohexenone derivatives. The formation of γ-pyran (1)[6] in the zinc chloride catalyzed reaction of pulegone with ethyl acetoacetate (eq 1) under conditions which minimize the reconversion of pyran 1 to the intermediate δ-diketone 2 suggests that the cyclization of δ-diketones to γ-pyrans might be a general reaction which has been long overlooked. We have in fact found that the condensation of α,β-unsaturated aldehydes and ketones with β-dicarbonyl compounds provides a general route to substituted γ-pyran derivatives (eq 2).



2 1

(1)



3

(2)

$R_1 = R_2 = R_3 = CH_3$

a, $X = OEt$, $Y = CH_3$

b, $X = OCH_3$, $Y = CH_3$

c, $X = Y = CH_3$

d, $Y = C_6H_5$, $X = OEt$

Mesityl oxide condenses with ethyl or methyl acetoacetate, 2,4-pentandione, and ethyl benzoyl acetate to give γ-pyrans **3a**, **b**, **c**, and **d**, respectively. Although the yields are relatively low, 10–25%, the ready availability of the starting material and the lack of an alternate route to these compounds makes this an attractive synthetic procedure.

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[1] Based on the thesis submitted by H. S. H. in partial fulfillment of the requirements for the Ph.D. degree from Purdue University, Jan 1969.

[2] R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1950, p 127.

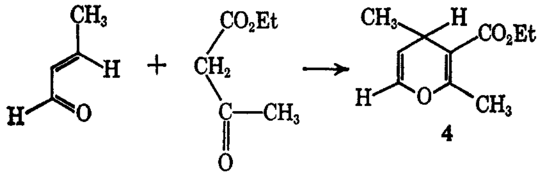
[3] (a) E. Knoevenagel, *Ann.*, **281**, 25 (1894); (b) R. E. Fargher and W. H. Perkin, *J. Chem. Soc.*, **105**, 1353 (1914).

[4] E. Blaise and H. Gault, *Bull. Soc. Chim. Fr.*, **1**, 129 (1907); C. F. Huebner, W. R. Sullivan, M. A. Stahmann, and K. P. Link, *J. Amer. Chem. Soc.*, **65**, 2292 (1943); P. deCarvalho, *Ann. Chim.* (Paris), **4**, 449 (1935).

[5] E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

[6] J. Wolinsky and H. Hauer, *J. Org. Chem.*, **34**, 380 (1969).

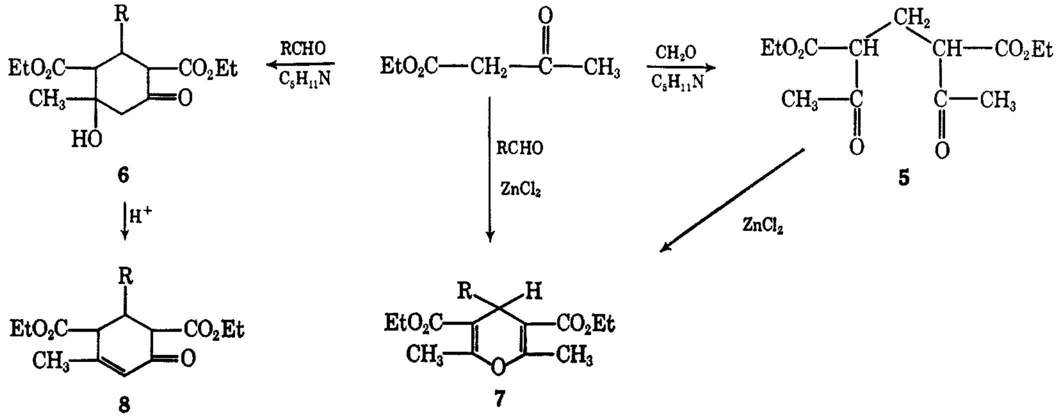
Crotonaldehyde reacts with ethyl acetoacetate to give 3-carbethoxy-2,4-dimethyl-4H-pyran (**4**). This pyran, unlike **3a–d**, is quite unstable and difficult to obtain in a state of high purity.



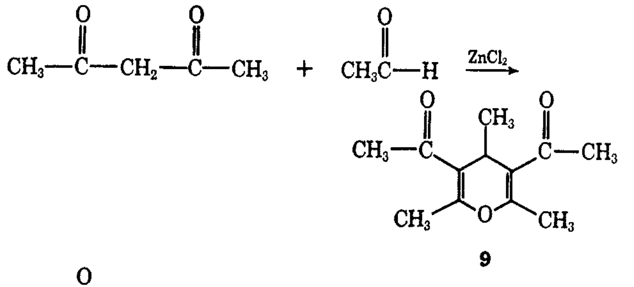
An attempt to react dypnone[7] with ethyl acetoacetate resulted in the recovery of starting materials.

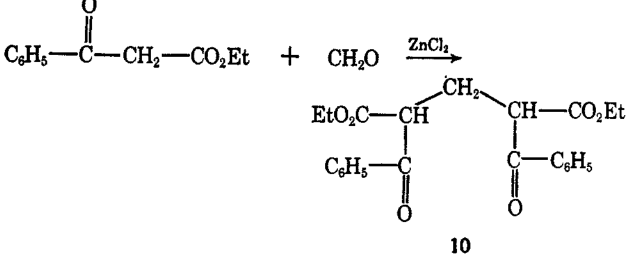
δ-Diketones are also available by the condensation of aldehydes with β-dicarbonyl compounds.[3a] Formaldehyde reacts with ethyl acetoacetate in the presence of piperidine to afford diketone **5**. Benzaldehyde and acetaldehyde under the same conditions yield the aldol **6** and not the diketone claimed by Knoevenagel[3a] and other investigators.[8]

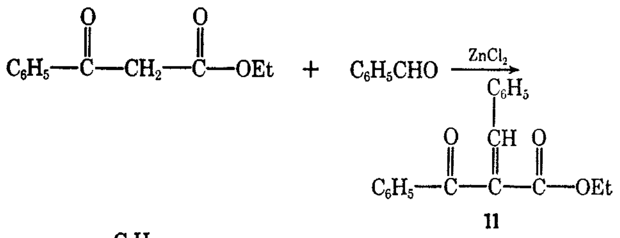
When aldehydes are condensed with ethyl acetoacetate in the presence of zinc chloride in acetic acid–acetic anhydride, γ-pyran derivatives **7** are produced in 35–50% yield. Furthermore, diketone **5** is converted to γ-pyran **7** (R = H) when subjected to these conditions.

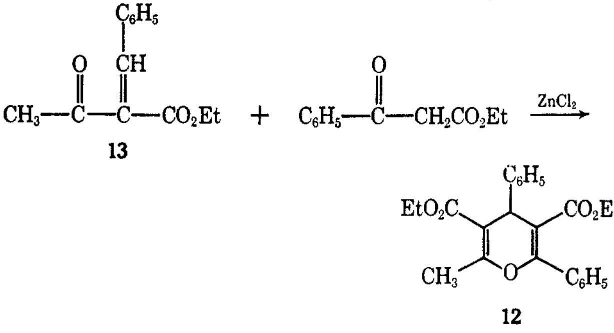


2,4-Pentanedione combined with acetaldehyde in the presence of zinc chloride to give 3,5-diacetyl-2,4,6-trimethyl-4H-pyran (**9**). However, ethyl benzoyl acetate condensed with formaldehyde to give the δ-diketone **10** and all attempts to cyclize **10** to a γ-pyran have been unsuccessful.









The condensation of benzaldehyde with ethyl benzoyl acetate also failed to give a pyran derivative; only the unsaturated keto ester **11** was isolated. However, a "mixed" pyran **12** could be obtained in 37% yield by condensing unsaturated ester **13**[9] with ethyl benzoylacetate.

Chemical Properties of γ-Pyrans.—4,4-Disubstituted 4H-pyrans with an electron-withdrawing substituent at position 3 are relatively stable and can be easily handled, providing contact with strong acid is avoided. 4-Monosubstituted 3-carbethoxy-4H-pyrans, by contrast, are quite unstable and decompose on standing at room temperature. Introduction of a second electron-withdrawing substituent at position 5 markedly increases the stability of the ring system, and even **7** (R = H), with two hydrogens at C-4, can be stored for some time at 4°.

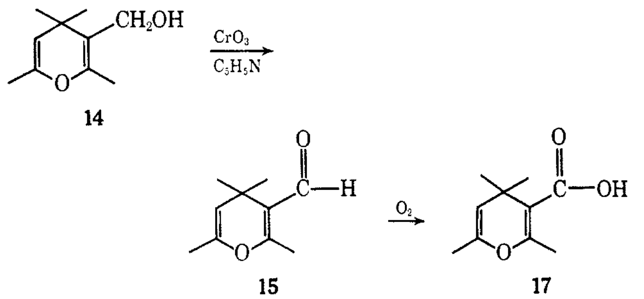
Lithium aluminum hydride reduction of 3-carbethoxy-2,4,4,6-tetramethyl-4H-pyran (**3a**) affords 3-hydroxymethyl-2,4,4,6-tetramethyl-4H-pyran (**14**). The pyran ring in **14** is far more reactive than that of its precursor **3a** and treatment of the alcohol with acid under mild conditions affords products which are currently under investigation.

(7) W. Wayne and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1953, p 367.

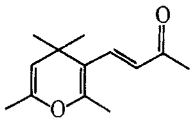
(8) L. Kuss and P. Karrer, *Helv. Chim. Acta*, **40**, 740 (1957); R. I. Reed and V. V. Takhistov, "Some Newer Physical Methods in Structural Chemistry," R. Bonnet and J. G. Davis, Ed., United Trade Press Ltd., London, 1967, p 39.

(9) L. Claisen and F. E. Matthews, *Ann.*, **218**, 170 (1883).

Oxidation of alcohol **14** with chromium trioxide in pyridine gives aldehyde **15**. Base-catalyzed aldol condensation of the aldehyde **15** with acetone affords the unsaturated ketone **16**. Further oxidation of **15** to the acid **17** is best performed by exposing it to air. When heated with a small amount of copper powder, the acid **17** undergoes decarboxylation and yields 2,4,4,6-tetramethyl-4H-pyran (**18**).



14 **15** **17**



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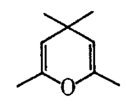
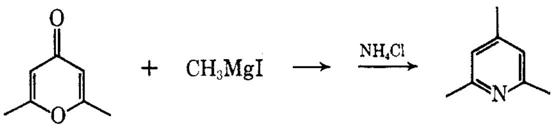
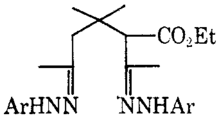


18

The synthesis of pyran **18** by the condensation of excess methylmagnesium iodide with 2,6-dimethyl-4-pyrone has been claimed by Gompper.[10] We have repeated this reaction and have found no trace of pyran **18** among the products. This observation is similar to those recorded by other investigators.[11] The only point worth noting is the production of a 40% yield of collidine when the reaction mixture is worked up with ammonium chloride instead of saturated salt solution,[12] suggesting that 2,4,6-trimethyl-4-hydroxy-4H-pyran is the major produt of the Grignard reaction.



γ-Pyrans react with 2,4-dinitrophenylhydrazine (2,4-DNP) reagent, but there seems to be no general trend in the type of derivative which will form. Pyran **3a** affords the bis-2,4-DNP **19**, whereas pyran **3d** gives a mono-2,4-DNP formulated as **20**. By contrast, pyran **1** yields a dihydropyridine derivative.[6]



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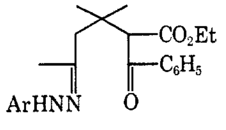

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Spectral Properties.—Owing to the small number of γ-pyrans described in the literature, there is a paucity of spectral data available. With a large number of pyrans now on hand, certain spectral correlations are worth mentioning as guidelines for future work involving the identification of the γ-pyran ring system.

The infrared spectra of pyrans are summarized in Table I. These compounds are all characterized by absorption at 5.80 and 6.0 μ. In 2,4,4,6-tetramethyl-4H-pyran (**18**), the 5.80-μ peak is of medium intensity and could be mistaken for a carbonyl group, while the 6.0-μ peak is weak and could be overlooked if the sample is too dilute. The absorption of carbonyl groups generally coincides with the 5.80-μ peak; an additional peak at 5.85–6.0 μ may also be noted; and the double-bond stretching band is shifted to 6.10–6.15 μ or as high as 6.40 μ in acid **17**. The pyrans with two carbonyl substituents at positions 3 and 5 show a trio of strong peaks at 5.8, 6.0, and 6.15 μ.

The ultraviolet spectra of γ-pyrans (see Table I) are characterized by a weak shoulder at *ca.* 225 mμ; they do not show absorption at *ca.* 240–250 mμ, as claimed by Gompper.[10] Introduction of a carbethoxy or acetyl group at position 3 causes a shift to 270 and 284 mμ, respectively. These maxima are considerably displaced from those of ordinary β-alkoxy-α,β-unsaturated esters and ketones,[13] suggesting additional conjugation with the second double bond in the molecule. The presence of a second carbethoxy or acetyl group at position 5 provides a further bathochromic shift to 285 and 296 mμ, respectively.

The nmr spectra of γ-pyrans are unexceptional. It is worth noting that the vinyl hydrogen at position 5 gives rise to a signal at 4.27–4.43 ppm. In most instances, homoallylic coupling with a methyl group at position 6 is clearly resolved (see Table I), whereas in other cases, *i.e.*, acid **17**, the vinyl hydrogen signal appears as a broad singlet.

The mass spectra of various γ-pyran derivatives are collected in Tables II and III. The major mode of fragmentation in 4,4-dimethyl-3-carboethoxypyrans involves loss of a methyl group and formation of a stable pyrylium ion (A) (see Scheme I). 4-Monosubstituted pyrans lose methyl or phenyl from position 4 in preference to hydrogen and also give rise to stable pyrylium ions A. Further fragmentation appears to be limited to the carboethoxy group, which loses ethylene in a McLafferty rearrangement to give acid B. Acid B loses a water molecule to yield ion C, which also arises from pyrylium ion A by a McLafferty rearrangement involving loss of an alcohol molecule. If a second carbethoxy group is present, the fragmentation of another ethylene molecule is observed. The original parent ion also ejects an alkoxy radical to give ion D, which eliminates carbon monoxide to form ion E.

The fragmentation of derivatives with other substituents at position 3 or 5 follows the same pattern mentioned above. The hydroxymethyl and carboxylic acid derivatives lose a methyl group and a water molecule, while the acetyl derivatives eject methyl and then a fragment of *m/e* 42, which is probably ketene.

These fragmentation patterns are documented by high-resolution studies and by the appearance of metastable ions. For example, in the mass spectrum of **3a**, metastable ions at *m/e* 143 (195 − 167), 133 (167 − 149), and 114 (195 − 149) establish paths A → B, B → C, and A → C.

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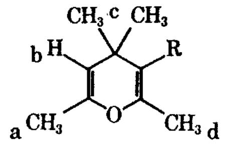
[10] R. Gompper and O. Christmann, *Chem. Ber.*, **94**, 1784 (1961).

[11] *Cf.* A. Hinnen and J. Dreux, *Compt. Rend.*, **255**, 1747 (1962); A. Hinnen and J. Dreux, *Bull. Soc. Chim. Fr.*, 1492 (1964); J. Royer, and J. Dreux, *Compt. Rend.*, **258**, 2895 (1964); J. Royer and J. Dreux, *Tetrahedron Lett.*, 5589 (1968).

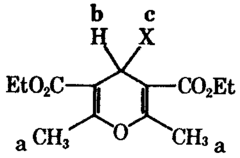
[12] *Cf.* K. Dimroth, *Angew. Chem.*, **72**, 331 (1960), for a review of reactions of pyrones with nucleophiles.

[13] A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957); F. E. Bader, *Helv. Chim. Acta*, **36**, 215 (1953).

Table I
Infrared, Ultraviolet, and Nuclear Magnetic Resonance Spectra of Substituted γ-Pyran Derivatives



Registry no.	R	Ir, μ	Uv, λ_{max}^{MeOH} (log ε)	Nmr, ppm (J, Hz) H$_a$	H$_b$	H$_c$	H$_d$	H$_R$
21298-98-6	H	5.8 (m), 6.0 (w)	225 (3.08)	s, 1.78	s, 4.41	s, 1.01		
21298-99-7	CH_2OH	2.95 (m–w), 5.8 (m), 6.0 (w)						
21299-00-3	$\overset{\overset{O}{\|}}{C}{-}CH_3$	5.80 (s), 5.89 (s), 6.03 (m)	215 (3.21) 284 (2.93)	d, 1.73 (1)	q, 4.35 (1)	s, 1.13	s, 1.83	s, 2.23
21298-97-5	$\overset{\overset{O}{\|}}{C}{-}OH$	5.8 (m), 6.0 (m), 6.4 (m)		s, 1.78	s, 4.43	s, 1.32	s, 2.20	s, 12.53
21299-01-4	$\overset{\overset{O}{\|}}{C}{-}OCH_3$	5.73 (s), 5.85 (s), 6.15 (m)		d, 1.77 (1.5)	m, 4.40 (1.5)	s, 1.18	s, 2.02	s, 3.70
21299-02-5	$\overset{\overset{O}{\|}}{C}{-}OCH_2CH_3$	5.80 (s), 6.15 (m)	208 (3.45) 270 (3.34)	d, 1.73 (1.0)	m, 4.32	s, 1.18	s, 1.98	q, 4.12 (τ) t, 1.28 (τ)
21299-03-6	$CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3$	5.8 (m), 5.9 (w), 6.1 (s)	216 (4.52) 336 (4.70)	d, 1.75 (1.0)	q, 4.33 (1)	s, 1.23	s, 2.02	d, 6.17 (16) d, 7.18 (16) s, 2.15



Registry no.	R	Ir, μ	Uv, λ_{max}^{MeOH} (log ε)	H$_a$	H$_b$	H$_c$	H$_d$	H$_R$
21299-10-5	H	5.80 (s), 5.95 (s), 6.1 (s)		t, 2.28 (1.5)	m, 3.15 (1.5)			q, 4.32 (7) t, 1.33 (7)
21299-04-7	CH_3	5.80 (s), 5.95 (s), 6.1 (s)	214 (4.04) 221 (4.04) 285 (3.46)	s, 2.27	q, 3.57	d, 1.07		q, 4.23 (7) t, 1.15 (7)
21299-05-8	C_6H_5	5.85 (s), 6.00 (s), 6.15 (s)		s, 2.33	s, 4.78	m, 7.18		q, 4.67 (7) t, 1.15 (7)

SCHEME I

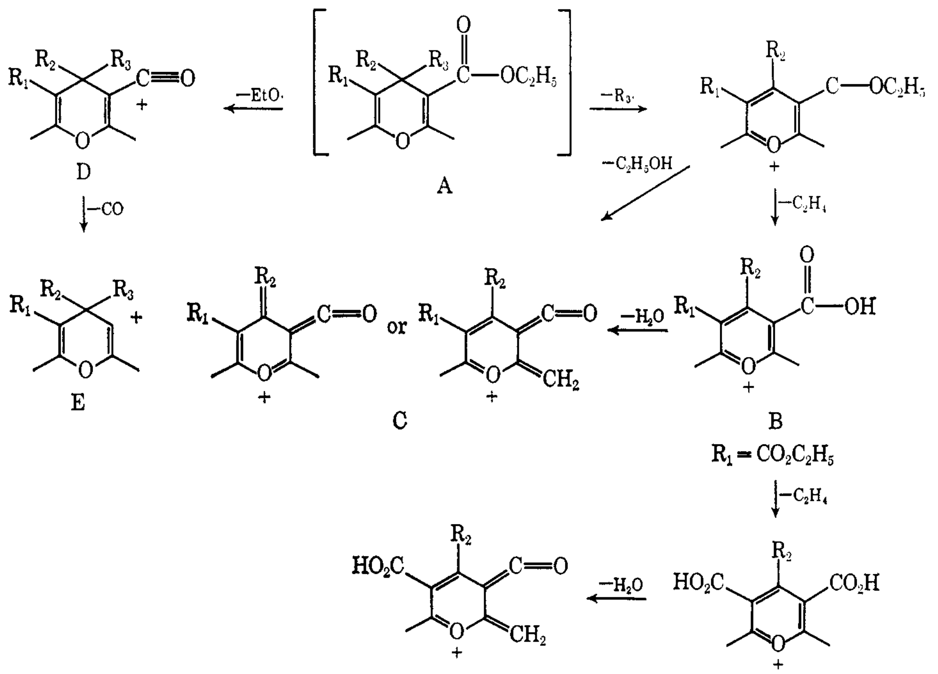
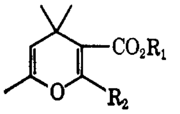


TABLE II

IMPORTANT IONS IN THE MASS SPECTRA OF 3-CARBOALKOXY-4,4-DIMETHYL-4H-PYRANS



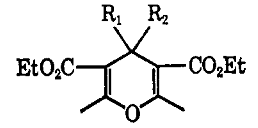
Registry no.	R₁	R₂	P	P − CH₃	P − CH₃ − C₂H₄	P − CH₃ − C₂H₅ − H₂O	P − OR	P − OR − CO	
	CH₂CH₃	CH₃	210 (2)	195 (100)	167 (46)	149 (25)	165 (19)	137 (3)	43 (11)
	CH₃	CH₃	196 (3)	181 (100)		149 (44)[a]	165 (11)	137 (2)	43 (57)
	H	CH₃	182 (2)	167 (100)		149 (20)[b]			43 (50)
21299-09-2	CH₂CH₃	C₆H₅	272 (3)	257 (100)	229 (23)	211 (5)	227 (8)	199 (3)	43 (33)

m/e (% relative abundance) spans columns P through the last.

[a] Established by high-resolution studies. [b] $P - CH_3 - H_2O$.

TABLE III

IMPORTANT IONS IN THE MASS SPECTRA OF 3,5-DICARBETHOXYPYRANS



R₁	R₂	P	P − R₁	P − R₂	P − R₂ − C₂H₄	P − R₂ − 2C₂H₄	P − R₂ − 2C₂H₄ − H₂O	P − OC₂H₅	P − OC₂H₅ − CO	
H	H	254 (8)	253 (3)		225 (100)	197 (41)	179 (9)	209 (20)	181 (18)	43 (91)
H	CH₃	268 (2)	267 (0.2)	253 (100)	225 (18)	197 (15)	179 (6)	223 (17)	195 (1)	43 (31)
H	C₆H₅	330 (24)	329 (1)	253 (100)	225 (2)	197 (18)	179 (7)	285 (15)	257 (19)	43 (41)

Experimental Section[14]

A. General Procedure for Pyran Synthesis.—A mixture of α,β-unsaturated aldehyde or ketone and the appropriate β-dicarbonyl compound was added dropwise to a vigorously stirred solution of fused $ZnCl_2$ in *ca.* 80 ml of acetic acid and *ca.* 100 ml of acetic anhydride. The solution was kept at room temperature for 1-3 weeks and was then poured into 400 ml of water and extracted with ether. The ether extracts were washed with water, 5% $NaHCO_3$ solution, and saturated salt solution. The ether solution was dried over anhydrous $MgSO_4$ and the ether was removed. The pyran was isolated by distillation *in vacuo.* Analytical samples were generally obtained by vpc using a DEGS column at 180°.

B.—A mixture of aldehyde and β-dicarbonyl compound was added dropwise to a vigorously stirred solution of fused $ZnCl_2$ in *ca.* 40 ml of acetic acid and *ca.* 50 ml of acetic anhydride. The solution was kept at room temperature for 1-2 weeks and was worked up as described in general procedure A. The products were purified by recrystallization.

3-Hydroxymethyl-2,4,4,6-tetramethyl-4H-pyran (14).—A solution of 9.39 g of 3-carboethoxy-2,4,4,6-tetramethyl-4H-pyran (**3a**) in 20 ml of ether was added slowly under a nitrogen atmosphere to a stirred suspension of 1.52 g of lithium aluminum

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[14] All boiling and melting points are uncorrected. Infrared spectra were measured with Perkin-Elmer Infracord or 221 spectrophotometers. Nuclear magnetic resonance spectra were determined with a Varian Associates A-60 spectrometer. Mass spectra were measured with a Hitachi RMU-6A and a CDC-110 high-resolution mass spectrometer by the Purdue University Spectral Service Department. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505. Microanalysis were performed by Dr. C. S. Yeh and associates.

TABLE IV

γ-PYRANS PREPARED BY THE CONDENSATION OF ALDEHYDES AND α,β-UNSATURATED KETONES AND ALDEHYDES WITH β-DICARBONYL COMPOUNDS

Pyran	Yield, %	Bp, °C (mm)	n_D	Mp, °C	Calcd, % C	Calcd, % H	Found, % C	Found, % H
3a	15	52 (0.3)	1.4703		68.54	8.63	68.47	8.81
3b	15	48–54 (0.5)	1.4714		67.32	8.22	67.58	8.31
3c	10	49–54 (0.2)	1.4758		73.30	8.95	73.21	9.20
3d	20			49–50	74.97	7.40	75.12	7.53
4		90–100 (~10)			65.91	7.74	65.44	7.88
7a	38			76.5–78	69.07	6.71	69.30	6.79
7b	50			42–43	62.67	7.51	62.81	7.47
7c				40–45	61.41	7.14	60.91	6.91
9	21	86–100 (0.15)	1.5071		69.21	7.74	68.92	7.57
12	35			60–62	73.45	6.16	73.41	6.08

hydride and 50 ml of ether containing 0.52 ml of absolute ethanol.[15] The mixture was heated for 30 min, and saturated ammonium chloride solution was added to the cooled mixture. The salts were removed by filtration, and the ether solution was dried over anhydrous magnesium sulfate and distilled to yield 7 g of alcohol **14**, bp 62° (0.2 mm); mass spectrum *m/e* (rel intensity) 168 (0.5), 153 (1), 150 (7), 135 (43), and 43 (100).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.63; H, 9.75.

2,4,4,6-Tetramethyl-4H-pyran-3-carboxylic acid (**17**).—A solution of 7.0 g of alcohol **14** in 20 ml of pyridine at 0° was added to a solution of 12.2 g of chromium trioxide in 140 ml of pyridine.[16] The mixture was stirred for 30 min and then kept at room temperature for 20 hr. The mixture was poured into 600 ml of water and extracted with ether. The ether extracts were washed with dilute hydrochloric acid, water, and saturated salt solution. The ether solution was dried and the ether was removed to leave 4.4 g (64%) of crude aldehyde **15** which was used directly in the next step.

The crude aldehyde was stirred at room temperature in an open flask for *ca.* 20 hr and was then taken up in ether. The ether solution was extracted with 5% sodium carbonate solution. The basic extract was acidified with 5% hydrochloric acid and extracted with ether. The ether extracts were dried and the ether was removed to leave 1.8 g of crude acid. Recrystallization of the acid from pentane gave 1.04 g of a white solid, mp 132–134°. The aldehyde recovered from the original ether solution could be recycled to provide additional acid **17**; mass spectrum *m/e* (rel intensity) 182 (2), 167 (100), 149 (20), and 43 (50).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.21; H, 7.79.

3-(3-oxo-2-butenyl)-2,4,4,6-tetramethyl-4H-pyran (**16**).—A solution of 9.72 g of crude aldehyde **15** in 50 ml of ether was treated in a nitrogen atmosphere with 0.63 g of sodium hydride and 10 ml of dry acetone. The mixture was heated to reflux for 30 min, let stand at room temperature for 90 min, and then washed with water. Distillation gave **16**, bp 70–85° (0.26 mm), which was crystallized from pentane to afford a white solid, mp 42.5–44.5°. An analytical sample was prepared by sublimation *in vacuo;* mass spectrum *m/e* (rel intensity 206 (8), 191 (100), 149 (12), and 43 (59).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.70; H, 8.92.

2,4,4,6-Tetramethyl-4H-pyran (**18**).—A mixture of 0.4 g of acid **17** and 0.4 g of copper powder was heated at 230–280° until distillation of 0.15 g of colorless liquid, bp *ca.* 193°, was complete; mass spectrum *m/e* (rel intensity) 138 (4), 123 (100), and 43 (40).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.78; H, 10.43.

Reaction of 3a with 2,4-Dinitrophenylhydrazine.—A solution of 1 ml of pyran **3a** in 10 ml of ethanol was added to a solution of 0.85 g of 2,4-dinitrophenylhydrazine in 30 ml of 65% aqueous ethanol containing 5 ml of concentrated sulfuric acid. A solid precipitated within 1 min. After standing overnight, the solid was collected and recrystallized from 3:1 ethyl acetate–ethanol to give orange-yellow crystals of **19**, mp 154–155.5°; uv λ_{max}^{MeOH} 228 and 357 mμ (log ε 4.0 and 4.2); nmr ($CDCl_3$) 1.30 (t, 3, CH_3CH_2O), 2.20 and 2.30 (s, 6, 2 CH_3CO), and 4.27 ppm (q, 2, CH_3CH_2O).

Anal. Calcd for $C_{24}H_{28}N_8O_{10}$: C, 48.98; H, 4.80; N, 19.04. Found: C, 48.90; H, 4.77; N, 19.18.

Reaction of Pyan 3d with 2,4-Dinitrophenylhydrazine.—A solution of 0.5 g of **3d** in 10 ml of ethanol was added to a solution of 0.43 g of 2,4-dinitrophenylhydrazine and 2.5 ml of concentrated sulfuric acid in 15 ml of 65% aqueous ethanol. After standing overnight, the orange-yellow solid which separated was collected and recrystallized from ethyl acetate–ethanol to give crystals of **20**, mp 94–96°; ir 5.8 and 5.9 μ.

Anal. Calcd for $C_{23}H_{26}N_4O_7$: C, 58.72; H, 5.57; N, 11.91. Found: C, 58.64; H, 5.93; N, 11.98.

2,4-Dicarbethoxy-1,5-diphenyl-1,5-pentanedione (**10**).—A mixture of 9.3 g (0.31 mol) of paraformaldehyde, 97.1 g (0.50 mol) of ethyl benzoylacetate, and 19.5 g of fused zinc chloride in acetic acid–acetic anhydride was stirred at room temperature for 4 days. The mixture was worked up as described under general procedure A to give an oil which slowly solidified. Recrystallization from 1:1 hexane–ethyl acetate gave 32.5 g (33%) of diketone **10**, mp 91.5–92.5° (lit. mp 86°); ir (Nujol) 5.7, 5.8, and 5.95 μ; nmr ($CDCl_3$) 1.27 (t, 6, J = 7.5 Hz, CH_3CH_2O), 2.64 (t, 2, J = 8 Hz, $CHCH_2CH$), 4.28 (q, 4, J = 7.5 Hz, CH_3CH_2O), 4.72 (t, 2, J = 8 Hz, $CHCH_2CH$), 7.67 (m, 6 *meta* and *para* H), and 8.17 ppm (m, 4, *ortho* H).

Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.51; H, 6.18.

Attempts to cyclize this diketone with zinc chloride in acetic acid–acetic anhydride, *p*-toluenesulfonic acid in benzene, or diphenylphosphoryl chloride failed.

Ethyl β-Benzoylcinnamate (**11**),—The reaction of 13.6 g (0.13 mol) of benzaldehyde, 48.6 (0.25 mol) of ethyl benzoylacetate, and 9.3 g of fused zinc chloride, following general procedure B, gave an oil which solidified on scratching. Recrystallization from 1:1 hexane–ethyl acetate gave 23.4 g (33%) of a white solid, mp 95.5–97.5° (lit.[17] mp 98–99°); ir (Nujol) 5.9 and 6.0 μ; nmr 1.13 (t, 3, J = 7 Hz, CH_3CH_2O), 4.20 (q, 2, J = 7 Hz, CH_3CH_2O), 7.3 and 7.9 ppm (m, 11).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.91; H, 5.50.

Registry No.—**4**, 21299-13-8; **9**, 21299-14-9; **10**, 21299-15-0; **11**, 17451-18-2; **12**, 21299-17-2; **19**, 21299-18-3; **20**, 21299-19-4.

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