Condensation of Carbon Suboxide with α-Diketones by Means of the Oxyphosphorane Reaction

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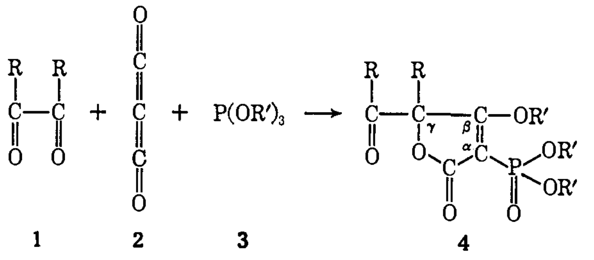
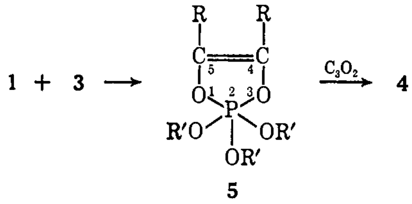
Abstract: The condensation of carbon suboxide, C_3O_2, with biacetyl was carried out in two steps: (1) reaction of biacetyl with either trimethyl phosphite, dimethyl phenylphosphonite, or methyl diphenylphosphinite to give the corresponding derivative of a 2,2-dihydro-4,5-dimethyl-1,3,2-dioxaphospholene, and (2) reaction of the dioxaphospholene with carbon suboxide to give the corresponding derivative of a β-methoxy-γ-acetyl-γ-methyl-$\Delta^{\alpha,\beta}$-butenolide, with either a dimethoxyphosphoryl, a methoxyphenylphosphoryl, or a diphenylphosphoryl group at the α position. This is a new type of molecular rearrangement in the general *carbon–carbon oxyphosphorane condensation*. The butenolides underwent hydrolysis to α-phosphoryl-β-methoxy-γ-acetyl-γ-methyl-γ-hydroxycrotonic acids (*cis–trans* isomers). Two of the crotonic acids cyclized to lactones of phosphonic and phosphinic acids (unsaturated phostones).

The discovery[2] of carbon suboxide was followed by the development of methods of preparation from derivatives of malonic acid[3] and of tartaric acid,[4] and by the elucidation of the molecular structure.[5] The behavior of the suboxide toward a number of substances has been investigated.[6] A significant contribution to the mechanism of its reactions resulted from a study of its behavior toward phenylmagnesium bromide.[7] The photochemical decomposition of carbon suboxide has been investigated recently.[8]

This paper decribes a new reaction which achieves the condensation of an α-diketone **1** with carbon suboxide **2** by means of a trialkyl phosphite (**3**) with the formation of an α-phosphorylated β-alkoxy-γ-acyl-$\Delta^{\alpha,\beta}$-butenolide (**4**).

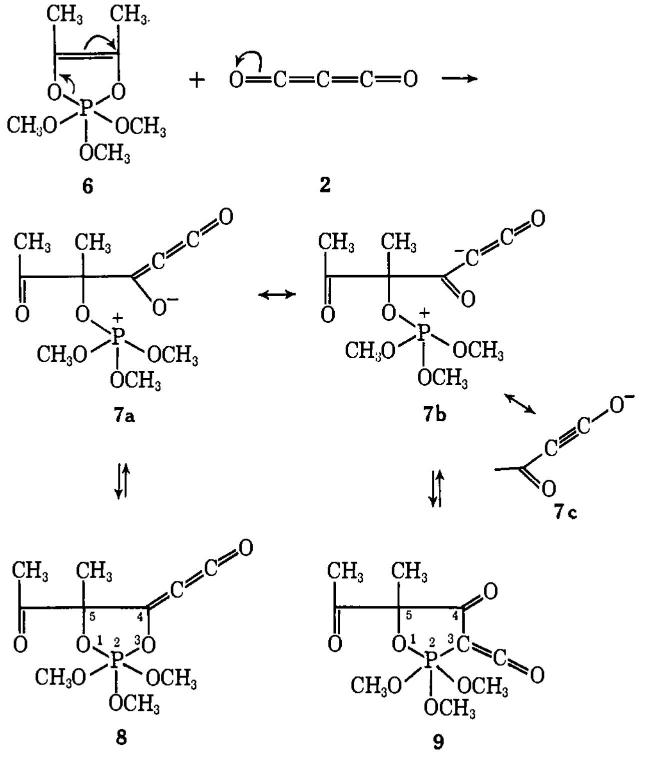


The condensation was carried out in two steps. First, the α-diketone **1** was combined with the phosphite **3** to give the 2,2,2-trialkoxy-2,2-dihydro-1,3,2-dioxaphospholene[9] **5**. Then, the phospholene was added to carbon suboxide to form the butenolide **4**. This step involved the transfer of phosphorus from an oxygen of the phospholene **5** to the central carbon of the suboxide. This paper discusses the mechanism of this new type of rearrangement.



Reaction of Carbon Suboxide with the Biacetyl–Trimethyl Phosphite Adduct 6. This reaction (Scheme I) took place in methylene chloride solution at about 0°. The first step was probably a nucleophilic addition of

Scheme I



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(1) John Simon Guggenheim Fellow, 1968. This work was supported by Public Health Service Grant No. CA-04769-09 from the National Cancer Institute, and by the National Science Foundation Grant GP-6690.

(2) (a) B. C. Brodie, *Proc. Roy. Soc.* (London), **21**, 245 (1873); (b) B. C. Brodie, *Ann.*, **169**, 270 (1873).

(3) O. Diels and B. Wolf, *Ber.*, **39**, 689 (1906).

(4) (a) E. Ott, *ibid.*, **47**, 2388 (1914); (b) K. A. Kobe and L. H. Ryerson, *J. Phys. Chem.*, **35**, 3025 (1931).

(5) F. A. Miller, D. H. Lemmon, and R. E. Witkowsky, *Spectrochim. Acta*, **21**, 1709 (1965), and references therein.

(6) (a) L. B. Dashkevich and V. G. Beiliv, *J. Gen. Chem. USSR*, **34**, 2808 (1964); (b) see the comprehensive review by H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967; Chapter 3; (c) L. B. Dashkevich, *Russ. Chem. Rev.*, **36**, 391 (1967).

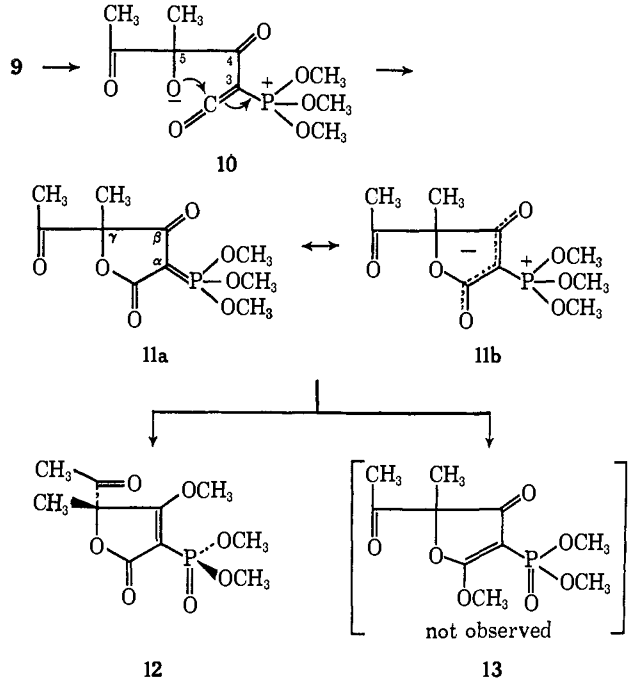
(7) D. J. Cram and R. L. Zimmerman, *J. Am. Chem. Soc.*, **74**, 2646 (1952).

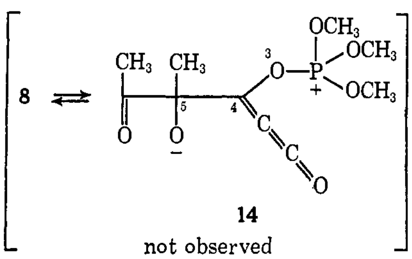
(8) (a) A. P. Wolf, *ibid.*, **84**, 3214 (1962); (b) K. D. Bayes, *ibid.*, **84**, 4077 (1962); (c) D. G. Williamson and K. D. Bayes, *ibid.*, **90**, 1957 (1968).

(9) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

the phospholene 4-carbon to the terminal carbon of the suboxide with the formation of a resonance-stabilized dipolar adduct **7a–c**. This adduct can form a 4-ketenylidene-1,3,2-dioxaphospholane (**8**) or a 3-carbonyl-4-oxo-1,2-oxaphospholane (**9**). Rupture of the P2–O1 bond in the 1,2-oxaphospholane **9** led to a new dipolar adduct **10**, which cyclized to the resonance-stabilized β-oxoalkylideneophosphorane **11a, b** (or ylide) (Scheme II). This step establishes the carbon skeleton of the final product, *i.e.*, the butenolide phosphonate **12**, which was derived from **11a, b** by a methyl group translocation.[10] The less likely isomer **13** was not observed. The dipolar adduct **14**, which would have resulted from the rupture of the P2–O1 bond in the 1,3,2-dioxaphospholane **8**, did not play a role in the rearrangement because the subsequent cyclization of **14** can not occur for steric and electronic reasons.

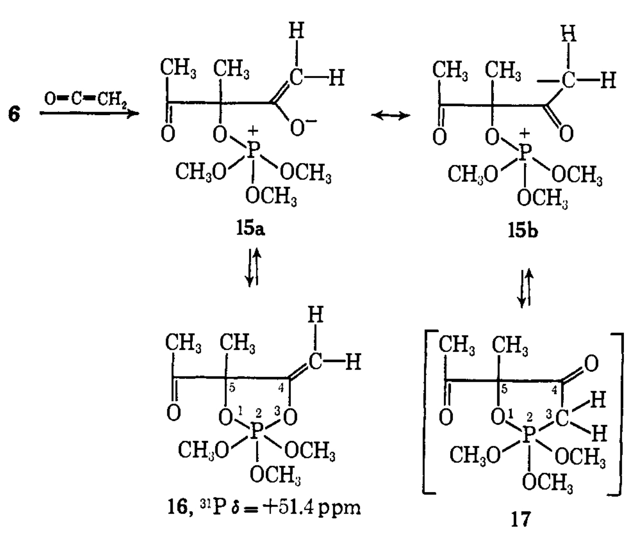
Scheme II





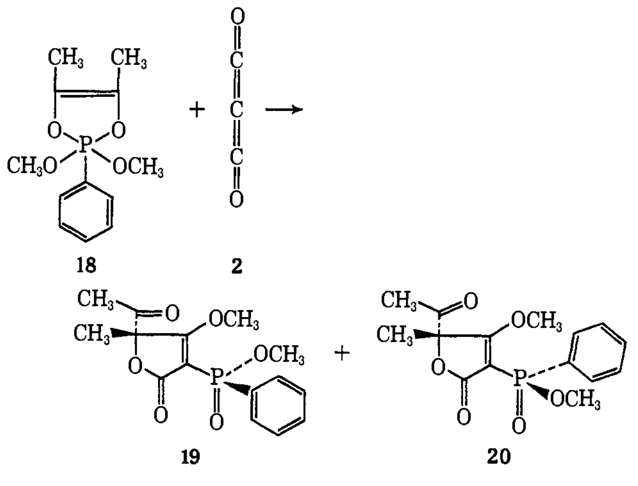
The nucleophilic addition of the phospholene **6** to ketene gave the 4-methylene-1,3,2-dioxaphospholane[11a] **16** (Scheme III). The latter, **16**, with five oxygens on phosphorus, was more stable than the 4-oxo-1,2-oxaphospholane **17**, with only four oxygens on phosphorus.[9] Rupture of the P2–O1 bond of **17** can not produce intermediates analogous to **10** and **11**, capable of leading to stable final products like **12**.

Scheme III



The phospholene **6** added to isocyanates, $O{=}C{=}NAr$, and gave the 4-imino-1,3,2-dioxaphospholanes[11b] analgous to **16**. The formation of small amounts of the 4-oxo-1,3,2-oxaazaphospholane analogous to **17** was demonstrated[11c] in some cases.

Reaction of Carbon Suboxide with Biacetyl–Phosphonite and Biacetyl–Phosphinite Adducts. The mechanism suggested for the reaction of carbon suboxide with the phospholene **6** predicted the possible formation of two diastereomeric butenolides **19** and **20**, differing in the configuration of the tetracoordinated phosphorus, when the phospholene was made from the reaction of biacetyl with dimethyl phenylphosphonite, as shown in formula **18**. When gaseous suboxide was introduced into a solution of phosphonite adduct **18** in methylene chloride at −78°, the two expected diastereomeric butenolide phosphinates **19** and **20** were produced in approximately 60:40 proportion. When a methylene chloride solution of the adduct **18** was added to the liquid suboxide, only one butenolide **19** was formed. The stereochemistry of **19** and **20** should be established during the methyl group translocation of the β-oxoylide **21**.



The addition of suboxide to a solution of the adduct **22** made from biacetyl and methyl diphenylphosphinite gave, as expected, one butenolide phosphine oxide **23**.

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[10] F. Ramirez, O. P. Madan, and C. P. Smith, *J. Org. Chem.*, **30**, 2284 (1965).

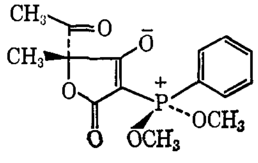
[11] (a) F. Ramirez, S. B. Bhatia, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 3026 (1967); (b) *ibid.*, **89**, 3030 (1967); (c) *Tetrahedron*, **25**, 771 (1969).

Table I. Analyses[a] of the Products of the Reaction of Carbon Suboxide with 2,2,2-Trisubstituted 4,5-Dimethyl-2,2-dihydro-1,3,2-dioxaphospholenes and of Their Hydrolysis Products

2,2,2 substituents on parent phospholene			No.	Mp, °C	Formula	Calcd, %			Found, %		
						C	H	P	C	H	P
α-Phosphoryl-β-methoxy-γ-acetyl-γ-methyl-$\Delta^{\alpha,\beta}$-butenolides											
CH_3O	CH_3O	CH_3O	**12**	99–100[b]	$C_{10}H_{15}O_7P$	43.2	5.4	11.4	43.2	5.5	11.0
CH_3O	CH_3O	C_6H_5	**19**[c]	141–142[b]	$C_{15}H_{17}O_6P$	55.6	5.2	....	54.8	5.3	....
			19 + **20**[d]	105–128[d]	$C_{15}H_{17}O_6P$	55.6	5.2	9.6	55.9	5.2	9.5
CH_3O	C_6H_5	C_6H_5	**23**	172–173[e]	$C_{20}H_{19}O_5P$	64.9	5.2	8.4	64.9	5.5	....
α-Carboxy-β-methoxy-γ-acetyl-γ-methyl $\Delta^{\alpha,\beta}$-Unsaturated Phostones											
CH_3O	CH_3O	CH_3O	**27**	70–71[f]	$C_9H_{13}O_7P \cdot 0.5H_2O$	39.5	5.1	11.3	39.5	5.3	11.3
			28	*g*	$C_9H_{13}O_7P$	40.9	4.9	11.7	40.9	5.1	11.7
CH_3O	CH_3O	C_6H_5	**32**	109–140[h]	$C_{14}H_{15}O_6P$	54.2	4.9	10.0	54.1	4.9	9.8
			35								
α-Carbomethoxy-β-methoxy-γ-acetyl-γ-methyl $\Delta^{\alpha,\beta}$-Unsaturated Phostones											
CH_3O	CH_3O	CH_3O	**39**	94–97[i]	$C_{10}H_{15}O_7P$	43.2	5.4	11.2	43.0	5.4	1.11
			40								
CH_3O	CH_3O	C_6H_5	**41**	96–105[j]	$C_{15}H_{17}O_6P$	55.5	5.3	9.6	55.4	5.4	9.5
			42								
			37								
α-Phosphoryl-β-methoxy-γ-acetyl-γ-methyl-γ-hydroxycrotonic Acids											
CH_3O	C_6H_5	C_6H_5	**36**	104–105[k]	$C_{20}H_{21}O_6P \cdot 0.5H_2O$	60.4	5.5	7.8	60.4	5.5	7.8

[a] Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. [b] From benzene–hexane. [c] One diastereomer. [d] Mixture of diastereomers (60:40, **19**:**20**). [e] From benzene. [f] From ether. Two diastereomers at phosphorus. [g] Noncrystalline anhydrous acids. [h] Trituration with ether. Mixture of two diastereomers at phosphorus. [i] The crude ester consisted of two diastereomers at phosphorus; one isomer was obtained crystalline from ether. [j] The crude ester and the material obtained by crystallization from ether were a mixture of two diastereomers at phosphorus. [k] From ether. *cis–trans* isomers about C═C.

The reverse addition of the adduct **22** to liquid suboxide produced only polymers of the suboxide.



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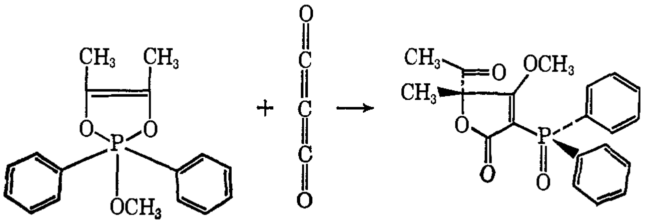


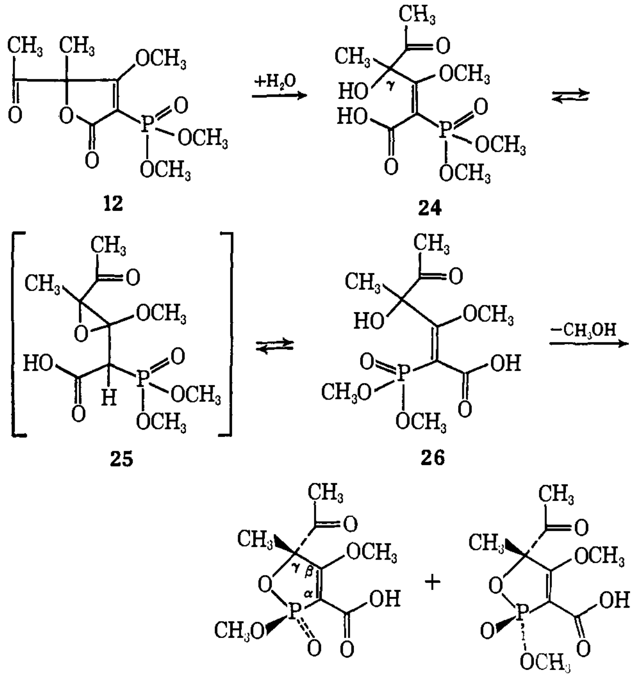
22 **2** **23**

The elemental analyses of the butenolides are given in Table I. The spectral properties, which are discussed in another section, are summarized in Table II.

Hydrolyses of the Butenolides by 1 Mole Equiv of D_2O in $CDCl_3$ Solution.[12] The course of these hydrolyses was followed by ^1H nmr spectroscopy. The phosphonate **12** was completely hydrolyzed within 25 min, but the phosphinates **19**, **20** and the phosphine oxide **23** required about 20 and 35 hr, respectively, for complete hydrolysis under comparable conditions.

The hydrolysis of the butenolide phosphonate **12** gave a transient *cis*-γ-hydroxycrotonic acid[12] (**24**) (Scheme IV), which was recognized by an ^1H nmr signal at τ 8.43 (CH_3 on γ-carbon). The *cis* acid **24** underwent a very rapid isomerization to the *trans* acid **26**; this process may be subject to acid catalysis and could proceed *via* the epoxy ether intermediate **25**. The *trans* acid **26** was not detected in this case (as it was in others) due to a *rapid cyclization to the two diastereomeric α-carboxyphostones* **27** and **28**. These isomers differed in the configuration at phosphorus; their properties are given in Tables I and II. Their configuration will be discussed below.

Scheme IV



The phostones **27** and **28** were formed in *ca.* 60:40 proportion, which did not change within 24 hr. Either the cyclization yielded directly both phostones in that

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(12) The hydrolyses were also carried out with H_2O. Deuterium atoms are omitted from the subsequent formulas. The appearance of CH_3OD was clearly seen in the ^1H nmr spectra.

Table II. Spectral Data[a] of the Products of the Reaction of Carbon Suboxide with 2,2,2-Trisubstituted 4,5-Dimethyl-2,2-dihydro-1,3,2-dioxaphospholenes and of Their Hydrolysis Products

2,2,2 substituents on parent phospholene			No.	$^{31}P\ \delta$	τ_{Ac}	τ_{CH_3C}	τ_{CH_3OC}	τ_{CH_3OP}	J_{CH_3OP}, cps	$\bar{\nu}$, cm^{-1}	λ, mμ	$\epsilon \times 10^{-3}$
				α-Phosphoryl-β-methoxy-γ-acetyl-γ-methyl-$\Delta^{\alpha,\beta}$-butenolides								
CH_3O	CH_3O	CH_3O	**12**	−65.8	7.65	8.21	6.28	6.03[b] 5.96	12.8 13.0	1726(m), 1660(s), 1440(m), 1231(w), 1186(w), 1051(m)	212 242	5.1 10.6
CH_3O	CH_3O	C_6H_5	**19**[c]	−80.9	7.58	8.16	6.35	5.95	13.2	1734(m), 1663(s), 1451(m), 1237(w), 1187(w), 1049(m)	216 244	14.4 11.0
			20[c]	−84.0	7.63	8.12	6.32	6.08	13.0			
CH_3O	C_6H_5	C_6H_5	**23**	−81.7	7.67	8.19	6.33	None	None	1717(m), 1644(s), 1446(m), 1262(m), 1236(m), 1100(m)	225 246	24.8 13.2
				α-Carboxy-β-methoxy-γ-acetyl-γ-methyl $\Delta^{\alpha,\beta}$-Unsaturated Phostones								
CH_3O	CH_3O	CH_3O	**27**[d]	−30.4	7.66[f]	8.32	6.09	6.12	11.8	1738(m), 1672(m), 1615(s), 1282(m), 1237(m), 1047(s)	236	9.3
			28[e]	−29.8	7.71[f]	8.26	6.09	6.05	11.8			
CH_3O	CH_3O	C_6H_5	**32**[d]	−43.5	7.52	8.22	6.28	None	None	1738(m), 1667(m), 1607(s), 1260(s), 1236(s), 1122(m)		
			35[e]	−42.2	7.74	8.08	6.28	None	None			
				α-Carbomethoxy-β-methoxy-γ-acetyl-γ-methyl $\Delta^{\alpha,\beta}$-Unsaturated Phostones								
CH_3O	CH_3O	CH_3O	**39**[d]	−35.5	7.70[g]	8.42	6.17	6.11	11.8	1732(s), 1617(s), 1278(s), 1236(m), 1198(m), 1053(m)		
			40[e]	−34.9	7.77[g]	8.38	6.17	6.07	11.8			
CH_3O	CH_3O	C_6H_5	**41**[d]	−49.8	7.53[h]	8.28	6.39	None	None	1730(s), 1610(s), 1258(s), 1200(m), 1123(m), 1027(m)		
			42[e]	−50.8	7.78[i]	8.14	6.39	None	None			
				α-Phosphoryl-β-methoxy-γ-acetyl-γ-hydroxycrotonic Acids								
CH_3O	C_6H_5	C_6H_5	**36**[j]	−28.2	7.78	8.51	6.47	None	None	1737(s), 1713(s), 1676(vw), 1286(s), 1202(s), 1150(s)	223 265	19.6 7.4
			37[k]	−29.1	7.88	8.61	6.49	None	None			

[a] ^{31}P nmr signals are given in parts per million *vs.* H_3PO_4 as zero, in CH_2Cl_2 or $CDCl_3$ at 40.5 Mcps. ^1H nmr signals are given in parts per million *vs.* TMS = 10 (τ values), in $CDCl_3$ at 60 Mcps. Main infrared bands were taken in CCl_4 or CH_2Cl_2, ultraviolet spectra in acetonitrile. [b] Two doublets due to nonequivalent methoxys on phosphorus. [c] Two diastereomers at phosphorus. [d] Major diastereomer assumed to have the acetyl *cis* to the phosphoryl oxygen. [e] Minor diastereomer assumed to have the acetyl *trans* to the phosphoryl oxygen. [f] The signals due to the COOH were at τ 1.98 in the hemihydrate, and at τ 1.13 in the anhydrous acids. [g] τ_{COOCH_3} at 5.76. [h] τ_{COOCH_3} at 5.71. [i] τ_{COOCH_3} at 5.75. [j] Formed in slightly higher proportion. [k] Formed in slightly lower proportion.

proportion, or one phostone was formed initially and then underwent rapid stereomutation. A mechanism which is capable of explaining the rapid cyclization of the crotonic acid **26** to the phostones **27** and **28**, directly and without stereomutation among the phostones, is based on the previous interpretation of the hydrolysis of α-ketol phosphates[13a] and phosphonates[13b] and of five-membered cyclic phosphates[14,15] and phosphonates.[14] It was suggested that oxyphosphoranes were involved as *intermediates* in those reactions, and that certain selection rules[13b,14c] operated during the conversion of tetracoordinated into pentacoordinated phosphorus and during the positional exchange of groups on trigonal bipyramidal phosphorus by pseudorotation.[16] The cyclization of the hydroxyphosphonate **26** can give bipyramids **29a** and **29b**, which differ in configuration at phosphorus and which have a carbon atom and the phosphoryl oxygen in equatorial positions. Ejection of the CH_3O group from the apical positions of bipyramids **29a** and **29b** gives, respectively, the phostones **27** and **28** (Scheme V). Note that one pseudorotation of **29a** about the equatorial $CH_3O(6)$ group would give bipyramid **29c**, with a carbon in an apical position. Pseudorotation of **29c** about the $CH_3O(7)$ group would give **29d**, which is equivalent to **29b** and would, therefore, yield a phostone equivalent to **28** by loss of the apical $CH_3O(6)$ group. The stereomutation among the phostones **27** and **28** would involve the reverse of these transformations.[17] If bipyramid **29c**, with the apical carbon, is of relatively high energy, the barrier for the corresponding pseudorotation could be sufficiently high to prevent stereomutation under the experimental conditions. It was possible to show (*vide infra*) that a stereochemically pure phostone carboxylic ester derived from the acid **27** did not undergo stereomutation in $CDCl_3$ in the

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(13) (a) F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962); (b) D. S. Frank and D. A. Usher, *ibid.*, **89**, 6360 (1967).

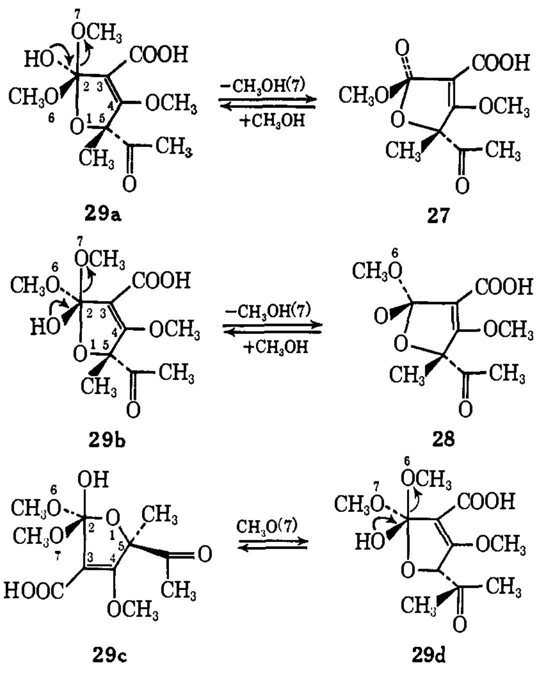
(14) (a) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961); (b) E. A. Dennis and F. H. Westheimer, *ibid.*, 88, 3432 (1966); (c) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(15) (a) F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banas, *J. Am. Chem. Soc.*, **85**, 2681 (1963); (b) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *ibid.*, **89**, 6503 (1967); (c) F. Ramirez, H. J. Kugler, A. V. Patwardhan, and C. P. Smith, *J. Org. Chem.*, **33**, 1185 (1968).

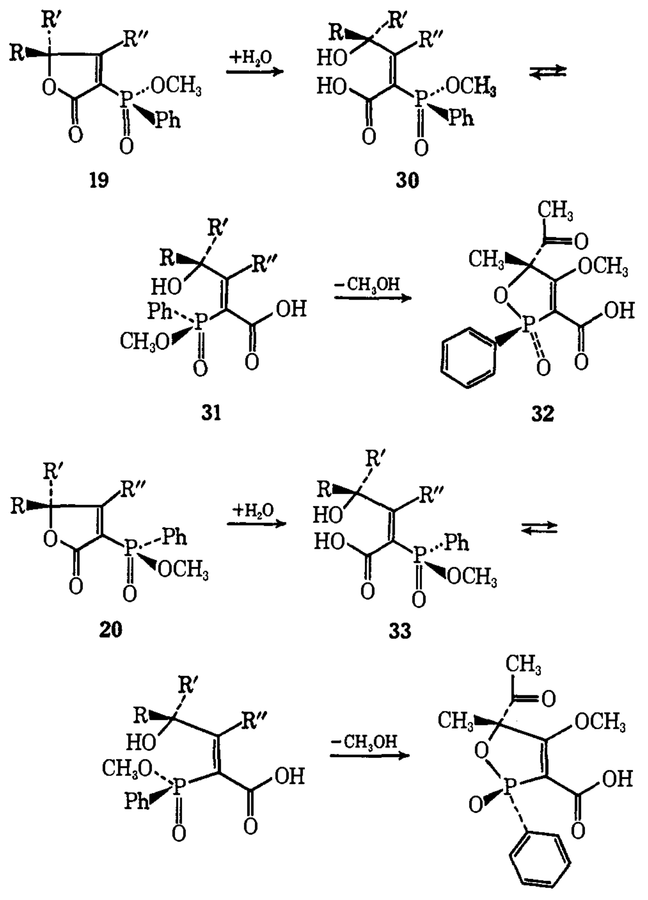
(16) (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); (c) P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, 90, 6722 (1968).

(17) F. Ramirez, N. B. Desai, and N. Ramanathan, *ibid.*, **85**, 3465 (1963).

Scheme V



Scheme VI

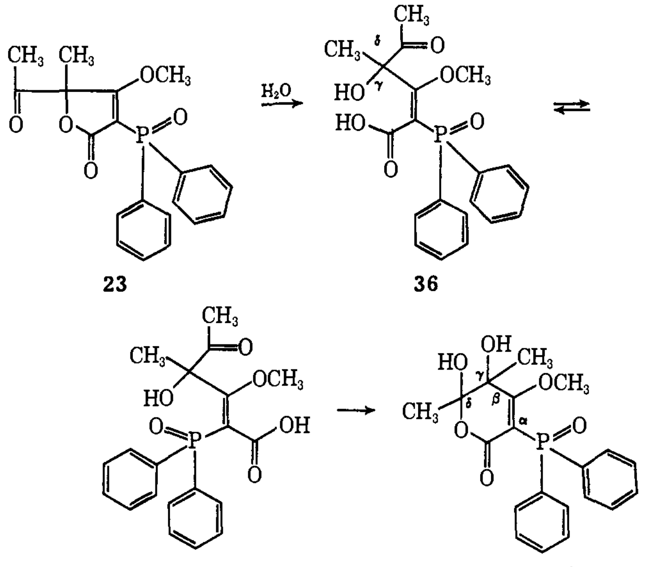


34, R = CH_3; R′ = CH_3CO; R″ = CH_3O

presence of methanol; the ester was not affected by 4 mole equiv of D_2O in $CDCl_3$ within 24 hr.

The hydrolysis of one diastereomeric butenolide phosphinate **19** gave the transient *cis*-γ-hydroxycrotonic acid **30**, with ^1H nmr signals at τ 8.48 (CH_3C), 7.87 (CH_3CO), and 6.40 (CH_3O). The isomerization of **30** to the *trans* acid **31** was followed, again, by a rapid cyclization to *one diastereomeric*[18] *α-carboxyphostone* **32**. *The cyclic phosphinate* **32** *did not undergo significant stereomutation to its isomer* **35** *within* **50** *hr in* $CDCl_3$ *solution.* The hydrolysis of a mixture of the two butenolide phosphinates **19** and **20** (*ca.* 40:60 proportion) gave a mixture of the two diastereomeric phostones **32** and **35** (*ca.* 40:60 proportion). There was no observable stereomutation among the phostones within 30 hr in $CDCl_3$ solution. These results showed that the crotonic acids **30**, **31**, **33**, and **34** retained their configurations at the phosphorus and at the γ-carbon during the hydrolysis and the cyclization. Note that cyclization of **31** would give a bipyramid analogous to **29a** (with phenyl in place of $CH_3O(6)$). Ejection of the apical CH_3O group gives phostone **32**. Cyclization of **34** would give a bipyramid analogous to **29b** (with phenyl in place of $CH_3O(6)$). Ejection of the apical CH_3O group gives phostone **35**. Inhibition of pseudorotation is reasonable in this case.[9,13–15]

The hydrolysis of the butenolide phosphine oxide **23** gave the two hydroxycrotonic acids **36** and **37** in almost equal proportion. The spectral data for these acids are given in Table II. After about 45 hr, both acids had been transformed into the two diastereomers of the pseudoacid **38a** and **38b**, in $CDCl_3$ solution. The pseudoacids were not isolated and their structures rest exclusively on the proton nmr spectral data:[19] τ 6.42 (CH_3O at β-carbon), 7.65 (CH_3 at δ-carbon), and 8.26 (CH_3 at γ-carbon) for the *trans* isomer **38a**; and τ 6.67 (CH_3O at β-carbon), 7.68 (CH_3 at δ-carbon), and 8.32 (CH_3 at γ-carbon) for the *cis* isomer **38b**.



38a, *trans* CH_3/CH_3
38b, *cis* CH_3/CH_3

Isolation of Hydrolysis Products of the Butenolides. The procedure described in the Experimental Section afforded a mixture of the two diastereomeric carboxyphostones **27** and **28** from the hydrolysis of the butenolide phosphonate **12**. These acids formed a crystal-

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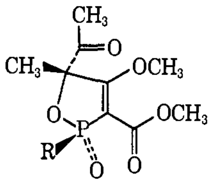
[18] Very small amounts of the diastereomeric phostone 35 were observed, but probably arose from small amounts of the isomeric butenolide phosphinate 20.

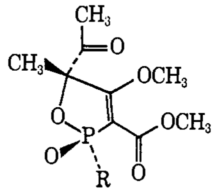
[19] The OH groups were deuterated since D_2O was used. The final spectrum of the hydrolysis after 50 hr was complicated by signals probably due to some deuterium–proton exchange involving the acetyl group.

line hemihydrate, which became noncrystalline on dehydration. The analytical and spectral data are given in Tables I and II. The mixture of acids **27** and **28** was converted into a mixture of esters **39** and **40** by diazomethane. One of the diastereomers, assumed to be **39**, was isolated nearly free from its isomer by crystallization from ether. Stereomutation of one phostone ester (**39**) into another (**40**), if it occurred at all, was very slow in $CDCl_3$ solution at 30° in the presence of catalytic amounts of methanol.

A mixture of the two diastereomeric carboxyphostones **32** and **35** was obtained in crystalline form from the butenolide phosphinates **19** and **20**. A mixture of two diastereomeric esters **41** and **42** was prepared from the acids and diazomethane. The esters were not separated, and there was no evidence for stereomutation in $CDCl_3$ solution.



39, R = OCH_3
41, R = C_6H_5



40, R = OCH_3
42, R = C_6H_5

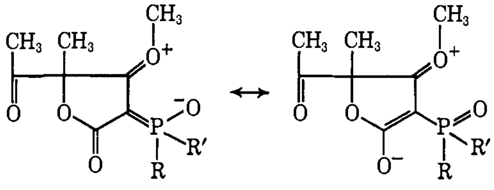
Stereochemistry. The tentative assignment of configurations to the phostone acids **27**, **28**, and **32**, **35**, and to the corresponding esters **39**, **40**, and **41**, **42**, was based on these assumptions. (a) A phosphoryl oxygen, P=O, should have a deshielding effect[17] *vs.* the P-OCH_3 group on the protons of an acetyl or of a methyl group situated on the γ-carbon of the phostone ring. (b) The P=O was also deshielding *vs.* the P-C_6H_5 on the protons of the same acetyl and methyl groups. For example, note in Table II that the acetyl (τ 7.66) *cis* to the P=O oxygen in **26** was at a lower field than the acetyl (τ 7.71) *cis* to the P-OCH_3 methoxy in **28**. The methyl (τ 8.26) *cis* to the P=O oxygen in **28** was at a lower field than the methyl (τ 8.32) *cis* to the P-OCH_3 methoxy in **27**. The same relationships held in the other cases shown in Table II. These assumptions were consistent with analogous ones in related cyclic phosphate esters.[17]

Spectral Properties of the Butenolides 12, 19, 20, and 23. The ^1H nmr spectra were unexceptional (*cf.* Table II). The ^{31}P nmr signals appeared at rather low magnetic fields relative to other phosphonates, and phosphine oxides.[20] Note the displacement of the P shift to high field, $-81.7 \rightarrow -29.1$, -28.2 ppm, when the butenolide phosphine oxide **23** was converted into the crotonic acids **36** and **37**.

The infrared bands due to the butenolide carbonyls (1660, 1663, and 1664 cm^{-1}) appeared at significantly lower frequencies than those of unsubstituted $\Delta^{\alpha,\beta}$-butenolides (*ca.* 1750 cm^{-1}).[21] The band due to the acetyl CO was at the expected frequency (1717–1734 cm^{-1}).

The ultraviolet spectra of the butenolides **12**, **19**, **20**, and **23**, had maximum absorption at relatively long wavelength (in the range 241–250 mμ). The bathochromic effect of certain substituents at the β position of $\Delta^{\alpha,\beta}$-butenolides has been discussed.[22]

A number of resonance structures, for example **43a** and **b**, can be written to represent the butenolide hybrid. These structures account for the effects noted in the infrared and ultraviolet spectra. Note also the "pseudo-alkylidenephosphorane character" of these structures. The ^{31}P nmr shifts of alkylidenephosphoranes with oxygen atoms attached to the phosphorus[20a] were at *ca.* -56 ppm.



43a **43b**

The carboxylic acids **27** and **28** derived from the butenolide **12** were relatively strong. The pH of a 0.54 *M* aqueous solution of the butenolide **12** was 0.72, that of a 0.27 *M* solution was 0.95. These solutions contained the acids **27** and **28**, the approximate pK_a at 20°, from titration with 0.5 *N* NaOH, was 1.2.

Experimental Section

Dioxaphospholenes. A solution of biacetyl in CH_2Cl_2 was added to a CH_2Cl_2 solution of 1 mole equiv of $(CH_3O)_2PC_6H_5$ (at 0°) and of $CH_3OP(C_6H_5)_2$ (at 20°) to obtain, respectively, the 2,2-dimethoxy-2-phenyl- and 2-methoxy-2,2-diphenyl-4,5-dimethyl-2,2-dihydro-1,3,2-dioxaphospholenes (**18** and **22**) in theoretical yield. The properties agreed with published ones.[23] The biacetyl-$(CH_3O)_3P$ adduct **6** was made as described.[9,11]

Carbon Suboxide. The suboxide was generated[4] *in vacuo* in an all-glass apparatus consisting of a round-bottomed flask, three traps, and suitable three-way stopcocks, connected in series. Diacetyltartaric anhydride[24] (60 g) was vaporized at 220° (0.5 mm); its vapors were passed over the coils of a "ketene generator" (Ace Glass Co.) at *ca.* 750°; the resulting mixture of acetic acid, carbon suboxide, and carbon dioxide was collected in trap 1 (liquid N_2 temperature). The suboxide and the dioxide were transferred by vacuum distillation from trap 1 (at -35°) to trap 2 (at liquid N_2 temperature). The dioxide was evaporated from trap 2, with little loss of suboxide, when this trap was kept 30 min at -110°, under oil-pump vacuum. The amount of pure suboxide left in trap 2 was determined by its volume, measured in a calibrated 15-mm wide constriction of this trap. The suboxide was obtained in 30% of the theoretical yield, and was characterized by its infrared spectrum. *Caution:* carbon monoxide is a by-product of the pyrolysis.

Reaction of Carbon Suboxide with Dioxaphospholenes. Procedure A. The suboxide was transferred by vacuum distillation from trap 2 (at -78° to trap 3 (at liquid N_2 temp). A solution of the biacetyl-$(CH_3O)_3P$ adduct **6** (66 mmoles) in CH_2Cl_2 (17 ml) was added, dropwise over a 30-min period, to the liquid suboxide (44 mmoles) in trap 3, at -78° and atmospheric pressure. The solution was stirred 2 hr at 0°, allowed to reach 20°, and evaporated at 20 mm. The butenolide phosphonate **12** was recrystallized from benzene–hexane and was obtained in 65% of the theoretical yield. The properties are given in Tables I and II.

A similar procedure was employed with the biacetyl-$(CH_3O)_2$-PC_6H_5 adduct **18**. The reaction was allowed to proceed 30 min at 0° and 5 hr at 20°. One of the two possible diastereomeric butenolide phosphinates **19** was obtained in 65% of the theoretical yield. Some polymerization of the suboxide was observed.

This procedure failed to yield any butenolide phosphine oxide **23** when applied to the biacetyl-$CH_3OP(C_6H_5)_2$ adduct **22**. The suboxide was converted into its red-brown polymer.

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(20) (a) F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, **22**, 567 (1966); (b) F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Am. Chem. Soc.*, **90**, 6726 (1968).

(21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 186.

(22) (a) J. A. Moore and J. Binkert, *J. Am. Chem. Soc.*, **81**, 6033 (1959); (b) E. Shaw, *ibid.*, **68**, 2510 (1946).

(23) F. Ramirez, *Trans. N. Y. Acad. Sci.*, **30**, 410 (1968).

(24) A. Wohl and C. Oesteilin, *Ber.*, **34**, 1144 (1901).

Procedure B. A solution of the biacetyl-$(CH_3O)_2PC_6H_5$ adduct **18** (75 mmoles) in CH_2Cl_2 (40 ml) was placed in trap 3 of the apparatus described above. Carbon suboxide (74 mmoles) was allowed to evaporate, over a 20-hr period, from trap 2 (first at −35°, finally up to +10°) into trap 3 containing the phospholene solution at −78°. (The evaporation can be expedited under slight vacuum for 30 sec.) The solvent was removed and the residue was recrystallized from benzene. A mixture of two diastereomeric butenolide phosphinates **19** and **20** (60:40) was obtained in 65% of the theoretical yield.

A similar procedure was applied to the biacetyl-$CH_3OP(C_6H_5)_2$ adduct **22** and gave the butenolide phosphine oxide **23** in 65% of the theoretical yield. Very little suboxide polymer was observed.

Phostone Carboxylic Acids. The properties are given in Tables I and II. Five grams of the butenolide phosphonate **12** dissolved instantaneously in 1 ml of water. The solution was evaporated at 20° (0.2 mm). The residue was dissolved in 150 ml of ether; traces of insoluble orange oil were pipetted out. The solution was concentrated to 50 ml, cooled at 5°, and filtered, yielding 3.7 g of the **hemihydrate of 27 and 28** (about 50:50). Anhydrous **27** and **28** were obtained at 56° (0.1 mm).

A mixture containing 2 g of both diastereomeric butenolide phosphinates **19** and **20** (60:40 proportion), 5 ml of CH_2Cl_2, and 1 mole equiv of water was stirred 20 hr at 30°. The solvent was removed *in vacuo;* the residue was triturated with 75 ml of ether, and the first crop of acids **32** and **35** was filtered off. The filtrate was concentrated to give the second crop of **32** and **35**, total yield 70%.

Phostone Carboxylic Esters. The properties are given in Tables I and II. Diazomethane in ether was added to a solution containing both diastereomeric acids **27** and **28** (1.5 g), ether (50 ml), CH_2Cl_2 (2 ml), and methanol (0.5 ml). The solvent was evaporated *in vacuo;* the residue contained two diastereomeric esters **39** + **40**, according to ^1H and ^{31}P nmr spectra. This residue was stirred with ether (5 ml), and the crystals were filtered off. The ester **39** was obtained in *ca.* 40% yield and contained about 5% of diastereomer.

The same procedure gave the mixture of diastereomeric esters **41** and **42** from the mixture of diastereomeric acids **32** and **35**.

Preparation of Crotonic Acids from the Butenolide. The properties are given in Tables I and II. A mixture containing the butenolide phosphine oxide **23** (1 g), CH_2Cl_2 (5 ml), and water (5 mole equiv) was stirred 15 hr at 20°. The solvent was removed *in vacuo* and the residue was extracted with ether (100 ml). The filtered solution was kept 24 hr at 0° to give acids **36** and **37** (0.3 g, mp 104–105°). The spectral data of Table II were obtained on this sample. Another crystallization from ether gave the analytical sample of Table I (also a mixture of **36** and **37** as shown by the ^1H nmr spectra).

Condensations of 4-Methyl-4-dichloromethyl-2,5-cyclohexadienone

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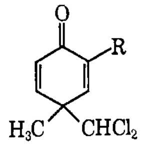
Abstract: The determination of the structure and stereochemistry of the products of base-induced condensations of 4-methyl-4-dichloromethyl-2,5-cyclohexadienone with dimethyl malonate and with methyl acetoacetate is presented. Facile syntheses of polyfunctional bicyclo[3.3.1]nonanes and *cis*-decalins are introduced.

The Reimer–Tiemann reaction, an interaction of phenols with chloroform and base, has been known for over half a century to lead to phenolic aldehydes and dichloromethylcyclohexadienones.[1] While it has been used to advantage for the preparation of aromatic aldehydes, only little attention has been paid to the cyclohexadienone products,[2,3] usually obtained in low yield. The presence of many, diverse functional groups encompassed in a small molecular framework in close proximity to each other make the cyclohexadienones interesting substances for general chemical study. Our previous utilization of a naphthalenone, prepared by the Reimer–Tiemann reaction of an α-naphthol derivative, in diterpene synthesis[4] and our discovery of an interesting rearrangement of another naphthalenone, derived from a β-naphthol derivative,[5] encouraged our further investigation of the chemistry of such compounds. The present communication illustrates the chemical behavior of cyclohexadienone **1a**[6] derived from *p*-cresol.



1a, R = H
b, R = Me

In analogy with the conversion of ketone **2** into tricyclic ketone **3**,[4a] whose first step involved a Michael condensation of acetoacetic ester with **2**, the transfor-

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[1] H. Wynberg, *Chem. Rev.*, 60, 169 (1960).

[2] A. J. Waring, *Advan. Alicyclic Chem.*, 1, 129 (1966).

[3] These compounds have been described usually as *abnormal Reimer–Tiemann products* and reactions leading to them have been designated frequently as *abnormal Reimer–Tiemann reactions.* Since the term *abnormal* is only of historical significance, reflecting the concern of early workers about the unexpected formation of nonaromatic compounds [K. Auwers, *Ber.*, 17, 2976 (1884), and later papers], and since present-day mechanistic interpretation of the reaction and its products places them into the well-understood context of carbene chemistry [J. Hine and J. M. van der Veen, *J. Am. Chem. Soc.*, 81, 6446 (1959)], it is suggested that the Reimer–Tiemann reaction not be described henceforth in terms of *normal* or *abnormal* processes or products.

[4] (a) E. Wenkert and T. E. Stevens, *ibid.*, 78, 5627 (1956); (b) E. Wenkert, A. Afonso, J. B-son Bredenberg, C. Kaneko, and A. Tahara, *ibid.*, 86, 2038 (1964).

[5] R. M. Dodson, J. R. Lewis, W. P. Webb, E. Wenkert, and R. D. Youssefyeh, *ibid.*, 83, 938 (1961).

[6] K. Auwers and F. Winternitz, *Ber.*, 35, 465 (1902); K. Auwers and G. Keil, *ibid.*, 35, 4207 (1902).