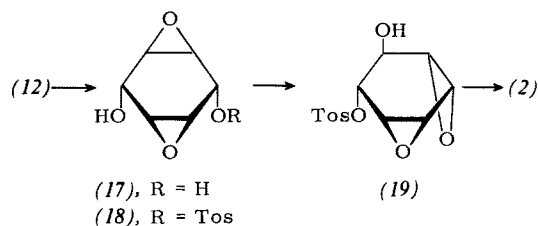


Both these variants, although not the first choice for the synthesis of (2), are by far the best routes for the synthesis of the dianhydro inositols (13)–(18). For example actinamine (*N,N'*-dimethyl-*myo*-inoso-1,3-diamine), a subunit of



antibiotics, is obtained in high yield from (15) by the method described by Suami *et al.* and proven in our total syntheses of deoxystreptamine and hyosamine^[9].

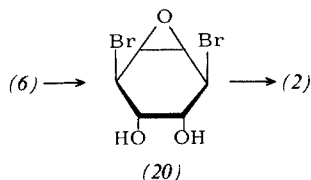
The new compounds (7)–(13), (16), and (18) have been confirmed by elemental analyses, IR, MS, ¹³C-NMR, and additional ¹H-NMR data.

Received: May 20, 1975 [Z 249 b IE]
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CAS Registry numbers:

(2), 39078-13-2; (5), 39573-56-3; (6), 56084-54-9; (7), 50473-94-4;
 (8), 55990-81-3; (9), 55990-82-4; (10), 55990-83-5; (11), 55990-84-6;
 (12), 55990-85-7; (13), 56084-55-0; (16), 55990-86-8; (18), 56084-56-1

- [1] H. Prinzbach, C. Kaiser, and H. Fritz, Angew. Chem. 87, 248 (1975); Angew. Chem. internat. Edit. 14, 253 (1975); R. Schwesinger and H. Prinzbach, Angew. Chem. 87, 625 (1975); Angew. Chem. internat. Edit. 14, 630 (1975); earlier literature cited therein.
- [2] E. Vogel, H.-J. Altenbach, and C.-D. Sommerfeld, Angew. Chem. 84, 986 (1972); Angew. Chem. internat. Edit. 11, 939 (1972); C. H. Foster and G. A. Berchtold, J. Amer. Chem. Soc. 94, 7939 (1972).
- [3] The route corresponding to that for the synthesis of (1) from (4) is thwarted by the fact that (6) can not be hydroxylated uniformly to (20); see, however, the synthesis of (2) from (1) via the 1,2:3,4-dianhydro-*epi*-inositol [8].



- [4] (6) is formed together with (4) and (5) in yields of only ca. 1% in the radical bromination of 4,5-epoxycyclohexene (NBS, CCl₄).
- [5] R. Schwesinger and H. Prinzbach, Angew. Chem. 84, 990 (1972); Angew. Chem. internat. Edit. 11, 942 (1972).
- [6] T. Suami, S. Ogawa, and S. Oki, Chem. Lett. 1973, 901.
- [7] Hence, (14) is prepared from (13), since diacyl esters of the type (11) react with peracids to give complex mixtures.
- [8] H. Prinzbach and H.-W. Schneider, Tetrahedron Lett. 1975, in press.
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Simple Synthesis of Ketenylidenetriphenylphosphorane and Its Thioanalogs

By Hans Jürgen Bestmann and Dieter Sandmeier^[*]

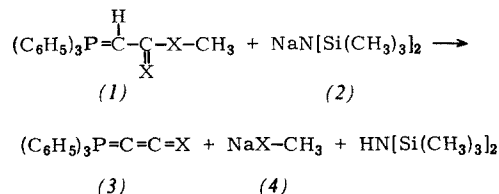
We recently reported a novel method for the synthesis of imino- and thioketenylidene-triphenylphosphoranes (3), X=N–R and X=S, from 3 moles methylidenetriphenylphosphorane and 1 mole isocyanide or thiophosgene, respectively

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vely^[1]. The analogous reaction with phosgene, affords only low yields of the expected ketenylidenetriphenylphosphorane (3), X=O.

We have now found a particularly simple synthesis for (3), X=O, namely reaction of the methoxycarbonylmethylidenetriphenylphosphorane (1), X=O, with the sodium salt of hexamethyldisilazane (2).



The sodium methoxide (4) (X=O) formed on reaction of (1) (X=O) with (2), *e.g.* in benzene, precipitates out and after its separation by filtration or centrifugation compound (3) (X=O) can be recovered by concentration of the filtrate and precipitation with ether or petroleum ether [yield 80%; m.p. 171–172°C^[2]; ³¹P-NMR; $\delta = -5.37$ ppm^[3]; IR: 2080 cm⁻¹ (C=C=O)].

Analogous reaction of the methylthio(thiocarbonyl)methylidenetriphenylphosphorane (1), X=S^[4], and (2) affords the sodium mercaptide (4). X=S, and the thioketenylidenetriphenylphosphorane (3), X=S [yield 76%; m.p. 220–222°C^[5]; ³¹P-NMR: $\delta = +8.11$ ppm^[3]; IR: 1950, 2110 cm⁻¹ (C=C=S)].

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CAS Registry numbers:

(1) (X=O), 2605-67-6; (1) (X=S), 54985-87-4; (2), 1070-89-9; (3) (X=O), 15596-07-3; (3) (X=S), 17507-47-0

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- [3] 100-MHz PFT spectrum. H₃PO₄ as external standard. In footnote [4] of our communication in Angew. Chem. 87, 35 (1975), Angew. Chem. internat. Edit. 14, 53 (1975) the external standard should also read H₃PO₄.
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- [5] M.p. = 224–226°C [2].

Mechanism of Electrochemical Pinacolization. The First Asymmetric Synthesis in a Chiral Medium^[**]

By Dieter Seebach and Hok An Oei^[*]

Electrochemical reduction of ketones such as acetophenone (1) can lead to formation of the alcohol (3) and pinacols (5)^[1]. It is assumed that the alcohol is formed by transfer of two electrons and two protons in the cathodic double layer, whereas the pinacols are formed in the solution from ketyl (2) which escapes from the electrode in the form of radicals (4) (depending upon the pH of the solution R is H or the cation of the electrolyte). This mechanism is supported, *inter alia*, by the fact that, a) the ratio of *meso* to *d,l* form in the isolated mixture of pinacols (5) is independent of the

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[illegible]

The experiments described here are not only a further, stronger indication for the formation of pinacols in the electrochemical reduction of arylalkyl ketones *in the solution*, but, to our knowledge, constitute the first asymmetric electrodiminization in a chiral medium with achiral supporting electrolyte^[8].

Table 1. Formation of 2,3-diphenyl-2,3-butanediol (acetophenone pinacol) (5) by photolysis and by electrolysis of acetophenone (1) (2g) in (S,S)-(+)-DDB-containing medium [4]. (R,R)-(+)-5 is formed in excess in each case. Double values denote parallel experiments.

No.	Solvent and salt [g]	<i>T</i> [°C]	(5) Yield [%]	<i>meso</i> <i>d,l</i>	
			Chem. [a]	Opt. [b]	
<i>Photolysis</i>					
1	DDB	25	52	8.3	1.04
	(25)	27	57	8.1	1.14
2	DDB/pentane	− 72	41	23.5	1.10
	(40/200)				
3	DDB/CH ₃ OH	29	44	2.9	0.85
	(25/10)	27	42	3.0	0.93
4	DDB/CH ₃ OH/LiBr	25	52	3.3	0.50
	(25/10/5)	27	27	3.7	0.55
5	DDB/CH ₃ OH/LiBr	29	34	0.2	0.58
	(10/25/5)				
6	DDB/CH ₃ OH/LiBr/LiOCH ₃	26	24	4.7	0.38
	(25/10/4.3/0.26)	27	31	5.9	0.33
7	DDB/CH ₃ OH/LiBr/LiOCH ₃				
	(10/25/4.3/0.26)	29	29	0.2	0.25
<i>Electrolysis</i>					
8	DDB/CH ₃ OH/LiBr	31	91	4.8	0.36
(60 mA)	(25/10/5)	33	88	4.8	0.35
9	DDB/CH ₃ OH/LiBr	29	84	6.3	0.36
(20 mA)	(25/10/5)	26	93	5.6	0.35
10	DDB/CH ₃ OH/LiBr	26	97	5.8	0.33
(4 mA)	(25/10/5)	24	95	6.4	0.37
11	DDB/CH ₃ OH/LiBr				
(20 mA)	(10/25/5)	25	90	0.2	0.26

[b] Referred to *d,l* fraction.

We were able to show some time ago that hydroxy radicals (4), R=H, generated photochemically from acetophenone (1) dimerize in the chiral amino-ether DDB to pinacol (5), the *d,l* fraction of which exhibits up to 23 % optical activity⁽⁴⁾ (Table 1, Nos. 1 and 2). The above theory of electrochemical pinacol formation can therefore be subjected to the following stringent test: electrolysis and photolysis performed under identical conditions must afford the pinacols with the *same meso/d,l* ratio, with the *same* optical yields in the *d,l* fraction, and with enrichment of the *same* enantiomer. In the photolysis experiment⁽⁵⁾ we first tested whether addition of protic solvent (Table 1, No. 3), of supporting electrolyte (Nos. 4 and 5),

(1), 98-86-2; meso-(5), 4217-65-6; d,l-(5), 22985-90-6; (R,R)(+)-(5), 33603-65-5; (S,S)-(+)-DDB, 26549-21-3

- 635

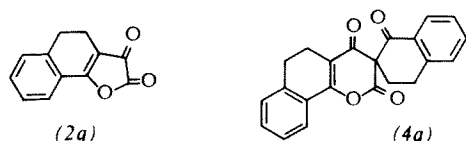
and H₂O; finally, chromatography (silica gel, benzene/10% ethyl acetate) without separation of *meso*- and *d,l*-(5); determination of *meso*/*d,l* ratio by NMR spectroscopy [J. H. Stocker, J. Am. Chem. Soc. 88, 2878 (1966)].

- [6] Conditions: magnetically stirred 15-ml-Hg cathode having an effective surface area of 10 cm², 40 ml total volume of solution in the cathode space, 0.5 cm² platinum leaf anode, 5 ml anode solution, 1 cm diameter G-3 frit diaphragm, Philips controller PE1527, constant current density of 4–60 mA, 6–80 volt potential, N₂ atmosphere.
- [7] According to NMR analysis of the crude products in the photolyses and electrolyses described here, the alcohol (3) is formed in less than 5% yield.
- [8] Electroreduction of phenylglyoxylic acid in the presence of alkaloids see: M. Juhault, E. Raoult, and D. Peltier, *Electrochim. Acta* 19, 865 (1974).

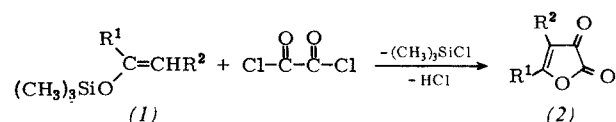
Synthesis and Thermal Decarbonylation of 2,3-Furandiones^[1]

By Shinji Murai, Kiichi Hasegawa, and Noboru Sonoda^[*]

We wish to report the first general method for the synthesis of 2,3-furandiones (2), topological isomers of maleic anhydride, and their subsequent thermal decomposition via α -oxoketenes (3) to 3H-pyran-2,4-diones (4) (Table 1). Hitherto only three compounds of type (2) have been known^[2].



Addition of oxalyl chloride to a solution of alkenyloxysilanes



(1)^[3] in dry ether at room temperature gave (2) in good yields. Furandiones (2) are all yellow in color having UV_{max}^{CH₃CN} at 354–392 nm ($\epsilon = 10000$ –19000). Three intense IR absorption bands, 1832–1815, 1743–1713, and 1613–1588 cm⁻¹, have been observed. The highest frequency band can reasonably be attributed to the lactone carbonyl of (2). The latter two bands would be those of enone moieties. Interestingly, mass spectra of all of 2,3-furandiones showed a base peak at $m/e = [M - 28]^+$ indicating predominant loss of carbon monoxide from molecular ions.

The facile loss of carbon monoxide has also been shown by thermal decomposition of (2). Smooth evolution of carbon monoxide was observed and pyrandiones (4) were obtained in high yields when (2) were heated without solvent at their respective melting points for 30 minutes. IR data (Table 1) show that the compounds (4) which have R² = H are virtually completely enolized and have 4-hydroxy-2-pyrone structures. Cheletropic fragmentation of (2) gives in addition to carbon monoxide, an α -oxoketene (3), which then undergoes $[4\pi + 2\pi]$

Table 1. Yield and physical properties of the furandiones (2a)–(2g) and pyrandiones (4a)–(4g).

	R ¹	R ²	(2)	Yield [%] [b]	M. p. [°C] [a]	(4)	Yield [%]
			M. p. [°C] [a] B. p. [°C/torr]			IR (nujol) [cm ⁻¹]	
a	C ₆ H ₅	H	130–132 [c]	85	167.5–168 [d]	1742 [4] 1625 1545	95
b	<i>p</i> -CH ₃ C ₆ H ₄	H	130–131 [c]	80	199–200	1739 1620 1541	90
c	<i>p</i> -CH ₃ OC ₆ H ₄	H	133–134 [c]	78	194–195	1740 1621 1541	88
d	<i>p</i> -BrC ₆ H ₄	H	145–146 [c]	83	268–269	1745 1624 1538	86
e	C ₆ H ₅	CH ₃	107.5–109.5	64	130–131	1760 1702 1674 1623	83
f	C(CH ₃) ₃	H	50.5–52 73–75/2	32	95–96	1768 1650 1555	83
g	see above		118–119.5 [c]	76	108–109	1772 1678 1657 1630	84

[a] Purification: (2a) by sublimation at 100°C/0.2 torr; (2b)–(2d) and (2g) by recrystallization from acetonitrile; (2e), (4a) and (4g) by recrystallization from benzene/hexane, (2f) by distillation, (4b)–(4f) by recrystallization from methanol. Recrystallization of compounds (2) should be carried out very quickly.

[b] Based on oxalyl chloride used.

[c] Decomposition at melting point.

[d] Lit. M. p. 171°C [4].

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cyclodimerization to afford the pyrandiones (4). Such an intermediate from (2a) has been trapped by chloral as 1,3-dioxin-4-one (5)^[5,6].