60 MHz, using 30–35 mg of steroid per 0.6 ml of solvent, either $CDCl_3$ or pyridine-d_5, and TMS as internal standard. The methyl signals of the cholestane side chain at C-21 and C-26,27 were centered at 0.84 ± 0.02 ppm, respectively, each with J = 6–8 cps for all compounds reported in both solvents. The assignment of these bands and the C-19 signal was based on the coupling constants and the relative peak intensities. Mass spectra were determined on an Hitachi RMU-6B single-focusing mass spectrometer. ORD curves were recorded on a Jasco 5A spectropolarimeter. The authors are indebted to Dr. R. B. Treptow and to Procter and Gamble, Co., Miami Valley Laboratories, for the use of their spectropolarimeter.

Oxidation of 5α-Cholestan-3β-ol (4) to 5α-Cholestan-3-one (5) by Jones Reagent.—5α-Cholestan-3-one (**5**) was prepared as previously described.[10] The ketone was recrystallized from acetone: mp 128–128.5°; $[\alpha]D$ +44.4° (*c* 4.27, $CHCl_3$) (lit.[11] mp 129°; $[\alpha]D$, +42–44°); ir (KBr) 1709 cm^{-1}; nmr ($CHCl_3$) δ 1.00 s (19-CH_3), 0.65 s (18-CH_3) (lit.[12] δ 1.01, 0.67).

2,3-*seco*-5α-Cholestan-2,3-dioic acid (6) was prepared according to the method of Rull and Ourisson.[13] After adding a solution of the ketone **5** (6.00 g, 13.8 mmol) in 120 ml of glacial acetic acid to CrO_3 (5.54 g, 55.4 mmol) suspended in 100 ml of HOAc at 70°, the reaction mixture was maintained at 85° for 26 hr. Subsequent work-up gave **6**: 4.60 g (68%); mp 194.5–195° (EtOAc), $[\alpha]D$ +35.5° (*c* 0.013) (lit.[14] mp 195–196°; $[\alpha]D$ +35.7°; ir (KBr) 3700–3100 (OH), 1705 (C=O), 925 cm^{-1} (diacid); nmr ($CDCl_3$) δ 0.68 s (18-CH_3), 0.84 s(19-CH_3), 8.2–10.7 s (COOH).

Dimethyl 2,3-*seco*-5α-cholestan-2,3-dioate (2) was prepared by methylation by a method analogous to that of Ourisson[15] except that *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide (Diazald, Aldrich Chemical Co., Milwaukee) was used as a CH_2N_2 precursor. The reaction gave **2** which was recrystallized (MeOH): mp 59–60°, $[\alpha]D$ +23.5° (lit.[16] mp 59–60°; $[\alpha]D$ +20°); ir (KBr) 1745 cm^{-1} (C=O ester); nmr ($CDCl_3$) δ 0.81 s (19-CH_3), 0.65 s (18-CH_3), 3.67 s ($COOCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 464 (1), 428 (2), 380 (24).

3α-Carbomethoxy-*A*-nor-5α-cholestan-2-one (1b) was prepared according to the method of Fuchs and Loewenthal[2] except that the solvent contained benzene and DMSO in a ratio of 5:1 by volume. The product gave the following data: mp 108–109°; $[\alpha]D$ +111° (*c* 0.10, $CHCl_3$) (lit.[2] mp 110–111°; $[\alpha]D$ +109°); ir 3700–3200 weak (enol OH), 1765 (cyclopentanone C=O), 1727 cm^{-1} (ester C=O); uv max (EtOH) 294 nm (ε 4.25); nmr ($CDCl_3$) 0.68 s (18-CH_3), 0.87 s (19-CH_3), 3.73 s (methyl ester), 3.08 d (C-3, J = 13 Hz); nmr (pyr) 0.75 s (19-CH_3), 0.63 s (18-CH_3); ORD (*c* 0.10, MeOH) Φ × 10^{-3} (nm), +3.66 (375), +10.52 (335), +16.55 (326), +14.82 (321), +16.32 (316), +5.80 (305), 0 (300), −12.03 (278), −10.54 (255); a +283; mas spectrum (70 eV) *m/e* (rel intensity) 430 (62), 415 (46, M − CH_3), 399 (34, M − CH_3O), 275 (105).

3α-Carbomethoxy-*A*-nor-5α-cholestan-2β-ol (3b) was prepared by reduction of **1b** as previously described.[2] The crude product recovered was chromatographed on neutral alumina and gave **3b**: mp 119–122.5° (lit.[2] 121.5–122.5°); ir 3500 (broad, OH), 1728 cm^{-1} (C=O, ester); nmr ($CDCl_3$) 0.68 s (18-CH_3), 0.97 s (19-CH_3); nmr (pyr) 1.17 s (19-CH_3), 0.68 s (18-CH_3).

***A*-Nor-5α-cholestan-2-one (7)** was prepared from the diacid **6** by the method of Castells, *et al.*[17] The crude product recovered gave **7**: mp 96–97° (lit.[17] 101–102°); ir (KBr) 1745 (cyclopentanone C=O); uv (MeOH) 237.5 nm (ε 253), 297.5 (97); nmr ($CDCl_3$) δ 0.65 s (18-CH_3), 0.83 s (19-CH_3); nmr (pyr) δ 0.64 (18-CH_3), 0.73 (19-CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 372 (6.8), 357 (2.61), 202 (1.11), 214 (1.0); ORD (*c* 0.10, MeOH) Φ × 10^{-3} (λ, nm) +2.64 (375), +4.38 (350), +10.69 (325), +10.57 (322), +12.20 (315), +7.85 (308), +5.00 (302), 0 (297.5), −8.53 (285), −10.57 (275), −8.53 (2.60); a +228 (lit.[18] +234).

Registry No.—**1b**, 27460-19-1; **2**, 1180-24-1; **3b**, 30157-81-4; **4**, 80-97-7; **6**, 1178-00-3; **7**, 2310-36-3.

(10) A. Bowers, T. Halsal, E. Jones, and A. Lemin, *J. Chem. Soc.*, 2548 (1953).

(11) O. Diels and E. Abderhalden, *Ber.*, **39**, 884 (1906).

(12) P. C. Cherry, R. T. Cottrell, G. D. Meakins, and E. E. Richards, *J. Chem. Soc. C*, 181 (1967).

(13) T. Rull and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1573 (1958).

(14) B. H. Brown, I. M. Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 1482 (1940).

(15) A. Giroud, A. Rassat, P. Witz, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 3240 (1964).

(16) B. B. Smith and H. R. Nace, *J. Amer. Chem. Soc.*, **76**, 6119 (1954).

(17) J. Castells, G. Fletcher, E. Jones, G. Meakins, and R. Swindells, *J. Chem. Soc.*, 2627 (1960).

(18) W. Klyne, *Tetrahedron*, **13**, 29 (1961).

The Thienylfurans

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The scope and limitations of the photochemically induced valence bond isomerization has been reasonably well defined.[1-3] Nevertheless a number of intriguing questions remain particularly in the area of heteroaromatic-substituted thiophenes.[2]

This note describes the synthesis of the four isomeric thienylfurans (**1**,[3a] **2**,[3a] **3**, and **4**) and preliminary irradiation experiments (Scheme I).

2-(2-Thienyl)furan (**1**), a straw-colored oil, bp 46–47° (17 mm), was prepared in 20% overall yield starting with ethyl-2-thenoylacetate (**5**).[4] The latter (**5**) was condensed with α,β-dichloroethyl ethyl ether,[5] and the ester **6** thus formed could be hydrolyzed and decarboxylated to **1**.

3-(2-Thienyl)furan (**2**), 2-(3-thienyl)furan (**3**), and 3-(3-thienyl)furan (**4**) were prepared by a route developed earlier by us for the synthesis of 2,3-diethienyl,[6] 3-phenylfuran,[7] and 3,3′-difuryl.[8] The starting materials **7**, **11**, and **15** have been described previously,[9-11] while the ketones **8** and **12** are also available by tested procedures.[7,12,13] Dehydration of the carbinols **9**, **13**, and **16** was carried out *in situ*[10,11] by distillation from dilute sulfuric acid. In each case a mixture of bond isomers, the thienyldihydrofurans **10**, **14**, and **17**, was ob-

(1) (a) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis *J. Amer. Chem. Soc.*, **89**, 3501 (1967); (b) R. M. Kellogg, J. K. Dik, H. van Driel, and H. Wynberg, *J. Org. Chem.*, **35**, 2737 (1970).

(2) H. Wynberg, T. J. van Bergen, and R. M. Kellogg, *ibid.*, **34**, 3175 (1969).

(3) R. M. Kellogg, T. J. van Bergen, and H. Wynberg, *Tetrahedron Lett.*, 5211 (1069).

(3a) NOTE ADDED IN PROOF.—It has just come to my attention that D. J. Klinke [Dissertation Abstracts, University Microfilms, Inc., Ann Arbor, Mich., 1964; Ph.D. Thesis, University of Michigan, 1963 (thesis director Dr. R. D. Schuetz)] described the synthesis and several reactions of **1** and **2**. The physical properties agree.

(4) R. Levine and C. R. Hauser, *Tetrahedron Lett.*, **66**, 1768 (1944).

(5) F. Reichstein, A. Grusssner, and H. Tschokke, *Helv. Chim. Acta*, **15**, 1066 (1932).

(6) H. Wynberg, A. Logothetis, and D. Verploeg, *J. Amer. Chem. Soc.*, **79**, 1972 (1957).

(7) H. Wynberg, *ibid.*, **80**, 364 (1958).

(8) H. Wynberg and J. W. van Reijendam, *Recl. Trav. Chim. Pays-Bas*, **86**, 381 (1967).

(9) H. Gilman and D. A. Shirley, *J. Amer. Chem. Soc.*, **71**, 1870 (1949).

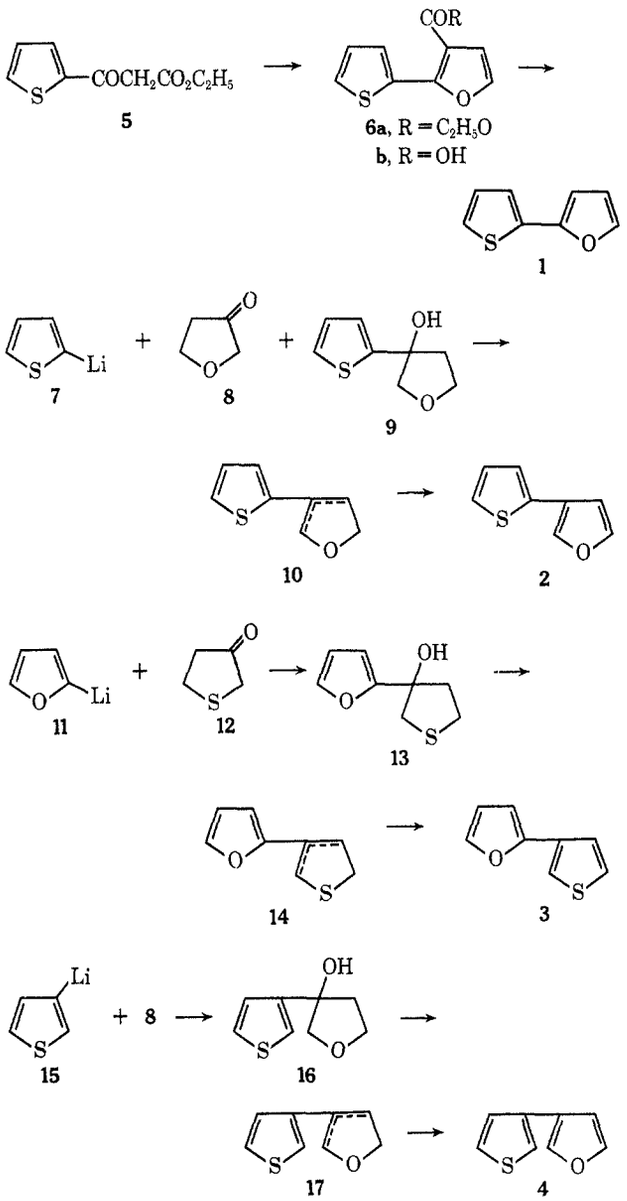
(10) S. Gronowitz, *Ark. Kemi*, **7**, 361 (1954).

(11) V. Ramananthan and R. Levine, *J. Org. Chem.*, **27**, 1216 (1962).

(12) Yu. K. Yur'ev, I. K. Korobitsyna, and L. A. Savina, *Dokl. Akad. Nauk SSSR*, **86**, 91 (1952) [*Chem. Abstr.*, **47**, 7478 (1953)]; J. H. S. Weiland, H. Dijkstra, and A. B. Pik, *Recl. Trav. Chim. Pays-Bas*, **82**, 651 (1963).

(13) P. Karrer and A. Kiese, *Helv. Chim. Acta*, **27**, 1285 (1945); R. B. Woodward and R. H. Eastman, *J. Amer. Chem. Soc.*, **68**, 2229 (1946). The most convenient preparation of ketone **12** consists of pyrolysis of the barium salt of 3-thiaadipic acid at 230° using the method developed by R. M. Acheson, J. A. Barltrop, H. Hichens, and R. F. Hichens, *J. Chem. Soc.*, 650 (1961), for alkylsubstituted thiaadipic acids. See also F. A. Buiter, *Diss.*, Groningen (Holland), 1966.

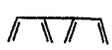
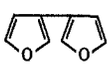
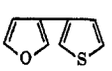
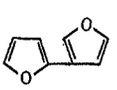
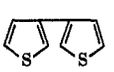
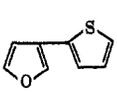
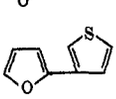
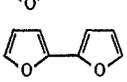
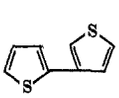
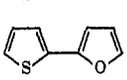
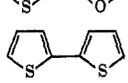
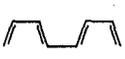
SCHEME I



tained. Gas chromatographic analysis of the ratio of one isomer to the other was relatively easy. The thienyldihydrofurans as well as the thienylfurans are quite volatile compounds. No attempts were made at this time to separate and identify each individual dihydrofuran since the mixture could be dehydrogenated smoothly using sulfur in dimethylformamide, yielding in each case one single compound (**2**, **3**, or **4**). All of the four isomers, **1**, **2**, **3**, and **4**, appeared to be sensitive to light, heat, and moisture. Even storage at −20° under nitrogen and in the dark resulted in darkening after several days. The stability of a negatively substituted derivative, *viz.*, **6**, was considerably greater.[14] In principle all of the four isomers are photochemically intraconvertible. Initial attempts were made to determine whether 2-(2-thienyl)furan (**1**) would yield any of the other isomers **2**, **3**, or **4** upon irradiation under conditions similar to those described for 2-phenylthiophene.[1] Although in one experiment a 2–5% conversion to 2-(3-thienyl)furan (**3**) was detected by gas chromatography (that is, a new compound having the retention time of **3** was observed), no positive identification could be made. Longer irradiation times led to decomposition of starting material. In fact, it appears that none of the four isomers are photochemically sufficiently stable to permit preparatively useful rearrangements. This phase of our work obviously requires further study.

Spectra.—In view of the current interest[17,18] in the structure and bonding in dithienyls, Table I summarizes the ultraviolet absorption spectra of all of the ten dithienyls, difuryls, and thienylfurans. For comparison, 2,3-divinylbutadiene (**18**) and 1,3,5,7-octatetraene (**25**) are included in this chart. Note that 2,3′-difuryl (**20**) has not been reported previously.

TABLE I

Compd	No.	Uv spectrum,[a] λ_{max} (mμ) (*E*)	Ref
	**18**	223 (20,800)	*b*
	**19**	239 (sh), 231, 220 (5,420, 7,780, 7,770)	*c*
	**4**	242 (7,500)	*d*
	**20**	259, 254, 214, 270 (sh) (11,500)	*e*
	**21**	260, 212 (cyclohexane) (11,300, 22,300)	*f*
	**2**	273 (7,800)	*d*
	**3**	279, 270, 228 (13,500, 13,300, 12,300)	*d*
	**22**	281 (18,500)	*g*
	**23**	282, 235 (cyclohexane) (13,100, 9,400)	*f*, *h*
	**1**	296, 230 (10,950, 1,300)	*d*
	**24**	301, 246 (12,900, 6,100)	*h*
	**25**	304, 290, 278, 267	*i*

[a] Solvent 96% ethanol unless noted otherwise. [b] K. Greiner, *Diss.*, Erlangen (1960). [c] Reference 8. [d] This work. [e] Prepared in 35% overall yield from 3-furyllithium and **8** as an unstable yellow oil, $n^{28}D$ 1.5297 (Found: C, 71.1; H, 4.50, by Mr. B. Greydanus of this laboratory). [f] H. van Driel, *Diss.*, Groningen (1967). [g] R. Grigg, J. A. Knight, and H. V. Sargent, *J. Chem. Soc. C*, 976 (1966). [h] Reference 6. [i] G. F. Woods and L. H. Schwartzman, *J. Amer. Chem. Soc.*, **71**, 1396 (1949).

(14) The purification and stability of the dithienyls have been the source of concern in ours and other laboratories. The known reactivity of dithienyls under the influence of light[1] and oxygen[15] as well as the reaction of oxygen with furans[16] are undoubtedly involved in the instability.

(15) P. Caralieri d'Oro, A. Mangini, G. F. Pedulli, P. Spagnolo, and M. Tiecco, *Tetrahedron Lett.*, 4179 (1969).

(16) G. O. Schenk, *Naturwissenschaffen*, **31**, 387 (1943).

(17) G. J. Visser, G. J. Heeres, J. Wolters, and A. Vos, *Acta Crystallogr.*, **24**, 467 (1968).

(18) H. J. S. Dewar and N. Trinajstic,[1] *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

The compounds can empirically but usefully be divided into three groups: those compounds whose chromophore resembles that of 2,3-divinylbutadiene (**18**), *i.e.*, compounds **19**, **4**, and **21**; those compounds whose chromophore is similar to that of a vinylhexatriene, *i.e.*, compounds **20**, **2**, **3**, and **23**; and finally compounds **22**, **1**, and **24** whose chromophore resembles an octatriene (**25**).

As recorded earlier by others,[8,19] the resonances of the β hydrogens in five-membered heterocyclics occur at higher fields than those of the α hydrogens. This difference is most pronounced in furans,[8,19] and consequently the nmr spectra of the four diaryl **1**, **2**, **3**, and **4** are all characterized by an absorption at τ 3.6–3.7 due to the β hydrogen(s) of the furan ring and a resonance at τ 2.4–2.5 for compounds **2** and **4** due to H_2 of the furan ring. The hydrogens of the thiophene ring as well as the H_5 hydrogens of the furan ring form a complex multiplet between τ 2.67 and 3.2. The spectra, including the ir and mass spectra, are available on request.

Experimental Section

Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 instrument using tetramethylsilane (TMS) as internal standard. Ir spectra were run on a Perkin-Elmer 257 or 137 instrument. Ultraviolet spectra were obtained with a Zeiss PHQ II spectrophotometer while mass spectra were run on an AEI MS 9. Melting points using a Reichert hot-stage are uncorrected. Microanalyses were carried out in the analytical section of our department under the direction of M. W. Hazenberg.

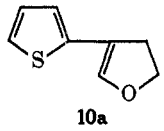
2-(2-Thienyl)furan (1).—Ethyl β-keto-β-(2-thienyl)propionate[4] (**5**) (19.8 g, 0.1 mol) and 18.0 g (0.13 mol) of 1,2-dichloroethyl ethyl ether were condensed by stirring at 30–40° in 60 ml of ether to which 11 g of sodium hydroxide in 170 ml of water was added with cooling. Following the work-up as described by Reichstein[5] for 2,2′-difuryl, we obtained 6.6 g (30%) of ethyl 2-(2-thienyl)furan-3-carboxylate (**6a**), bp 115° (0.8 mm), $n^{22}D$ 1.5765, as a pale yellow oil. Saponification with potassium hydroxide in ethanol–water for 45 min furnished a solid. Recrystallization from petroleum ether (bp 140–160°) gave 4.0 g of slightly yellow needles, mp 154.5–156°, of 2-(2-thienyl)furan-2-carboxylic acid (**6b**).

Anal. Calcd for $C_9H_6O_3S$: C, 55.66; H, 3.10; S, 16.42. Found: C, 55.7; H, 3.3; S, 16.5.

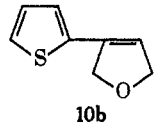
Decarboxylation of 1.5 g of the acid **6b** using 2.4 g of cupric oxide in 30 ml of quinoline at 245° for 7 min furnished 0.9 g (78%) of 2-(2-thienyl)furan (**1**) as a yellow oil which darkened upon standing. Purification was achieved by preparative gas chromatography (Carbowax SE-30 at 170°).

Anal. Calcd for C_8H_6OS: C, 63.97; H, 4.02. Found: C, 63.4; H, 5.1.

3-(2-Thienyl)furan (2).—Using an equivalent amount of *n*-butyllithium in ether, thiophene (3.7 g, 0.044 mol) in 100 ml of ether was lithiated[9] under nitrogen at −20° over a period of 1.5 hr. 3-Ketotetrahydrofuran[7,12] (**8**) (3.3 g, 0.044 mol) in 50 ml of ether was added at 0° with stirring. The reaction mixture was worked up as described in detail previously[6-8] and the mixture of dihydrofurans **10a** and **10b** was isolated as a yellow oil (3.5 g).



10a



10b

Glc analysis (diisodecyl phthalate) showed the two isomers in a ratio of 1:6. Dehydrogenation using 75 ml of dimethylformamide and 1.6 g of sulfur furnished 1.7 g (26% based on thiophene) of oil which could be purified by chromatography over alumina (benzene as eluent).

Anal. Calcd for C_8H_6OS: C, 63.97; H, 4.02; S, 21.34. Found: C, 64.1; H, 4.1; S, 21.5.

2-(3-Thienyl)furan (3).—Using 2-furyllithium[9] prepared from 16.5 g (0.24 mol) of furan and 25.2 g (0.24 mol) of 3-ketotetrahydrothiophene in 100 ml of ether at 0° yielded, after a similar work-up as above, 13.0 g (36%) of a mixture of bond isomers of 2-(3-thienyl)dihydrofuran as a yellow oil (ratio of isomers 5:4). Aromatization proceeded in 62% yield and after chromatography on alumina, 2-(3-thienyl)furan (**3**) was obtained as colorless solid, mp 24–26°.

Anal. Calcd for C_8H_6OS: C, 63.97; H, 4.02; S, 21.34. Found: C, 63.7; H, 4.4; S, 21.7.

3-(3-Thienyl)furan (4).—At −70° 3.7 g (0.05 mol) of 3-ketotetrahydrofuran (**8**) was added to a solution of 3-thienyllithium (from 7.2 g of 3-bromothiophene)[10] in 100 ml of ether. The reaction was worked up as described above to furnish, after steam distillation from dilute sulfuric acid, 4.0 g of a mixture of bond isomers of the 3-(3-thienyl)dihydrofurans (ratio 1:15) as a colorless solid. Aromatization gave 1.45 g (22% based on 3-bromothiophene) of pure 3-(3-thienyl)furan (**4**), mp 63–64°, one sublimation at 40° (0.2 mm).

Anal. Calcd for C_8H_6OS: C, 63.97; H, 4.02; S, 21.34. Found: C, 64.2; H, 4.3; S, 21.3.

Registry No.—**1**, 27521-80-8; **2**, 27521-81-9; **3**, 27521-82-0; **4**, 27521-83-1; **6a**, 27521-84-2; **6b**, 27521-85-3; **20**, 27521-86-4.

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The Reaction of Alkyl Diphenyl Phosphates with Potassium *tert*-Butoxide in Dimethyl Sulfoxide

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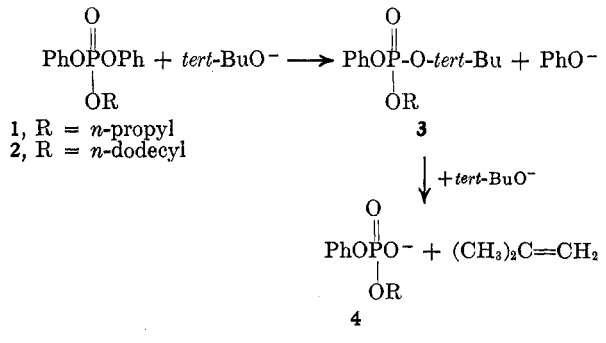
The reaction of 2-hexyl diphenyl phosphate with potassium *tert*-butoxide in dimethyl sulfoxide yields predominantly 2-methylpropene, instead of the hexene isomers anticipated from simple β elimination.[1] A two-step mechanism involving displacement of phenoxide from phosphorus by *tert*-butoxide and then β elimination in the *tert*-butyl group of the resulting ester was proposed[1] (Scheme I). It was not clear

SCHEME I



whether one or both phenoxy groups were cleaved. We wish to report a mechanistic investigation of

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