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.

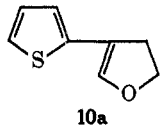
2-(2-Thienyl)furan (1).—Ethyl β-keto-β-(2-thienyl)propionate[4] (**5**) (19.8 g, 0.1 mol) and 18.0 g (0.13 mol) of 1,2-dichloroethyl ethyl ether were condensed by stirring at 30–40° in 60 ml of ether to which 11 g of sodium hydroxide in 170 ml of water was added with cooling. Following the work-up as 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.

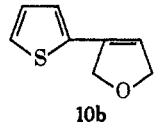
Decarboxylation of 1.5 g of the acid **6b** using 2.4 g of cupric oxide in 30 ml of quinoline at 245° for 7 min furnished 0.9 g (78%) of 2-(2-thienyl)furan (**1**) as a yellow oil which darkened upon standing. Purification was achieved by preparative gas chromatography (Carbowax SE-30 at 170°).

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.

(19) E. J. Corey, G. Slomp, S. Dev, S. Tobinaga, and E. R. Glatier, *J. Amer. Chem Soc.*, **80**, 1204 (1958); R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959); S. Gronowitz, A. B. Hörnfeldt, B. Gestblom, and R. A. Hoffman, *Ark. Kemi*, **18**, 133 (1961).

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

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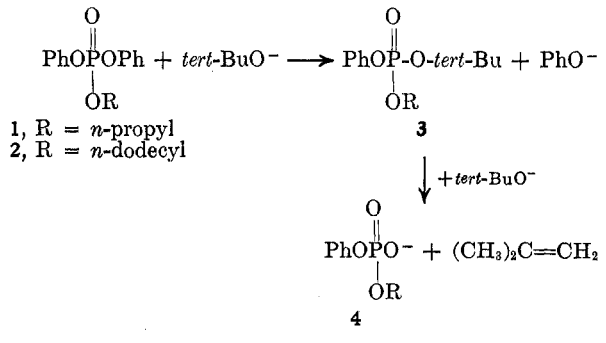
Received August 21, 1970

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

(1) R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, **91**, 1382 (1969).

TABLE I
YIELDS OF 2-METHYLPROPENE IN REACTIONS OF ALKYL DIPHENYL PHOSPHATE WITH POTASSIUM *tert*-BUTOXIDE IN DIMETHYL SULFOXIDE

Reaction no.	Alkyl diphenyl phosphate	Time, min	Temp, °C	Mmol of alkyl diphenyl phosphate	Mmol of potassium *tert*-butoxide	Yield of 2-methylpropene,[a] %
1	Dodecyl	12	50	0.73	2.6	56[b,c]
2	Dodecyl	30	50	0.71	4.9	106[d]
3	Dodecyl	30	100	0.79	4.9	105[d]
4	Dodecyl	30	50	0.78	0.78	55[c]
5	*n*-Propyl	30	50	0.91	4.6	86[d]
6	Methyl	30	50	1.32	4.9	30[c]

[a] Based upon cleavage of one phenoxy group. [b] Incomplete reaction. [c] Estimated uncertainty ±5%. [d] Estimated uncertainty ±10%.

this unusual reaction for primary alkyl diphenyl phosphates.

n-Propyl and *n*-dodecyl phosphates, **1** and **2**, respectively, were selected as representative starting materials. The yields of 2-methylpropene obtained from reactions of **1** and **2** with potassium *tert*-butoxide in dimethyl sulfoxide under various conditions are recorded in Table I. With an excess of base, approximately 1 mol of 2-methylpropene is produced per mole of **1** or **2** (reactions 2 and 5), even under forcing conditions (reaction 3). The slightly lower yield of 2-methylpropene from **1** might be due to minor incursion of a competing displacement of *tert*-butoxide upon carbon of the *n*-propyl group.[2] Support for this proposal is derived from the low yield of 2-methylpropene from methyl diphenyl phosphate (reaction 6).

Reaction of equivalent amounts of potassium *tert*-butoxide and **2** produced only a 50% yield of 2-methylpropene (reaction 4). Thus, a potassium *tert*-butoxide/alkyl diphenyl phosphate ratio of greater than 1 is required for formation of 1 mol of 2-methylpropene per mole of **2**. This result, as well as those from reactions employing a severalfold excess of potassium *tert*-butoxide, is compatible with the reaction sequence depicted in Scheme I, if β elimination from the *tert*-butyl alkyl phenyl phosphate, **3** (step 2), is more rapid than the initial displacement of *tert*-butoxide upon the alkyl diphenyl phosphate (step 1).[4]

An extraction technique was employed to determine the presence and amounts of two other anticipated reaction products (after acidification), phenol and alkyl phenyl phosphate. Emulsion formation during the extraction process prevented further studies on **2**. From the reaction of **1** with 4 equiv of potassium *tert*-butoxide, 1 mol of phenol per mole of **1** was liberated.

Several attempts to isolate and purify an oil, presumably *n*-propyl phenyl phosphate, recovered from the reaction of **1** with an excess of potassium *tert*-butoxide, as the cyclohexyl amine[6] or barium salts were unsuccessful. However, the pmr spectrum of this oil was nearly identical with that observed for *n*-propyl diphenyl phosphate except for the decreased ratio of aromatic to aliphatic protons expected for *n*-propyl phenyl phosphate.

The product studies of 2-methylpropene, phenol, and alkyl phenyl phosphate are all in accord with the mechanism outlined in Scheme I. Displacement of only one phenoxy group may be attributed to the unfavorable entropy for attack of *tert*-butoxide upon the negatively charged alkyl phenyl phosphate anion 4.[7]

Another conceivable mechanism that is consistent with the observed reaction products involves a nucleophilic aromatic substitution by *tert*-butoxide upon the alkyl diphenyl phosphate producing an alkyl phenyl phosphate anion and *tert*-butyl phenyl ether. Potassium *tert*-butoxide induced β elimination from the latter would form 2-methylpropene and phenoxide ion. However, the stability of *tert*-butyl phenyl ether to the action of potassium *tert*-butoxide in dimethyl sulfoxide[8] renders this proposal untenable.

Experimental Section

Reagents.—*n*-Propyl, *n*-dodecyl, and methyl diphenyl phosphate were synthesized by literature methods.[6,9,10] Sublimed potassium *tert*-butoxide (MSA) and reagent dimethyl sulfoxide from freshly opened bottles were used directly.

Procedure for Measuring 2-Methylpropene Yields.—A special apparatus designed to sweep the evolved 2-methylpropene from the reaction solution with nitrogen was employed. The sweeping nitrogen was passed first through an empty trap to remove any high boiling materials and then through a trap containing 5 ml of chloroform which was cooled in liquid nitrogen. The alkyl diphenyl phosphate was injected into the solution of potassium *tert*-butoxide in dimethyl sulfoxide (10 ml) with a syringe. After the desired reaction time, the liquid nitrogen-cooled trap was separated and an additional 5 ml of chloroform was added. The flask was warmed in cold water until the contents were half thawed, and a measured amount of bromine in acetic acid was added. Unconsumed bromine was determined by addition of 20 ml of 15% KI and titration with standard thiosulfate using starch indicator.

Extraction Procedure for Nonvolatile Products from 1.—The solution resulting from reaction of 0.73 g of **1** (2.49 mmol) with 10 ml of 1 *N* potassium *tert*-butoxide in dimethyl sulfoxide under nitrogen for 30 min at 50° was poured into 100 ml of water. After adjusting to pH 5 with concentrated HCl, the solution was extracted with CH_2Cl_2 (five 50-ml portions). The CH_2Cl_2 was evaporated from the combined organic extracts, and a phenol yield of 2.54 mmol (102%) was determined by uv spectroscopy. The pH of the aqueous layer was adjusted to 0.1 with concentrated HCl. Extraction with CH_2Cl_2 (four 75-ml portions),

(2) Bimolecular nucleophilic displacement of phosphate diester anions is very facile.[3]

(3) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, p 209.

(4) Alkaline cleavage of *tert*-butyl groups from tertiary phosphate esters occurs readily.[5]

(5) N. A. Milas, P. Davis, and L. Chiang, *J. Amer. Chem. Soc.*, **77**, 1640 (1955). However, see H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest," Wiley, New York, N. Y., 1961, p 20.

(6) J. Lecocq and A. R. Todd, *J. Chem. Soc.*, 2381 (1954).

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953, p 143.

(8) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, **82**, 6412 (1960).

(9) D. A. Brown, T. Malkin, and G. K. Maliphant, *J. Chem. Soc.*, 1584 (1955).

(10) D. W. Osborne, *J. Org. Chem.*, **29**, 3570 (1964).

drying the combined extracts ($MgSO_4$), and evaporation produced an oil. The pmr spectrum of this oil exhibited $\delta_{TMS}^{CCl_4}$ 0.88 (t, 3.0), 1.62 (sextet, 2.5, J = 7 Hz), 3.95 (apparent quartet, 2.0, J = 6 Hz), 7.15 (broad singlet, 5.0), which is consistent with that expected for *n*-propyl phenyl phosphate. For *n*-propyl diphenyl phosphate, the pmr spectrum was $\delta_{TMS}^{CCl_4}$ 0.88 (t, 2.9), 1.68 (sextet, 2.2, J = 7 Hz), 4.12 (apparent quartet, resolvable into overlapping triplets centered at 4.07 and 4.20 each with J = 6 Hz, 1.9), 7.23 (multiplet, 10.0).

Registry No.—**1**, 27460-01-1; **2**, 27460-02-2; potassium *tert*-butoxide, 865-47-4; methyl diphenyl phosphate, 115-89-9.

Acknowledgment.—We wish to thank R. R. Gibson and N. L. Bartsch for technical assistance.

α-Chlorodicyclopropyl Sulfone. Its Synthesis and Behavior toward Bases[1]

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Received August 8, 1970

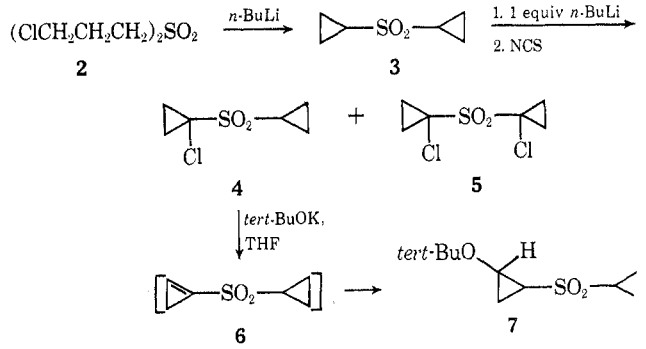
In 1940, Ramberg and Bäcklund demonstrated that exposure of acylic α-halo sulfones to the action of 2 *N* potassium hydroxide resulted in the production of alkenes with the concomitant ejection of hydrogen halide and sulfur dioxide.[3] Significantly, the new double bond unequivocally supplanted the sulfonyl group in each example studied. These findings, in conjunction with more recent mechanistic studies,[4] have resulted in broad application of the Ramberg–Bäcklund reaction to the preparation of many olefins, both cyclic and acyclic, which would be difficult to prepare by other methods.[5]

In the present instance, we felt that the α-halo sulfone rearrangement could offer an attractive opportunity for facile synthesis of bicyclopropylidene (**1**).

1

Hopefully, the approach would be entirely general in nature, in constrast to the limited number of highly specific methods known to date for this class of compounds.[6]

The scheme began with the *n*-butyllithium-induced cyclization of readily available γ,γ′-dichlorodipropyl sulfone (**2**) to give dicyclopropyl sulfone (**3**) in 85% yield. The nmr spectrum ($CDCl_3$) featured a multiplet of area 2 at δ 2.50 attributable to the α-sulfonyl protons and a second multiplet of area 8 centered at δ 1.08 for the remaining cyclopropyl hydrogens. Chlorination of sulfone **3** could be effected by initial treatment with slightly more than 1 equiv of *n*-butyllithium, followed by inverse addition of the α-sulfonyl carbanion



solution to excess *N*-chlorosuccinimide. Under these somewhat limiting conditions, the α,α′-dichloro derivative was produced in low (6%) yield. The nmr spectrum of this substance in deuteriochloroform was devoid of peaks in the δ 2.5–3.5 region; rather, two multiplets of equal area were displayed at approximately δ 1.97 and 1.56 for the two nonequivalent sets of ring protons. As expected, this method of chlorination also did give rise to the desired α-chloro sulfone (**4**) in fair (27%) yield. Its nmr spectrum in $CDCl_3$ displayed multiplets centered at δ 2.70 (1 H), 1.76 (2 H), 1.47 (2 H), and 1.18 (4 H), in full agreement with the structural assignment.

At the outset, sulfone **4** was found to be quite stable to the "normal" conditions of the α-halo sulfone rearrangement. Thus, **4** could be recovered intact from prolonged exposure to refluxing solutions of aqueous potassium hydroxide (1.2 *N*, 24 hr) and methanolic sodium methoxide (7 hr). Furthermore, it was noted that addition of *n*-butyllithium to dimethyl ether solutions of **4** at −20°, followed by controlled removal of low boiling components, afforded no volatile product other than solvent. In the presence of powdered potassium *tert*-butoxide in tetrahydrofuran at room temperature, however, **4** reacted readily to give not **1** but β-*tert*-butoxydicyclopropyl sulfone (**7**). The presence in **7** of the indicated β substituent is clearly revealed by the combination of a one-proton multiplet at δ 3.81, a two-proton multiplet at 2.20–2.70, a five-proton multiplet in the 0.80–1.70 region, and a sharp singlet (9 H) at 1.30.

It follows from these observations that **4** is particularly resistant to the α-halo sulfone rearrangement. Instead, potassium *tert*-butoxide is seen to promote dehydrochlorination to cyclopropene **6** and subsequent Michael addition of liberated *tert*-butyl alcohol to this reactive intermediate.[7] The inability of **4** to undergo

(1) This is paper XVI in the series entitled "α-Halo Sulfones." For the previous paper, see L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **93**, 944 (1971).

(2) NDEA Fellow, 1967–1970.

(3) L. Ramberg and B. Bäcklund, *Ark. Kemi, Mineral. Geol.*, **13A**, 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940).

(4) For comprehensive reviews of this subject, see (a) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); (b) L. A. Paquette, *Mech. Mol. Migr.*, **1**, 121 (1968); (c) F. G. Bordwell, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, Chapter 16.

(5) (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4383 (1964); (b) N. P. Neureiter, *J. Org. Chem.*, **30**, 1313 (1965); (c) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967); (d) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969); (e) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969); (f) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969); (g) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969); (h) R. E. Wingard and R. W. Houser, *ibid.*, in press.

(6) (a) W. R. Moore and H. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) B. du Laurens, A. Bezaguet, G. Davidovics, M. Bertrand, and J. Chouteau, *Bull. Soc. Chim. Fr.*, 799 (1967); (c) J. K. Crandall, D. R. Paulson, and C. A. Burnel, *Tetrahedron Lett.*, 4217 (1969); (d) P. Le Perchec and J. M. Conia, *ibid.*, 1587 (1970).

(7) A number of reports have appeared in which dehydrohalogenation of halo- and dihalocyclopropanes to cyclopropene intermediates has been achieved in somewhat analogous fashion: (a) T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 5425 (1967); (b) S. W. Tobey and R. West, *ibid.*, **88**, 2478 (1966); (c) K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, **79**, 4994 (1957); (d) T. C. Shields, B. A. Loving, and P. D. Gardner, *Chem. Commun.*, 556 (1967).