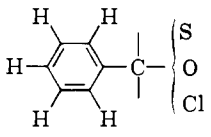
TABLE I

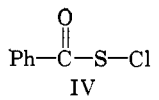
	Isomer **A** (m.p. 39°)	Isomer **B** (m.p. 5°)
Anal. Calcd. for C_7H_5SOCl: C, 48.70; H, 2.92; S, 18.54; Cl, 20.55	Found: C, 48.59; H, 3.02; S, 18.67; Cl, 20.81	Found: C, 48.88; H, 3.07; S, 18.85; Cl, 20.44
Molecular weight (cryoscopic, in cyclohexane) Calcd.: 172.6	170, 178	165, 170
Molecular weight (mass spectrometer)		172 (+174)
Refractive index, $n^{20}D$	1.605	1.657
Density, d^{20}_4	1.205	1.285
Molar refractivity, R_D	49.1	49.3
Ultraviolet (in cyclohexane)	229 mμ (ε 8000), 323 mμ (ε 9000)	226 mμ (ε 8000), 328 mμ (ε 14,000)
Infrared (0.6 *M* in CCl_4, values around 750 cm.$^{-1}$ determined in CS_2)	1446 (m), 1145 (vs), 1100 (m), 1025 (s), 920 (m), 753 (s), 688 (s) cm.$^{-1}$	1445 (m), 1269 (s), 1188 (m), 1120 (vs), 1005 (s), 910 (m), 758 (s), 683 (s) cm.$^{-1}$
H^1 n.m.r. (TMS, $\delta = 0$)	$\delta \sim 7.5$ (multiplet)	$\delta \sim 8.3$ and ~ 7.5 (multiplets, ratio 2:3)
C^{13} n.m.r.	$\delta_c = 12$ (singlet, nonaromatic C), and ~65 (complex absorption, aromatic C's)[3]	$\delta_c = 12$ (singlet, nonaromatic C), and ~67 (complex absorption, aromatic C's)[3]
Dipole moment, μ	3.97 D.	2.63 D.

reaction apparently belongs to the family of photochemical oxygen-transfer rearrangements discussed by Amin and Mayo.[4]

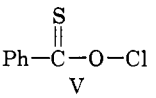
The chemical transformations, together with the presence of only aromatic absorption in the proton n.m.r. spectra and the infrared bands around 755 and 685 cm.$^{-1}$, require that both compounds have partial



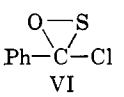
III



IV



V



VI

structure III. Structures IV, V, and VI are the only covalent structures, in addition to I and II, which can be derived by completing III without involving electron-deficient species or placing a formal positive charge on either carbon, oxygen, or chlorine. Structure IV, however, would require a carbonyl band in the infrared, V would be expected to absorb at longer wave lengths in the ultraviolet spectrum[5] than is observed, and VI would not account for the ultraviolet maxima around 325 mμ found in both **A** and **B**. Structure VI would also not be compatible with the C^{13} n.m.r. spectra; the observed chemical shift of the nonaromatic carbon (12 p.p.m. from CS_2 in both **A** and **B**) is close to that observed for carboxylic acids and some other functions in which the carbon atom is doubly bonded but is at substantially lower field than that reported for any saturated carbon.[6] Furthermore, if one isomer were IV, V, or VI, then the other isomer would have to have a completely different structure from the first, since neither IV, V, or VI is capable of geometrical isomerism or diastereoisomerism. However, the striking feature of the data summarized by Table I is the close similarity of many of the properties of **A** and **B**. The molar refractivities and the ultraviolet and C^{13} n.m.r. spectra are very similar, and the three strongest bands in the infrared spectrum of **A** (excluding those due to the phenyl group) at 1145, 1025, and 920 cm.$^{-1}$, respectively, have counterparts of comparable intensity in the spectrum of **B** at 1120, 1005, and 910 cm.$^{-1}$. We therefore assign structures I and II to the isomers.

Assuming that the S–O and C–Cl bonds are polarized so that the oxygen and chlorine atoms are each partially negatively charged, the dipole moment of I should be greater than that of II. On this basis we propose structure I for **A** (μ = 3.97 D.) and II for **B** (μ = 2.63 D.).

Geometrical isomerism about carbon–carbon, carbon–nitrogen, and nitrogen–nitrogen double bonds has been known for many years, and recently geometrical isomerism about a boron–nitrogen bond has been suggested.[7] I and II apparently represent the first case of geometrical isomerism about a double bond to an element outside the first short period of the periodic table.

Acknowledgment.—This work was supported by grants from the National Research Council of Canada. We thank Dr. W. A. Ayer (University of Alberta) for the mass spectrum, Dr. J. B. Stothers and Messrs. R. E. Klinck and K. S. Dhami for the n.m.r. data and their interpretation, and Dr. R. K. Chan for help in determining the dipole moments.

(3) Determined at 15.1 Mc./sec. in CCl_4 solution using enriched CH_3I as an external standard and given in p.p.m. relative to CS_2 (δ_c = 0): P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(4) J. H. Amin and P. de Mayo, *Tetrahedron Letters*, in press.

(5) Allyl thionbenzoates show a maximum at 420 mμ (ε 97): S. G. Smith, *J. Am. Chem. Soc.*, **83**, 4285 (1961). **A** and **B** even in 0.1 *M* solutions show no sign of a maximum around 420 mμ; at this wave length ε < 4 for both **A** and **B**.

(6) P. C. Lauterbur, Chapter 7 in "Determination of Organic Structures by Physical Methods," Vol. II, ed. by F. C. Nachod and W. D. Phillips, Academic Press, New York and London, 1962; also P. C. Lauterbur, *Ann. N.Y. Acad. Sci.*, **70**, 841 (1958).

(7) M. F. Lappert and M. K. Majumdar, *Proc. Chem. Soc.*, 88 (1963).

(8) Holder of National Research Council of Canada Scholarships, 1961–1963.

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A New, Stereospecific Olefin Synthesis from 1,2-Diols

Sir:

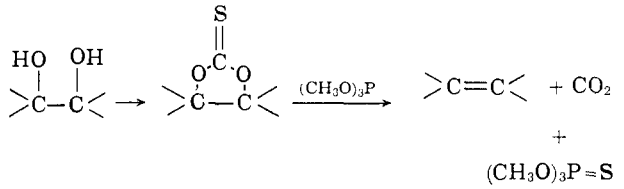
In the field of complex molecular synthesis, especially in the area of organic natural products, there is a need for new and general methods for position-specific *and* stereospecific introduction of carbon–carbon double bonds. We report here a new reaction which gives promise of broad practical application in stereospecific synthesis. Because the new method allows complete control of both the stereochemistry and the position of unsaturation, it possesses definite advantages in many synthetic problems over any of the presently known approaches.[1-10]

(1) G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954); this synthesis is both general and position-specific, but does not allow control of stereochemistry.

(2) R. C. Brandon, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **72**, 2120 (1950), and preceding papers there listed.

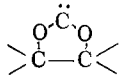
(3) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

In the present olefin synthesis, a 1,2-diol is converted to a cyclic thionocarbonate derivative which is then transformed into olefin by desulfurization–decarboxylation according to the equation



The first part of the two-step synthesis has been performed in two different ways. Simplest operationally and most efficient is the reaction of a diol with thiocarbonyldiimidazole,[11] in toluene or xylene at reflux for 30 min. This procedure gives the cyclic thionocarbonates directly, in excellent yields, and with essentially complete conversion. Alternatively, diols may be transformed into thionocarbonates by successive treatment in dry tetrahydrofuran solution with 1 equivalent of *n*-butyllithium (Foote Mineral Co., 15% solution in hexane), 1.2 equivalents of carbon disulfide, and 1 equivalent of methyl iodide.[12] Using this procedure, part (*ca.* 50%) of the diol is converted to thionocarbonate and part is recovered unchanged, the separation being accomplished simply by passage through a short column of alumina (Woelm neutral, activity III) in methylene chloride solution.[13]

The elimination reaction which comprises the second step of the olefin synthesis was devised from the hypothesis that a carbene of the type shown might be unstable



relative to olefin and carbon dioxide. Hence, the reagents which have been studied are those that are effective in the removal of sulfur from organic structures. Trimethyl- and triethylphosphite have proved to be both effective and convenient to use and most of our work has been carried out with these reagents.[14] With trimethylphosphite in excess (as solvent) at reflux for 70–80 hr. under nitrogen, cyclic thionocarbonates are converted cleanly to olefins.[15] Specific *cis*-elimination is observed. The stereospecificity and efficiency of the elimination are shown by the following examples (yields of isolated pure product in parentheses).

Thionocarbonate		Olefin
meso-Hydrobenzoin	⟶	*cis*-Stilbene (92%)
d,l-Hydrobenzoin	⟶	*trans*-Stilbene (87%)
cis-1,2-Cyclodecanediol	⟶	*cis*-Cyclodecene (84%)
trans-1,2-Cyclodecanediol	⟶	*trans*-Cyclodecene (81%)

Even highly substituted olefins can be prepared without difficulty. For example, pinacol was smoothly converted to 2,3-dimethyl-2-butene.

In view of the numerous syntheses of 1,2-diols which are available, often with control of stereochemistry, the thionocarbonate route to olefins is clearly of very broad scope. It constitutes, together with the *trans*-hydroxylation reactions, a general and unambiguous method for the interconversion of *cis* and *trans* olefins; in conjunction with the acyloin reaction it provides a synthesis of *cis* or *trans* cycloolefins in the medium- and large-ring classes.

We are continuing studies of this and other reactions for the synthesis of olefins from 1,2-diols. In addition, other aspects of the chemistry of carbenes from thionocarbonates are being investigated.

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(4) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 973 (1913).

(5) (a) F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082 (1954); (b) N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959).

(6) (a) L. Ramberg and B. Bäckland, *Arkiv. Kemi Mineral. Geol.*, **13A**, 27 (1940); (b) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951); (c) N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963).

(7) (a) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955); (b) C. B. Scott, *J. Org. Chem.*, **22**, 1118 (1957).

(8) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952).

(9) J. Fishman, M. Torigoe, and H. Guzik, *J. Org. Chem.*, **28**, 1443 (1963).

(10) The various syntheses of olefins from acetylenes by addition and from saturated precursors by classical E1, E2, and thermal cyclo-elimination reactions are also subject to a number of limitations which circumscribe their applicability in complex situations.

(11) H. A. Staab and G. Walther, *Ann.*, **657**, 98 (1962).

(12) The carbon disulfide is added *ca.* 5 min. after the lithium reagent and the reaction mixture is kept at 25° for 30 min. and at reflux for 30 min. Then methyl iodide is added and the reaction mixture is again maintained at 25° and at reflux for 30-min. periods.

(13) All the cyclic thionocarbonates which have been prepared to date are nicely crystalline compounds which characteristically exhibit two or more strong bands in the infrared at 7.3-7.9 μ; see R. Mecke, R. Mecke, and A. Lüttringhaus, *Z. Naturforsch.* **10b**, 367 (1955).

(14) Other trivalent phosphorus derivatives with comparable affinity for sulfur may be employed as well. Raney nickel which has been pretreated with acetone at reflux also brings about the elimination to form olefin, but only preliminary studies have been made of this alternative to date.

(15) Shorter reaction times can be used with triethylphosphite at reflux temperature, but the reactions are particularly clean with the trimethyl ester. The products can be isolated readily by addition of alkali to hydrolyze the excess phosphoesters and subsequent extraction.

Transition State Differences between Amides and Esters in Chymotrypsin-Catalyzed Hydrolysis[1]

Sir:

We have found that anilides show diametrically opposed responses to changes in charge density at the reaction site when compared to phenol esters. A previous study of substituent effects has shown that electron withdrawal facilitates the acylation of chymotrypsin by O-acyl-substituted phenols.[2]

The pseudo-first-order rate constants for the α-chymotrypsin-catalyzed hydrolysis of a series of three N-benzoyl-L-tyrosine anilides with substituents in the aniline portion of the substrate follow the Hammett equation with a ρ-value of −1.63 at an H_- value of 6.92 as calculated by least squares from the data shown in Table I.

TABLE I

Substrate	$E_0^a \times 10^5$ *M*	$S_0^b \times 10^3$ *M*	k/K_s,[c] min.$^{-1}$ *M*$^{-1}$
N-Benzoyl-L-tyrosine anilide	5.281	1.402	1483
N-Benzoyl-L-tyrosine-*p*-methoxyanilide	5.127	0.852	3490
N-Benzoyl-L-tyrosine-*m*-methoxyanilide	5.242	1.429	791
N-(*m*-Nitrobenzoyl)-L-tyrosine anilide	6.528	0.264	880
Hydrocinnamamide	4.191	4.872	95
Hydrocinnam-*p*-methoxyanilide	8.636	0.321	5.15
Hydrocinnamanilide	4.241	2.625	0.59

[a] Total enzyme concentration based on an assumed 24.8×10^3 g./mole of active enzyme. [b] Substrate concentration at zero time. [c] Pseudo-first-order rate constants.

The rate constant ratio for hydrogen-substituted to *meta*-nitro-substituted benzoyl of N-benzoyl-L-tyrosine anilide similarly indicates that electron donation from the α-acylamino group aids the catalyzed process. Details may be found in Table I. If the hydrolysis

(1) This research was supported by a National Institutes of Health grant, RG-8476.

(2) M. L. Bender and K. Nakamura, *J. Am. Chem. Soc.*, **84**, 2557 (1962).