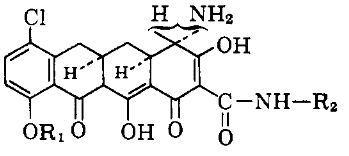
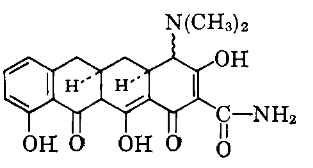
with $0.5B(OH)_3$ (m.p. 185–206° dec.; $\lambda\lambda_{max}$ m$\mu$ ($\epsilon$): 240 (12,500), 272 (10,800), 300 (11,200), 464 (44,000), and 490 (34,900) in MeOH–0.1 *M* $Na_2B_4O_7$ after 2-hr. equilibration).



IXa, $R_1 = CH_3$; $R_2 = C(CH_3)_3$
b, $R_1 = R_2 = H$

Treatment of IXa with HBr in acetic acid on a steam bath resulted in the formation of the epimeric pair (IXb) which was crystallized as the hydrobromide (dec. above 255°; $\lambda\lambda_{max}$ m$\mu$ ($\epsilon$): 272 (8,600), 287 (7,500), 471 (47,000), and 497 (34,100) in MeOH–0.1 *M* $Na_2B_4O_7$ after 2 hr.).

In order to alkylate the nitrogen in IXb, this compound was hydrogenated in methanol in the presence of 2 equiv. of triethylamine and an excess of formaldehyde with palladium-on-charcoal catalyst. By this procedure compound X was formed, crystallizing with 1 mole of dimethyl sulfoxide from dimethyl sulfoxide and acetone (m.p. 216–223° dec.; $\lambda\lambda_{max}$ m$\mu$ ($\epsilon$): 312 (6,100), 470 (46,800), and 496 (36,400) in MeOH–0.1 *M* $Na_2B_4O_7$ after 2 hr., 248 (16,000), 380 (12,600), 471 (20,200), and 495 (17,500) in MeOH–0.01 *N* NaOH after 14 min.). Both spectra are identical with spectra of optically active X, prepared by degradation of 6-demethyltetracycline, taken under exactly the same conditions.[10] The infrared absorption spectrum of synthetic X in KBr is identical with that of the known racemic synthetic X[3,11] but differs from optically active X prepared by degradation. Paper chromatographic behavior of synthetic X and X prepared by degradation is identical in several different solvent systems.



X

Compound X has already been transformed into racemic 6-deoxy-6-demethyltetracycline (I)[3] and can also be oxidized to this compound by the method developed in this laboratory[12] with platinum and oxygen.[13] It might be pointed out that resolution of the racemic mixture of either I or X seems to be extremely difficult, due to rapid equilibration at C-4. We have, therefore, resolved III. The transformation of optically active III into I will be the subject of a subsequent paper.

*Acknowledgment.* We thank Dr. Günter Grethe for the preparation of methyl N-*t*-butyl-3-oxoglutaramate and gratefully acknowledge financial support by the National Institutes of Health (Grant No. AI-04221-03 MCHA), the National Science Foundation (Grant No. 19 242), the Hofmann-LaRoche Anniversary Foundation, and Chas. Pfizer and Company, Inc.

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[10] The spectrum of X in 0.01 *N* methanolic sodium hydroxide differs somewhat from the published spectrum.[3] This is due to the rapid change of the spectrum with time.[3]

[11] We wish to express our thanks to Dr. J. J. Korst for sending us his ultraviolet and infrared spectra. For the comparison of the infrared spectra a sample containing no dimethyl sulfoxide was used.

[12] H. Muxfeldt, G. Buhr, and R. Bangert, *Angew. Chem.*, **74**, 213 (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 157 (1962).

[13] It has been reported erroneously and without our knowledge by a reporter in *Angew Chem.*, **76**, 791 (1964), that I has been synthesized by us in a different way.

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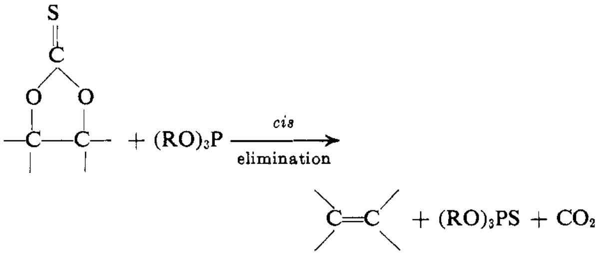
## Stereospecific Syntheses of Olefins from 1,2-Thionocarbonates and 1,2-Trithiocarbonates. *trans*-Cycloheptene

*Sir:*

A new stereospecific and orientationally specific synthesis of olefins from 1,2-thionocarbonates which proceeds according to eq. 1 has recently been reported from this laboratory.[1] In this note we present some new results which illustrate the power of the method as applied to the synthesis of relatively unstable olefins and a further generalization of the approach to the analogous elimination of [$CS_3$] from 1,2-trithiocarbonates.



(1)

*cis*-1,4-Diphenyl-2-butene was synthesized stereospecifically from the thionocarbonate derivative of *meso*-1,4-diphenyl-2,3-butanediol[2,3] (96% yield) by heating at reflux with trimethyl phosphite for 50 hr. with no evidence for formation of the thermodynamically more stable 1,4-diphenyl-1-butene by isomerization. Similarly, pure *trans*-1,4-diphenyl-2-butene was prepared from the corresponding racemic butane-2,3-diol in 99% yield without isomeric contaminants. Bicyclohexylidene was obtained free of isomeric impurities in 95% yield from the thionocarbonate derivative[4] of cyclohexanone pinacol.

Treatment of *trans*-1,2-cyclooctene thionocarbonate with triisooctyl phosphite at 135° for 24 hr. using a steady stream of argon through the reaction mixture to effect rapid removal of the volatile product afforded *trans*-cyclooctene of >99% purity (by v.p.c. analysis)

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[1] E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).

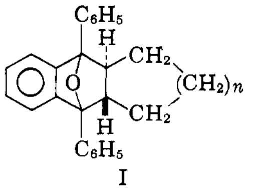
[2] Satisfactory elemental analyses and molecular weight data were obtained for all new compounds reported here. In addition the structures assigned are fully indicated by infrared and n.m.r. spectra. Homogeneity was established by v.p.c. or thin layer chromatographic analysis.

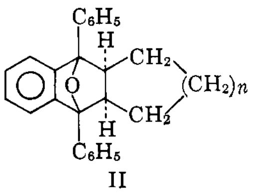
[3] Prepared from the diol and N,N′-thiocarbonyldiimidazole; see ref. 1 and H. A. Staab and G. Walther, *Ann.*, **657**, 98 (1962).

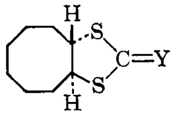
[4] This derivative was prepared from the dipotassium salt of the pinacol by sequential treatment in dry dioxane with 1 equiv. of carbon disulfide at 70° for 15 min. and 1 equiv. of methyl iodide at 0° initially, with gradual heating in a bath at 70° for 5 min. (see ref. 1). The thiocarbonyldiimidazole procedure is unsatisfactory for hindered diols such as the pinacols derived from ketones.

in 75% yield, the first reported stereospecific synthesis of this strained olefin. If the olefin was not removed continuously from the reaction mixture, isomerization occurred and only the *cis* isomer could be obtained. However, when the reaction was carried out in the presence of 2,5-diphenyl-3,4-isobenzofuran (in trimethyl phosphite at reflux for 30 hr.) the adduct of *trans*-cyclooctene, m.p. 129–130° (I, $n = 4$), was obtained in 80% yield.[5]

When an attempt was made to obtain *trans*-cycloheptene from *trans*-1,2-cycloheptene thionocarbonate by the procedure which was successful for the synthesis of *trans*-cyclooctene, only *cis*-cycloheptene was isolated. However, the reaction of *trans*-1,2-cycloheptene thionocarbonate with trimethyl phosphite in the presence of 2,5-diphenyl-3,4-isobenzofuran afforded an adduct, m.p. 148–150° (I, $n = 3$), isomeric with the known adduct of the isobenzofuran with *cis*-cycloheptene (II, $n = 3$), m.p. 183–185°,[6] m.m.p. 131–145°. It is apparent, therefore, that *trans*-cycloheptene is the primary product from *trans*-1,2-cycloheptene thionocarbonate in the elimination reaction. This is the first instance in which this highly strained olefin has been produced and detected; isolation in a pure state is obviously desirable and investigations toward this end are continuing. It is hoped that a sufficient quantity of this olefin can be obtained for the study of its chemistry and of the kinetics and thermodynamics of isomerization to *cis*-cycloheptene.


I

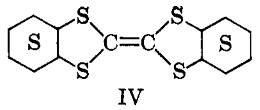

II

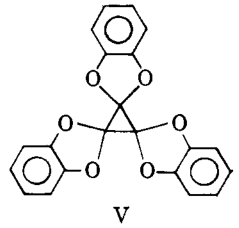

III

1,2-Trithiocarbonates, which are in general readily accessible substances, also undergo elimination when heated with trialkyl phosphites to form olefins by stereospecific *cis* elimination opening other routes to unsaturated structures. A practical synthesis of *trans*-cyclooctene from the *cis* isomer may be cited as an illustration. Addition of thiocyanogen to *cis*-cyclooctene affords stereospecifically *trans*-1,2-dithiocyanocyclooctane which is converted quantitatively to the imino dithiocarbonate III, Y = NH, by heating at reflux for 2 hr. with 47% hydrobromic acid followed by neutralization with sodium carbonate. The *trans*-thiocarbonate III, Y = S, is produced from this intermediate by reaction with hydrogen sulfide–ethanol (77% yield) and is converted to *trans*-cyclooctene of $>99\%$ purity in 99% yield by heating with triisooctyl phosphite at 135° (46 hr.) using the entrainment technique to remove product as formed.

Another route to the intermediate trithiocarbonates which can be of practical value for the synthesis of certain olefins is the reaction of *cis*- or *trans*-1,2-epoxides with potassium methyl xanthate to give *trans*- or *cis*-1,2-trithiocarbonates, respectively.[7-9] The geometrical relationship between substituents is changed in this process from *cis* to *trans*, or *trans* to *cis*, because of the occurrence of an odd number of inversions,[7-9] and hence still another method becomes available for interconversion of *cis*- and *trans*-olefins. Using 1,2-trithiocarbonates prepared from 1,2-epoxides in this way the following olefins have been synthesized stereospecifically (by heating at reflux with trimethyl phosphite for 24–30 hr.): *cis*- and *trans*-stilbene (94 and 100% yield, respectively), *cis*- and *trans*-2-butene.[10]

In some cases treatment of 1,2-thionocarbonates or 1,2-trithiocarbonates with trialkyl phosphites under the usual conditions does not lead to 1,2-elimination. Thus, *trans*-1,2-cyclohexene thionocarbonate affords neither cyclohexene nor carbon dioxide whereas the *cis* isomer yields *cis*-cyclohexene normally (77% yield). Similarly, *trans*-1,2-cyclohexene trithiocarbonate gives the coupling product of m.p. 298–299° (IV), but no *cis*-cyclohexene. *o*-Phenylene thionocarbonate was found to decompose to the interesting cyclopropane derivative V, m.p. 177.5–178.5°; no benzyne-derived products have been detected so far.


IV


V

All the data presently available on the new olefin synthesis indicate a concerted cycloelimination mechanism for the product-forming step. Further, elimination is effectively blocked in those cases in which *cis* elimination would lead to an excessively strained structure, *e.g.*, *trans*-cyclohexene. Investigations on the preceding stages of the reaction will be reported in due course as will the study of a photochemical modification of the olefin synthesis.

*Acknowledgment.* We thank the National Institutes of Health for the generous support of ths work.

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[5] This substance has been described previously by G. Wittig and R. Polster, *Ann.*, **612**, 102 (1958). It differs from the isomer, m.p. 180–182° (II, $n = 4$), which we have prepared from *cis*-cyclooctene and 2,5-diphenyl-3,4-isobenzofuran. See also G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3260 (1961).

[6] G. Wittig and T. F. Burger, *Ann.*, **632**, 85 (1960).

[7] A. M. Creighton and L. N. Owen, *J. Chem. Soc.*, 1024 (1960).

[8] S. M. Iqbal and L. N. Owen, *ibid.*, 1030 (1960).

[9] C. G. Overberger and A. Drucker, *J. Org. Chem.*, **29**, 360 (1964).

[10] We are indebted to Dr. C. G. Overberger for the samples of *trans*- and *cis*-2-butene trithiocarbonates from which the 2-butenes were prepared.

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## Pyrolysis of Salts of *p*-Tosylhydrazones. Simple Methods for Preparing Diazo Compounds and Effecting Their Carbenic Decomposition

*Sir:*

Diazoalkanes are usually prepared by nitrosation methods,[1a] oxidation of hydrazones,[1b] and reaction of