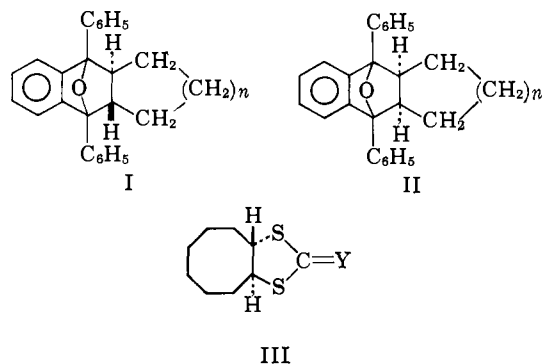


in 75% yield, the first reported stereospecific synthesis of this strained olefin. If the olefin was not removed continuously from the reaction mixture, isomerization occurred and only the *cis* isomer could be obtained. However, when the reaction was carried out in the presence of 2,5-diphenyl-3,4-isobenzofuran (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°, 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.

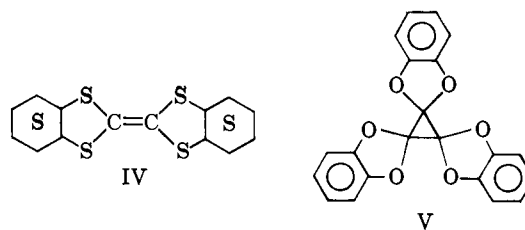
1,2-Trithiocarbonates, which are in general readily accessible substances, also undergo elimination when heated with trialkyl phosphites to form olefins by stereospecific *cis* elimination opening other routes to unsaturated structures. A practical synthesis of *trans*-cyclooctene from the *cis* isomer 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.

(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).

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.

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 this work.

(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.

E. J. Corey, F. A. Carey, Roland A. E. Winter
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received January 7, 1965

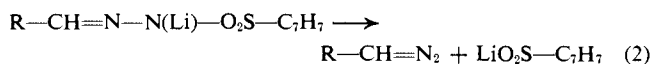
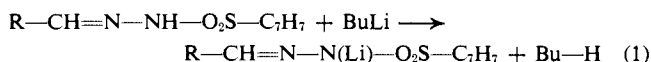
Pyrolysis of Salts of *p*-Tosylhydrazones. Simple Methods for Preparing Diazo Compounds and Effecting Their Carbenic Decomposition

Sir:

Diazoalkanes are usually prepared by nitrosation methods,^{1a} oxidation of hydrazones,^{1b} and reaction of

carbanionic reagents with chloramine,^{1c} hydroxylamine-O-sulfonic acid,^{1c} and *p*-tosyl azide.^{1d} These methods have limitations in preparation of pure diazo compounds in that the reactions are often inefficient, inconvenient, and hazardous, and separation of the diazo compounds from solvents is usually necessary.

p-Tosylhydrazones of aldehydes and ketones react with bases to yield salts of *p*-tosylhydrazones which thermolyze in suspension to give intermediate diazo compounds; the diazo compounds decompose *in situ* by carbenic mechanisms in aprotic solvents and by cationic processes in protic media.² Stabilized diazo compounds such as aryldiazomethanes^{2a,3a,b} and conjugated diazoalkenes^{3c} have been prepared in fair purity from *p*-tosylhydrazones and sodium alcoholates in alcohols,^{2a} glycols,^{2a,3a} glymes,^{3c} and pyridine,^{3b} respectively. It is presently reported that diazoalkanes and diazocycloalkanes can frequently be prepared conveniently and in high purity (eq. 1 and 2) by vacuum pyrolysis (0.2–3.0 mm.) of dry (preferred) or suspended lithium or sodium salts of *p*-tosylhydrazones (Table I) at 70–140°.⁴ The dry salts are obtained by precipita-



tion after neutralization of the *p*-tosylhydrazone with butyllithium (preferred) in tetrahydrofuran, sodium hydride in mineral oil, or sodium methoxide in absolute methanol-ether. With experience a *p*-tosylhydrazone can be prepared *in situ* from equivalent quantities of aldehyde or ketone and *p*-tosylhydrazine in tetrahydrofuran and then converted to its salt by reaction with the base. Lithium salts of *p*-tosylhydrazones prepared *in situ* from *p*-tosylhydrazones and butyllithium in tetraethylene glycol dimethyl ether at 0° may also be decomposed in suspension to diazo compounds by distillation at reduced pressures.

The methods developed are reasonably general and efficient for preparing primary diazoalkanes and aryldiazomethanes. Salts of *p*-tosylhydrazones of ketones frequently decompose at higher temperatures than those for aldehydes, and the secondary diazo compounds formed usually do not survive the pyrolytic conditions.⁵ Secondary diazo compounds, however, such as 1-diazo-2,2,4,4-tetramethylcyclobutane and cyclopropylphenyldiazomethane, can be prepared satisfactorily by the vacuum thermolytic methods. Minor reactions in pyrolysis result in carbenic decomposition to hydrocarbons with loss of nitrogen and formation of azines and salts of alkyl *p*-tolyl sulfones. The present methods are of particular value for preparing diazo

(1) (a) These methods are summarized by T. J. deBoer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954); (b) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916); (c) J. Meinwald, P. G. Gassman, and E. G. Miller, *J. Am. Chem. Soc.*, **81**, 4751 (1959); (d) W. von E. Doering and C. H. DePuy, *ibid.*, **75**, 5955 (1953).

(2) (a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) L. Friedmann and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (c) J. W. Powell and M. C. Whiting, *Tetrahedron*, **1**, 305 (1959).

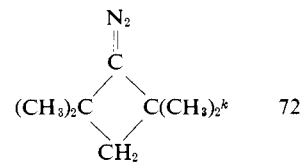
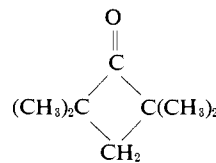
(3) (a) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964); (b) D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963); (c) G. L. Closs, L. E. Closs, and W. A. Boll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(4) Groups which leave at lower temperatures than does *p*-toluene-sulfonate ion are being studied.

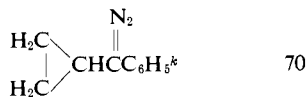
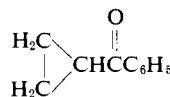
(5) 2-Diazopropane, diazocyclopentane, diazocyclohexane, and cyclopropyldiazomethane are formed in less than 5% yields by pyrolysis of lithium salts of *p*-tosylhydrazones.

Table I. Preparation of Diazo Compounds by Vacuum Pyrolysis of Salts of *p*-Tosylhydrazones

<i>p</i> -Tosylhydrazone of	Diazo compound	Yield, % ^a
CH ₃ CH ₂ CH=O ^{b-e}	CH ₃ CH ₂ CH=N ₂ ^f	46–56
CH ₃ CH ₂ CH ₂ CH=O ^{b-e}	CH ₃ CH ₂ CH ₂ CH=N ₂ ^f	75–80
(CH ₃) ₂ CHCH=O ^{b,e}	(CH ₃) ₂ CHCH=N ₂ ^f	65–75
CH ₃ CH ₂ CH ₂ CH ₂ CH=O ^{b,c,e}	CH ₃ CH ₂ CH ₂ CH ₂ CH=N ₂ ^f	52–53
CH ₃ CH ₂ CH(CH ₃)CH=O ^g	CH ₃ CH ₂ CH(CH ₃)CH=N ₂ ^f	63–65
(CH ₃) ₂ CHCH ₂ CH=O ^{b,e}	(CH ₃) ₂ CHCH ₂ CH=N ₂ ^f	46–59
(CH ₃) ₃ CCH=O ^b	(CH ₃) ₃ CCH=N ₂ ^f	85–95
C ₆ H ₅ CH=O	C ₆ H ₅ CH=N ₂ ^h	24 ⁱ
2-CH ₃ C ₆ H ₄ CH=O ^j	2-CH ₃ C ₆ H ₄ CH=N ₂ ^h	25 ⁱ
2,5-(CH ₃) ₂ C ₆ H ₃ CH=O ^j	2,5-(CH ₃) ₂ C ₆ H ₃ CH=N ₂ ^h	26 ⁱ
2,6-(CH ₃) ₂ C ₆ H ₃ CH=O ^j	2,6-(CH ₃) ₂ C ₆ H ₃ CH=N ₂ ^h	38 ⁱ
C ₆ H ₅ CH(CH ₃)CH=O ^b	C ₆ H ₅ CH(CH ₃)CH=N ₂ ^f	70–90



72



70

^a Analyzed volumetrically by the nitrogen evolved by excess benzoic acid in benzene and by conversion to the benzoate and titration of excess acid. ^b Prepared in warm methanol (5–10 min.); crystallized at –70°, washed with petroleum ether, vacuum dried, and refrigerated. ^c Deteriorates on recrystallization from methanol or acetic acid. ^d Better prepared by addition of aldehyde in petroleum ether to *p*-tosylhydrazine suspended in petroleum ether at 0° (3–6 hr.). ^e The lithium salt was also obtained from the tosylhydrazone prepared *in situ*. ^f By pyrolysis of the dry lithium salt. ^g Prepared in methylene chloride. ^h By pyrolysis of the sodium salt prepared from the *p*-tosylhydrazone and sodium hydride. ⁱ Purity rather than yield was emphasized. ^j Prepared at 25° in methanol (6–10 hr.) containing hydrochloric acid. ^k From the sodium salt prepared from sodium methoxide in methanol-ether.

compounds when their carbonyl precursors are more available than are amines. The diazo compounds may be used directly or purified by vacuum distillation. No serious hazards have been experienced in the systems of Table I; precautions were maintained at all times however.

A typical procedure is described for preparing 1-diazo-2,2-dimethylpropane. Butyllithium in hexane (35 ml., 1.6 N; 3.6 g., 0.056 mole) was injected in 5 min. to stirred trimethylacetaldehyde *p*-tosylhydrazone^{2b} (m.p. 112°; 12.7 g., 0.05 mole) under nitrogen in purified tetrahydrofuran (100 ml.) at 0–5°. A dense salt began separating near completion of addition. After 30 min. the mixture was concentrated at 35° on a rotary evaporator to give a white solid caked on the walls of the reaction flask. The flask was connected via an adapter⁶ to a series of traps and a vacuum system. The salt was heated to ~40° (0.3 mm.) to effect final drying and then to 80–135° (0.3 mm.) in diffuse light in 45 min. to effect its decomposition. Orange-red 1-diazo-2,2-dimethylpropane was condensed at –70°; redistillation (5 mm.) in darkness gave purified product (0.042–0.048 mole, 84–96% yield).

Reaction of *p*-tosylhydrazones with bases and decomposition of the subsequent salts in suspension to give

(6) Partially packed with glass wool to prevent spatter entrainment.

diazo compounds *in situ* which decompose carbenically to products^{2b} is frequently of limited preparative value. The yields may be poor, the system must be aprotic,^{2b} and the hydrocarbons may be difficult to separate from the solvent, particularly in small-scale experiments.⁷ It has been found that pyrolysis of dry salts of *p*-tosylhydrazones at reduced pressures (100–760 mm.) in distillation equipment is often of real advantage in effecting their carbenic decomposition to intramolecular products. At appropriate pressures and thermolytic

(7) (a) Metal alcoholates may cause complication in that the alcohols generated in formation of salts of the *p*-tosylhydrazones can lead to cationic decomposition of the intermediate diazo compounds. *N*-Methylpyrrolidone as a solvent when using metal alcoholates as bases frequently allows decomposition of the *p*-tosylhydrazones to intermediate alkyl *p*-tolylsulfonates which are saponified or transesterified to alcohols. (b) Similar observations have been made by J. W. Wilt and C. A. Schneider, *Chem. Ind.* (London), 865 (1963).

temperatures, the diazo compounds formed *in situ* decompose in the liquid and/or gaseous states to give products in good yields. The techniques are simple, rapid, free of many complications, and adaptable to small-scale experimentation. The method has been satisfactorily extended to injection in gas chromatographs of salts of tosylhydrazones as a dry powder or in suspension in a hydrocarbon; thermolysis is subsequently effected in a clean, heated injector unit and the products are separated, analyzed, and collected by usual techniques.

G. M. Kaufman, J. A. Smith
G. G. Vander Stouw, H. Shechter

Department of Chemistry, The Ohio State University
Columbus 10, Ohio

Received November 23, 1964

Book Reviews

Spectra-Structure Correlation. By JOHN P. PHILLIPS, Department of Chemistry, University of Louisville, Louisville, Ky. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1964. ix + 172 pp. 16 × 26 cm. Price, \$6.00.

As stated by the author in his preface, "The principal novelty of this book is its attempt to present a balanced survey of the data of absorption spectroscopy for organic compounds in all regions of the spectrum from far ultraviolet to far infrared." I believe that this is an excellent idea and it is indeed astonishing that until 1964 nobody seems to have undertaken the writing of a book of this type. The other surprising fact about this book is that it is so short. There is the other great merit of the author: he recognized the fact that, where analytical or other diagnostic work in spectroscopy is concerned, only relatively few correlations can be used for actual structure determination, the great majority of available data having little more than fingerprint value.

The reader whom this book will interest is clearly the chemist who uses the spectra as a tool, not the theoretically minded spectroscopist. It covers the spectra from 175 m μ to 35 μ , the range which is readily accessible to commercial instruments. The book is written in a vigorous personal style; nowhere does it become dull as so many other scientific books do.

The extreme brevity of the text (at places it is almost telegraphic) has not only advantages. Certain concepts such as the oscillator strength or "the cross-sectional area of the absorbing species" are literally parachuted into the text. On page 3, the inexperienced reader may get the impression that sodium chloride prisms can be used in the 16–18 μ area. On page 11, one may be led to believe that cumulative systems have stretching bands above 2000 cm.⁻¹ only. On page 12, symmetric and asymmetric bending frequencies are mentioned in relation with nonlinear XY₂-type molecules while there is only one bending (scissoring) vibration in this case. The out-of-plane bending vibrations of olefins are really treated too shortly (p. 40).

Even at such places, however, the work remains highly informative. Even though many things are not explained, almost every thing is at least mentioned, and good entries to the literature are given. On pages 13 to 19, a highly useful list of books and review papers is given. Many of the latter are not widely known. Only the absence of a somewhat larger number of "old" references in the text may be regretted. Concerning units, it would have been good, in the reviewer's opinion, to give both μ (or m μ) and cm.⁻¹ in characterizing the spectral location of bands. This may be cumbersome, but it is probably the only satisfactory solution in the present confused situation. It is somewhat unpleasant to be given the spectral location of a fundamental in cm.⁻¹ but that of its overtones in μ .

Summing up, it is rather nice to have spectral information for most typical organic compounds in only 160 pages covering the ultraviolet-visible, the near infrared, and the infrared, and even part of the far ultraviolet and the far infrared. I think that Dr. Phillips succeeded in writing something that will be useful for many. It may even encourage someone to write a book which will cover n.m.r. as well.

C. Sandorfy
Université de Montréal
Montreal, Canada

The Cyanine Dyes and Related Compounds. By FRANCES M. HAMER, Formerly Research Chemist, Kodak Ltd., London, and Honorary Lecturer, Imperial College of Science and Technology, London. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. xxxvi + 790 pp. 16 × 23.5 cm. Price, \$45.00.

A considerable body of work dealing with the cyanine and related dyes, including hundreds if not thousands of patent specifications, has issued over the years, particularly during the last three decades.

The cyanines are of special interest for several reasons. More than most dyes, they lend themselves to almost limitless structural variation, as a result of which they present by far the most diverse assemblage of absorption spectra (and hence of colors) of any known dye series. They are polymethine dyes, and in the sym-

metrical benzothiazole series $A=C(-C=C)_n-A$, where A represents the appropriate forms of the benzothiazole ring, dyes have been prepared where $n = 0, 1, 2, 3, 4, 5,$ and 6 . Since each successive increase in n has the effect of shifting the absorption maximum by about 100 m μ toward longer wave lengths, the extraordinary range of absorptions of this one series can be imagined.

On the practical side, the cyanines, with certain exceptions, are generally too fugitive to be useful in the dyeing of textiles, but happily this deficiency is balanced by their outstanding usefulness as color sensitizers in photography. For this purpose they are dyes of choice, and it is not too much to say that the elaborate edifice of photography could not exist without them in anything like the form in which we know it today.

The appearance of the present volume, the first to deal exclusively with these dyes, has accordingly been awaited with great interest, not only by the relatively small number of chemists actively working in the field but by the many others who would welcome an opportunity to become familiar with the main features of the