

Georgia Department of Experimental Statistics for the statistical adjustment of the data; and to Dr.

Leonard P. Spadafino, who prepared our sample of BDPA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH DAKOTA, GRAND FORKS, N. D.]

Chemistry of Ylids. X. Diphenylsulfonium Alkylides—A Stereoselective Synthesis of Epoxides¹

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The preparation and properties of diphenylsulfonium benzylide (8) and butylide (9) are described. Both ylids can be dissociated into carbenes and phenyl sulfide. The benzylide 8 reacts stereoselectively with benzaldehydes to form *trans*-stilbene oxides.

Introduction

From a study of the properties of phosphorus ylids² it became obvious that ylids containing heteroatoms other than phosphorus should be capable of existence. The major requirement appeared to be the ability of the heteroatom to stabilize the ylid carbanion, usually by overlap of the free electron pair with the vacant, low-energy d-orbitals of the heteroatom. In instances where this was not possible, such as many nitrogen ylids,³ the substances were capable of only fleeting existence. At an early date Ingold and Jessop,⁴ although apparently not using this line of reasoning, prepared a sulfur ylid, 9-dimethylsulfonium fluorenylide (1). In more recent years Johnson^{5a} and Wittig^{5b} have investigated the chemistry of ylids containing group V heteroatoms other than phosphorus.

Some time ago we undertook to investigate the physical and chemical properties of several new ylids and chose first to examine the chemistry of sulfonium ylids. We were particularly anxious to determine how these ylids would react with carbonyl compounds under the conditions of the well-known Wittig reaction.⁶ Since all ylids are nucleophiles, albeit of varying strength, we expected they would undergo at least the first step of the Wittig reaction, *i.e.* the attack of the ylid carbanion on the carbonyl carbon to form a betaine intermediate (*e.g.*, 2). Whether or not the betaine would dissociate into an olefin (*e.g.*, 3) and an oxide of the heteroatom group (*e.g.*, 4) was expected to depend on the bond energies involved.

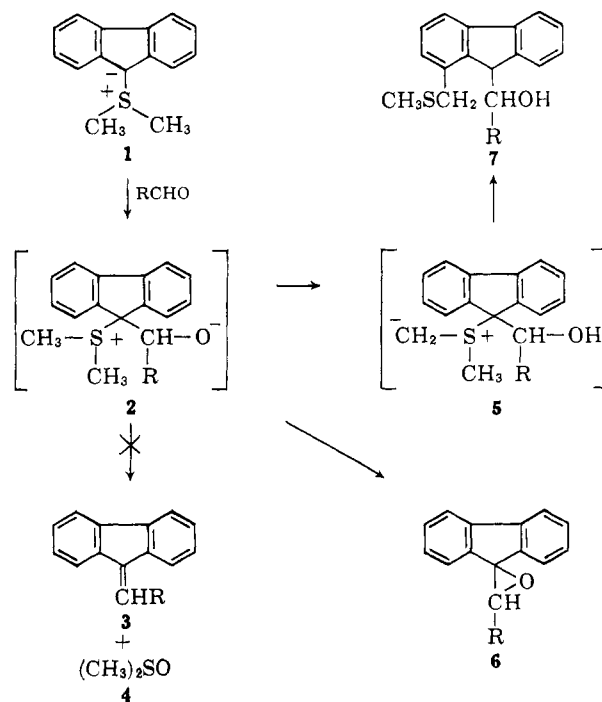
In our original work on the chemistry of sulfonium ylids⁷ we showed that 9-dimethylsulfonium fluorenylide (1) reacted with benzaldehydes to form a mixture of the benzalfluorene oxide (6, R = C₆H₄X) and a rearranged alcohol (7, R = C₆H₄X). The mechanism shown in Chart I was tentatively proposed to account for the observed products. This mechanism was based on the relative carbonyl reactivity sequence, analogy with other sulfonium salt displacements, and

the analogy with the known Sommelet rearrangement of the original ylid 1. Epoxide formation, rather than olefin formation as in the Wittig reaction, was not completely unexpected on the basis of the difference in bond dissociation energies of dimethyl sulfoxide (89 kcal./mole)^{8a} and triphenylphosphine oxide (128 kcal./mole)^{8b} and the known reluctance of hydroxide to attack trivalent sulfur but not tetravalent phosphorus.⁹

On the basis of this work we predicted that most, if not all, sulfonium ylids would form epoxides upon reaction with aldehydes and ketones. This expectation has been verified in the much later work reported by Corey, *et al.*, with dimethylsulfoxonium methylide^{10a} and dimethylsulfonium methylide^{10b} and the more recent reports by Franzen and co-workers using phenylmethylsulfonium methylide.^{10c}

To develop our original reaction between sulfonium ylids and carbonyl compounds into one of practical value for the synthesis of epoxides, two modifications would be required. First, the reactivity of the ylids would have to be increased since the fluorenylide (1)

CHART I



(1) (a) For paper IX in this series see A. W. Johnson, *Chem. Ind. (London)*, 1119 (1963). (b) Taken in part from the thesis of Victor J. Hruby presented to the Graduate School of the University of North Dakota in partial fulfillment of the requirements for the degree of Master of Science, August, 1962. (c) Part of this work was originally presented at the 142nd National Meeting of the American Chemical Society, Division of Organic Chemistry, Atlantic City, N. J., September 10, 1962. Another portion was announced in a preliminary communication, *J. Am. Chem. Soc.*, **84**, 3586 (1962). (d) We gratefully acknowledge the financial support of the National Science Foundation (Grants No. G-17345 and GP-1321).

(2) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

(3) G. Wittig and W. Tochtermann, *Chem. Ber.*, **94**, 1692 (1961).

(4) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

(5) (a) A. W. Johnson, *J. Org. Chem.*, **25**, 183 (1960); (b) M. C. Henry and G. Wittig, *J. Am. Chem. Soc.*, **82**, 563 (1960).

(6) S. Trippett, "Advances in Organic Chemistry," Vol. 1, R. A. Raphael, E. C. Taylor, and H. Wynberg, Eds., Interscience Publishers, Inc., New York, N. Y., 1960, p. 83.

(7) A. W. Johnson and R. B. LaCount, *Chem. Ind. (London)*, 1440 (1958); *J. Am. Chem. Soc.*, **83**, 417 (1961).

(8) (a) H. Mackle, *Tetrahedron*, **19**, 1159 (1963); (b) A. F. Bedford and C. T. Mortimer, *J. Chem. Soc.*, 1622 (1960).

(9) C. K. Ingold, *et al.*, *ibid.*, 531, 533 (1933).

(10) (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); (b) *ibid.*, **84**, 3782 (1962); (c) V. Franzen and H. E. Driessen, *Tetrahedron Letters*, 661 (1962); *Chem. Ber.*, **96**, 1881 (1963).

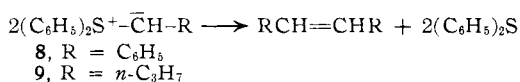
reacted only with benzaldehydes carrying electron-withdrawing groups.⁷ Since this lack of reactivity was probably due to the ability of the fluorenyl group to efficiently disperse the electron density on the ylid carbanion, any group which is less effective in this dispersal should provide a more reactive ylid.² Thus, we have prepared and studied the reactions of sulfonium ylids carrying a benzyl or a butyl group, both of which should be more reactive than 1.

Prevention of the formation of the rearranged alcohol 7 and analogous substances would be the second major requirement for a useful synthetic procedure. If the mechanism portrayed in Chart I is correct, replacement of the methyl groups on sulfur by groups with no α -hydrogen should prevent the Sommelet rearrangement. We chose, therefore, to study the chemistry of diphenylsulfonium alkylides 8 and 9.

Results and Discussion

Treatment of a slurry of silver tetrafluoroborate in benzyl chloride with phenyl sulfide afforded diphenylbenzylsulfonium tetrafluoroborate in 84% yield. Similarly, diphenylbutylsulfonium tetrafluoroborate was prepared in 56% yield from *n*-butyl bromide. Hydrolysis of the two salts afforded benzyl alcohol and 1-butanol, respectively, together with phenyl sulfide, a reaction characteristic of sulfonium salts but not of phosphonium salts. When a slurry of the salts in THF¹¹ under a blanket of nitrogen was treated with an equimolar quantity of *n*-butyllithium, the salts slowly dissolved and a yellow color appeared. This color, presumably due to the presence of the ylids 8 or 9, could be discharged by neutralization with acetic acid but could be made to reappear by the addition of butyllithium. The color would also rapidly vanish when the solution was allowed to stand at room temperature, but it persisted indefinitely at -70° .

Allowing a solution of diphenylsulfonium benzylide (8) to stand at -40° afforded 21% of recovered sulfonium salt together with a 61% yield of *cis*- and *trans*-stilbene and a 66% yield of phenyl sulfide. Two explanations may account for the stilbene formation. The ylid 8 could carry out a nucleophilic attack on the sulfonium salt to form a new sulfonium salt (10).

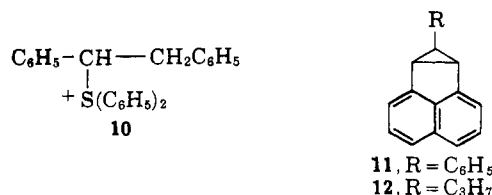


The *n*-butyllithium could then effect a β -elimination with phenyl sulfide as the leaving group, resulting in stilbene formation (mechanism A). Alternatively, the ylid 8 could dissociate into phenylcarbene and phenyl sulfide, the carbene then dimerizing to stilbene (mechanism B).

Franzen and Wittig¹² had previously reported the decomposition of trimethylammonium methylide into methylene and trimethylamine, the former being trapped with cyclohexene to form norcaradiene. Later, Franzen, *et al.*,¹³ postulated the analogous decomposition of several sulfonium ylids into carbenes. For example, on the basis of the isolation of triphenylmethane (42%), 1,1,1-triphenylpentane (15%), and 1-butene (7%) from the reaction of tritylsodium with *n*-butyldiphenylsulfonium tetrafluoroborate, they postulated the conversion of the latter salt into the corresponding ylid 9 followed by its decomposition to a carbene and phenyl sulfide. However, they failed to demonstrate unambiguously carbene formation since all of the above products can be accounted for by dis-

placement and/or elimination reactions, their conversion to ylid was low as indicated by the yield of the conjugate base, triphenylmethane, and they failed in their attempt to trap the carbene with olefins. More recently, Rothberg and Thornton¹⁴ have shown that decomposition of *p*-nitrobenzylidimethylsulfonium tosylate in aqueous sodium hydroxide does not proceed *via* the carbanion mechanism (mechanism A) but most likely proceeds *via* a carbene mechanism (mechanism B).

When the benzyl ylid 8 was formed in THF solution in the presence of one equivalent of acenaphthylene, a 43% yield of 7-phenyl-6b,7a-dihydrocycloprop[*a*]acenaphthylene (11) was obtained. The structure of 11 was proved by its inertness to cold permanganate



or bromine, its infrared spectrum (no olefinic absorption, monosubstituted aryl at 13.70 and 14.83 μ), its ultraviolet spectrum (λ_{max} 232 m μ (log ϵ 4.3), 296 (3.6), 310 (3.5), and 323 (3.1)), and by oxidation with chromic acid to benzoic acid and naphthalene-1,8-dicarboxylic acid anhydride. Likewise, the butyl ylid 9 reacted with acenaphthylene to afford a 60% yield of the corresponding propyl adduct 12 and its structure was proved in an analogous manner.

The isolation of the cyclopropane products 11 and 12 indicates that a carbene probably is formed by dissociation of the sulfur ylids 8 and 9. This process would not be unexpected since phenyl sulfide is such a good leaving group. However, it should be pointed out that our results do not provide conclusive proof of carbene formation since it is not inconceivable that the ylids 8 or 9 added to the double bond of acenaphthylene in a manner analogous to that proposed by Mechoulam and Sondheimer for the addition of phosphonium ylids to dibenzofulvenes.¹⁵ On the other hand, there is no evidence that the latter reaction does not proceed by carbene addition. In fact, Trippett¹⁶ has recently proposed the decomposition of a phosphorus ylid to triphenylphosphine and a carbene which then dimerized to an olefin.

When a THF solution of *p*-nitrobenzaldehyde was added to a solution of diphenylsulfonium benzylide (8) at -70° , the yellow color of the ylid disappeared. Chromatography of the products afforded an 85% yield of phenyl sulfide and a 72% yield of *trans*-*p*-nitrostilbene oxide. The ylid also formed the corresponding *p*-substituted *trans*-stilbene oxides when allowed to react with *p*-chlorobenzaldehyde (63%) and benzaldehyde (58%). The ylid 8 did not react with cyclohexanone or benzophenone under our conditions but it did react with *p*-nitroacetophenone to afford 1-(*p*-nitrophenyl)-1-methyl-2-phenyloxirane in 49% yield. Reaction with acetaldehyde afforded β -methylstyrene oxide in 48% yield which was purposefully rearranged to phenylacetone on the chromatographic column to facilitate isolation and identification.

Reaction of the benzylide 8 with *p*-methoxybenzaldehyde and work-up under our conditions afforded a 46% yield of *p*-methoxybenzyl phenyl ketone. We suspect

(11) THF = tetrahydrofuran.

(12) V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

(13) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

(14) I. Rothberg and E. R. Thornton, *J. Am. Chem. Soc.*, **85**, 1704 (1963).

(15) R. Mechoulam and F. Sondheimer, *ibid.*, **80**, 4386 (1958).

(16) S. Trippett, *Proc. Chem. Soc.*, 19 (1963).

that *p*-methoxystilbene oxide was, in fact, the initial product of this reaction but also was rearranged to the ketone on the alumina chromatographic column as reported by Campbell, *et al.*¹⁷ In addition, it should be noted that the reaction between the benzylide **8** and the other benzaldehydes afforded mixtures of the isomeric desoxybenzoins in varying amounts depending on the conditions employed for the reaction. For example, reaction of **8** with *p*-nitrobenzaldehyde at -70° followed by warming to room temperature gave only 3% of a mixture of *p*-nitrobenzyl phenyl ketone (**13**) and *p*-nitrophenyl benzyl ketone (**14**) along with 72% of the expected epoxide as mentioned previously. However, if the reaction was carried out at -70° , then followed by a 3-hr. heating under reflux, a 21% yield of **13** and a 19% yield of **14** were isolated but no trace of epoxide could be found. It was subsequently shown that the epoxide was stable to heat alone but would rearrange to a mixture of the ketones **13** and **14** upon heating with a solution containing butyllithium. The epoxides were stable to chromatography on neutral alumina but would rearrange to the ketones on acidic alumina.

Diphenylsulfonium butylide (**9**) also reacted with carbonyl compounds to afford epoxides. For example, it reacted with *p*-nitrobenzaldehyde to form 1-(*p*-nitrophenyl)-2-propyloxirane in 40% yield.

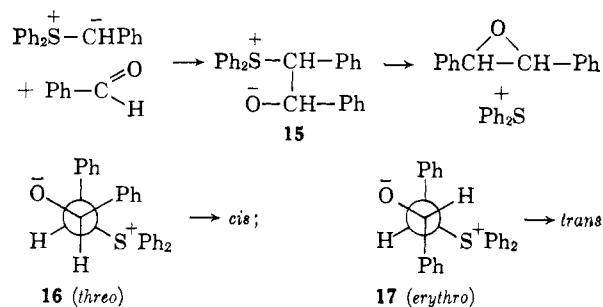
Thus, we have succeeded in widening the scope of the reaction of sulfonium ylids with carbonyl compounds. Furthermore, by using diphenylsulfonium alkylides we prevented the formation of sulfur-containing by-products. In effect, we have met our two outlined objectives and have made the reaction between such ylids and carbonyl compounds of considerable use for the synthesis of a variety of epoxides. It should be pointed out that this synthesis is extremely flexible since it permits varying the nature of the groups attached to both carbons of the oxirane product whereas use of Corey's or Franzen's ylids¹⁰ permits the synthesis of oxiranes substituted on only one carbon.

In the reaction of diphenylsulfonium benzylide (**8**) with benzaldehydes it was noted that in every case the resulting stilbene oxides were of the *trans* configuration. In spite of repeated and diligent searching, we were unable to find any trace of the *cis*-stilbene oxides. The question then arose as to whether the *cis*-oxides, if formed in the reactions at all, would have survived the reaction conditions and the subsequent work-up procedures. Therefore, an authentic sample of *cis*-stilbene oxide, prepared by peracetic acid oxidation of *cis*-stilbene, was subjected to the original reaction conditions, including the presence of one-half equivalent of butyllithium on the assumption that some excess was present at all times during the condensation reaction. Isolation of the products as described for the condensation reaction afforded 97% of the original *cis*-stilbene oxide. Repetition of this procedure but using one equivalent of butyllithium led to the recovery of 88% of the original *cis*-stilbene oxide. Thus, the *cis*-oxide, if formed in the ylid condensation, would have survived the reaction and work-up that followed and, on the basis of these results, we feel that we would have detected them if they had been formed in greater than 5% yield. Since we found no *cis*-stilbene oxides among the products of the reaction of the ylid **8** with benzaldehydes, we conclude that this reaction is stereoselective in producing the *trans*-stilbene oxides.

The mechanism illustrated in Chart II accounts for the results of the reaction between diphenylsulfonium benzylide (**8**) and benzaldehyde. The initial step is

assumed to be the nucleophilic attack of the ylid carbanion on the carbonyl carbon. The fact that **8** is more reactive than the fluorenylide **1**, analogy with the mechanism of the Wittig reaction,¹⁸ and the observation that the benzylide **8** is most reactive with carbonyl groups carrying electron-withdrawing groups, all are in agreement with this assumption. The second

CHART II



step is most likely a typical S_N2 backside displacement of the sulfonium group by the oxyanion. It is analogous, both mechanistically and stereochemically, to the formation of stilbene oxide from the methoxydioxide of 1,2-diphenyl-2-aminoethanol.¹⁹

The stereochemistry of the ylid reaction with carbonyl compounds is also accounted for by the above mechanism. In the first step, the betaine intermediate **15** could be formed in either a *threo* or *erythro* configuration. If the second step is, in fact, a backside displacement, the rotational conformations **16** and **17** would represent the two configurations required for that step. Examination of these two conformations reveals that the *threo* form **16** has the three bulky groups *gauche* to one another, whereas the *erythro* form does not. It might be expected, therefore, that the *threo* form would have a higher energy barrier for completion of the second step than would the *erythro* form. If the first step in the reaction were reversible, only the *erythro* form would then be converted to product, the *trans*-stilbene oxide, while the *threo* form of the betaine would revert to starting materials, the ylid **8** and benzaldehyde. Speziale and Bissing¹⁸ have recently shown that in the reaction between "stabilized" phosphonium ylids and carbonyl compounds, formation of an analogous betaine intermediate is reversible. Such may also be the case for the sulfonium benzylide **8** and may therefore account for the stereoselective formation of the *trans*-stilbene oxides.

Thus, the reaction between sulfonium ylids and carbonyl compounds has some potential as a general and stereoselective synthesis of epoxides. Application of this reaction to specific synthetic problems is continuing.

Experimental²⁰

Diphenylbenzylsulfonium Tetrafluoroborate.—By a method arrived at independently but essentially identical with that reported by Franzen, *et al.*,¹³ this salt was prepared as colorless microcrystals, m.p. 101–102° (lit.¹³ m.p. 102.5°), in 84% yield.

Diphenylbutylsulfonium tetrafluoroborate was prepared in a similar fashion from *n*-butyl bromide, phenyl sulfide, and silver tetrafluoroborate. It crystallized from ethanol as nearly colorless microcrystals, m.p. 85–86.5° (lit.¹³ m.p. 85.5–86°), in 56% yield.

(18) A. J. Speziale and D. E. Bissing, *ibid.*, **85**, 1888 (1963).

(19) J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 2377 (1930).

(20) Melting points are uncorrected. Analyses by Alfred Bernhardt, Mulheim (Ruhr), Germany. Ultraviolet spectra were recorded on a Bausch and Lomb 505 spectrophotometer and infrared spectra were recorded on a Perkin-Elmer Infracord as Nujol mulls unless otherwise specified. All chromatograms used Merck alumina, No. 71707, as the adsorbent. Phenyl sulfide was identified and estimated by its oxidation to phenyl sulfone, m.p. 125–126.5°, in 86% yield using 30% hydrogen peroxide–acetic acid mixture.

(17) D. R. Campbell, J. O. Edwards, F. MacClachlar, and K. Polgar, *J. Am. Chem. Soc.*, **80**, 5303 (1958).

Decomposition of the Benzylide 8 to Stilbene.—To a stirred slurry of 1.45 g. (4 mmoles) of diphenylbenzylsulfonium tetrafluoroborate in 50 ml. of THF which was cooled to -50° under a blanket of nitrogen was added, over 2 hr., a hexane solution containing 4.1 mmoles of butyllithium. The resulting yellow homogeneous solution was stirred for 2 hr. at -40° and for 2 hr. while warming to room temperature. Removal of the solvents *in vacuo* and pouring the residue into chloroform precipitated 0.26 g. (68%) of LiBF_4 . Chromatography of the chloroform filtrate afforded 0.49 g. (66%) of phenyl sulfide (hexane eluent); 0.22 g. (61%) of a mixture of *cis*- and *trans*-stilbene (hexane-benzene eluent), identified by its infrared and ultraviolet²¹ spectra ($\lambda_{\text{max}}^{\text{EtOH}}$ 283, 294, 307, and 319 (sh) μ ; and 0.30 g. (21%) of unreacted sulfonium salt.

7-Phenyl-6b,7a-dihydrocycloprop[a]acenaphthylene (11).—A solution of 4 mmoles of the benzylide 8 was prepared and handled as described above except in the presence of 0.61 g. (4 mmoles) of acenaphthylene. Pouring the reaction mixture into ether caused 0.38 g. (99%) of the LiBF_4 to precipitate. Removal of the ether left an oil from which phenyl sulfide (0.61 g., 82%) and unreacted acenaphthylene (0.18 g., 30%) were removed by extraction with hexane. The residue was crystallized from ether-ethanol to afford 0.30 g. (43% based on reacted acenaphthylene) of the adduct 11 as a pale yellow powder, m.p. 125–127°, λ_{max} 6.26, 12.84, 13.80, and 14.40 μ ; $\lambda_{\text{max}}^{\text{dioxane}}$ 232 μ ($\log \epsilon$ 4.3), 296 (3.8), 310 (3.7), and 323 (3.3). The adduct was inert to cold permanganate or bromine in CCl_4 . However, it yellowed on standing or heating and we were unable to obtain a satisfactory microanalysis.

Oxidation of 0.30 g. of the adduct 11 by heating under reflux with 2.0 g. of $\text{K}_2\text{Cr}_2\text{O}_7$ in glacial acetic acid for 30 hr. followed by quenching with water and filtration afforded 0.16 g. (67%) of naphthalene-1,8-dicarboxylic acid anhydride. It crystallized from chloroform-hexane as tan needles, m.p. 272.5–274° dec. (lit.²² m.p. 274° dec.), and was identified by mixture melting point and infrared spectral comparison with an authentic sample obtained by an analogous oxidation of acenaphthylene itself. Ether extraction of the aqueous filtrate afforded 0.02 g. (15%) of crude benzoic acid which sublimed as colorless needles, m.p. 120–121°, identical with an authentic sample.

7-Propyl-6b,7a-dihydrocycloprop[a]acenaphthylene (12).—To a stirred slurry of 1.32 g. (4 mmoles) of diphenylbutylsulfonium tetrafluoroborate and 0.61 g. (4 mmoles) of acenaphthylene in 60 ml. of THF, cooled to -40° under an atmosphere of nitrogen, was added, dropwise, a hexane solution containing 4.2 mmoles of butyllithium. After stirring for 2 hr. at -40° , 1.5 hr. with warming to room temperature, then an additional 1 hr., the solution was poured into ether affording a mixture of 0.25 g. (66%) of LiBF_4 and 0.37 g. (28%) of unreacted sulfonium salt. Evaporation of the ether and extraction of the residual oil with hexane afforded 0.35 g. (47%) of phenyl sulfide and 0.20 g. (33%) of unreacted acenaphthylene. Evaporation of the hexane and crystallization of the residue from benzene-hexane afforded 0.36 g. (60%) of the adduct 12 as a cream-colored powder, m.p. 276–279°, λ_{max} 6.27 and 12.81 μ ; $\lambda_{\text{max}}^{\text{dioxane}}$ 235 μ ($\log \epsilon$ 4.3), 296 (4.0), 309 (3.8), and 322 (3.5). The adduct was inert to cold permanganate and bromine in CCl_4 but again yellowed on standing or heating. We were unable to obtain a satisfactory microanalysis on this substance also.

Oxidation of 0.30 g. of the adduct 12 according to the procedure outlined above for the benzyl adduct 11 afforded 0.21 g. (74%) of naphthalene-1,8-dicarboxylic acid anhydride, m.p. 276–277° dec. (lit.²² m.p. 274° dec.), identified by comparison with an authentic sample.

Reaction of Diphenylsulfonium Benzylide (8) with Carbonyl Compounds.—The following general procedure was used in all of the reactions. To a stirred slurry of 1.45 g. (4 mmoles) of diphenylbenzylsulfonium tetrafluoroborate in 35 ml. of anhydrous THF cooled to -70° under an atmosphere of nitrogen was added, dropwise, a hexane solution containing 4.1 mmoles of butyllithium. The salt slowly dissolved and the solution became yellow. A solution of 4 mmoles of the carbonyl compound in 15 ml. of THF was then added dropwise during which time the color faded. After stirring for 2 hr. at -70° , while warming to room temperature over 2 hr. then for 1 hr. at room temperature, the colorless, homogeneous solution was poured into 100 ml. of distilled water. Extraction with ether followed by evaporation of the solvents afforded colorless viscous oils which were then chromatographed. The order of elution of the various products was: phenyl sulfide with hexane, the epoxides with 1:1 hexane-benzene, and the desoxybenzoins with 1:1 benzene-ether.

A. *p*-Nitrobenzaldehyde.—The aldehyde (0.61 g.) was treated with the benzylide 8 as described above to afford 0.63 g. (85%) of phenyl sulfide; 0.69 g. (72%) of *trans*-*p*-nitrostilbene oxide, which crystallized from chloroform-hexane as cream-colored needles, m.p. 125.5–126.5°, lit.²³ m.p. 125° (Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_3$:

C, 69.70; H, 4.60; N, 5.81. Found: C, 70.30; H, 4.96; N, 5.75); 0.03 g. (3%) of a mixture of the two desoxybenzoins 13 and 14, identified by comparison of its infrared spectrum with that of an authentic mixture; and 0.16 g. (26%) of *p*-nitrobenzyl alcohol, m.p. 89–90.5° (lit.²⁴ m.p. 93°), formed by the reduction of unreacted *p*-nitrobenzaldehyde on the alumina chromatographic column.²⁵

Repetition of the above reaction with the exception that after stirring for 2 hr. at -70° the reaction mixture was heated under reflux for 3 hr., led to the isolation of 0.61 g. (82%) of phenyl sulfide; 0.18 g. (19%) of *p*-nitrophenyl benzyl ketone (14) which crystallized from ethanol-water as pale yellow needles, m.p. 157–158° (lit.²⁶ m.p. 156–157°), $\lambda_{\text{max}}^{\text{EtOH}}$ 264 μ ($\log \epsilon$ 4.2), λ_{max} 5.94, 6.62, 7.46, 13.41, and 14.51 μ (Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_3$: N, 5.81. Found: N, 5.75); and 0.20 g. (21%) of *p*-nitrobenzyl phenyl ketone (13) which crystallized from benzene-hexane as colorless needles, m.p. 134–135° (lit.²⁷ m.p. 141–142°), λ_{max} 6.09, 6.64, 7.40, 13.64, and 14.48 μ , $\lambda_{\text{max}}^{\text{EtOH}}$ 265 μ ($\log \epsilon$ 4.6), shown to be identical with an authentic sample prepared *via* acylation of benzene with *p*-nitrophenylacetyl chloride.

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_3$: C, 69.70; H, 4.60. Found: C, 69.98; H, 4.74.

B. *p*-Chlorobenzaldehyde.—The aldehyde (0.56 g.) was treated with the benzylide 8 as described above to afford 0.60 g. (81%) of phenyl sulfide; 0.55 g. (63%) of *trans*-*p*-chlorostilbene oxide, which crystallized from hexane as colorless microcrystals, m.p. 98–99° (lit.²⁸ m.p. 99–100°), λ_{max} 9.03 μ , and gave a positive epoxide test²⁹ with periodic acid; traces of *p*-chlorophenylbenzyl ketone as identified by a comparison of infrared spectra; and 0.18 g. (32%) of *p*-chlorobenzyl alcohol which crystallized from methanol as colorless needles, m.p. 68–69° (lit.³⁰ m.p. 70°), again formed by reduction of unreacted aldehyde on alumina.²⁵

C. Benzaldehyde.—The aldehyde (0.43 g.) was treated with the benzylide 8 as described above to afford 0.59 g. (80%) of phenyl sulfide; 0.36 g. (58%) of *trans*-stilbene oxide, which crystallized from hexane as colorless plates, m.p. 66–67° (lit.²² m.p. 68°), identified by mixture melting point and infrared spectral comparison with an authentic sample, λ_{max} 9.05 μ ; 0.22 g. (53%) of benzyl alcohol, identified by its infrared spectrum; and 0.30 g. (21%) of unreacted sulfonium salt.

D. *p*-Anisaldehyde.—The aldehyde (0.54 g.) was treated with the benzylide 8 as described to afford 0.58 g. (76%) of phenyl sulfide; 0.41 g. (46%) of *p*-methoxybenzyl phenyl ketone which crystallized from ethanol as colorless plates, m.p. 93–94° (lit.³¹ m.p. 94–95°), λ_{max} 5.92 μ . The ketone formed a 2,4-dinitrophenylhydrazone which crystallized from ethanol as orange plates, m.p. 178–182° (lit.³¹ m.p. 179–182°).

E. *p*-Nitroacetophenone.—The ketone (0.86 g.) was treated with the benzylide 8 as described above to afford 0.60 g. (80%) of phenyl sulfide; 0.30 g. (45%) of unreacted ketone; and 0.44 g. (44%) of 1-(*p*-nitrophenyl)-1-methyl-2-phenyloxirane, which crystallized from ethanol as colorless microcrystals, m.p. 80–81°, λ_{max} 6.59, 7.43 and 9.04 μ , and which gave a positive epoxide test.²⁹

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{NO}_3$: C, 70.62; H, 5.14; N, 5.49. Found: C, 70.79; H, 5.38; N, 6.06.

F. Acetaldehyde.—An excess of the aldehyde (0.35 g.) was treated with the benzylide 8 as described to afford 0.61 g. (82%) of phenyl sulfide and 0.26 g. (48%) of phenylacetone as a colorless liquid, n_D^{20} 1.5187 (lit.³² n_D 1.5174), λ_{max} 5.80 μ . The ketone formed a semicarbazone which crystallized from 95% ethanol as colorless microcrystals, m.p. 188–189.5° (lit.³³ m.p. 188–189°).

1-(*p*-Nitrophenyl)-2-propyloxirane.—To a THF solution of 4 mmoles of diphenylsulfonium butylide (9), prepared as described for the benzylide 8, was added 0.61 g. (4 mmoles) of *p*-nitrobenzaldehyde. Use of the conditions and work-up procedures described above afforded 0.47 g. (65%) of phenyl sulfide; 0.32 g. (53%) of *p*-nitrobenzyl alcohol, m.p. 89–90°; and 0.38 g. (40%) of the desired oxirane which crystallized from hexane as colorless needles, m.p. 44–45°, λ_{max} 6.62, 7.47, 9.07, and 11.38 μ , and which gave a positive epoxide test.²⁹

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Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.72; H, 6.25; N, 6.85.

Stability of *cis*-Stilbene Oxide.—*cis*-Stilbene³⁴ (n_D^{25} 1.6185, lit.³⁴ n_D^{25} 1.6183) was oxidized to *cis*-stilbene oxide according to the procedure of Curtin and Kellom³⁵ except that peracetic acid³⁶ was used in place of the perbenzoic acid. The epoxide crystallized from 70% aqueous ethanol as a colorless mass, m.p. 37.5–38° (lit.³⁵ m.p. 37–37.5°).

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To a solution of 0.78 g. (4 mmoles) of *cis*-stilbene oxide in 35 ml. of anhydrous THF cooled to -70° under a blanket of nitrogen was added 2 mmoles of a hexane solution of butyllithium. The solution was stirred for 2 hr. at -70° , warmed to room temperature over 2 hr., then stirred for an additional hour before being poured into 100 ml. of water. Extraction with ether and chromatography of the organic products afforded, using a 1:1 benzene-hexane eluent, 0.76 g. (97%) of crude *cis*-stilbene oxide which crystallized from 70% aqueous ethanol, m.p. 37–38°, and was identified by its infrared spectrum and mixture melting point.

Repetition of the above reaction using 1.0 g. (5.1 mmoles) of *cis*-stilbene oxide and 5.1 mmoles of butyllithium solution led to the recovery of 0.88 g. (88%) of *cis*-stilbene oxide.

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The Structure of 2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl Cyanide and Some Derivatives Therefrom. Synthesis of 1-Deoxy-D-galacto-heptulose

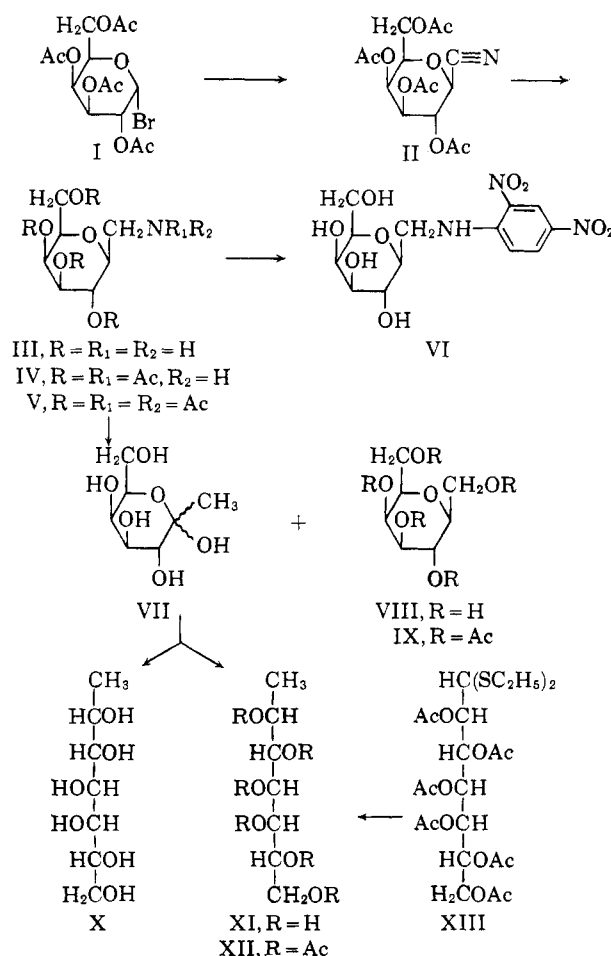
BY BRUCE COXON AND HEWITT G. FLETCHER, JR.

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Reduction of 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl cyanide with lithium aluminum hydride has led to the isolation of 1-amino-2,6-anhydro-1-deoxy-D-glycero-L-manno-heptitol. Deamination of this amine with nitrous acid gives two substances. One of these is an anhydroheptitol which periodate oxidation studies have shown to be 2,6-anhydro-D-glycero-L-manno-heptitol. The structure of this anhydride confirms the structure assigned to the parent cyanide. The second product from the deamination is a reducing sugar which was isolated as its 2,5-dichlorophenylhydrazone. Reduction of the sugar with sodium borohydride affords a mixture of 1-deoxy-D-glycero-L-manno-heptitol and 1-deoxy-D-glycero-L-gulo-heptitol; the sugar is, therefore, 1-deoxy-D-galacto-heptulose. The mechanism of the formation of this 1-deoxyheptulose from 1-amino-2,6-anhydro-1-deoxy-D-glycero-L-manno-heptitol is discussed.

It has recently been shown¹ that condensation of 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide with mercuric cyanide in nitromethane solution results in the formation of 2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl cyanide in 12% yield and of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)- α -D-glucopyranose in 11.5% yield. Under similar conditions 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide (I) has been reported^{2–4} to yield only one product; the presence of four alkalisaponifiable ester groups and the presumed mechanism of the condensation is the basis for the assumption that the substance is 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl cyanide (II). We have now repeated this condensation and obtained a substance whose physical properties agree with those reported by the earlier authors.^{2,3} Particularly noteworthy is the marked contrast here between the glucose and the galactose series; in the latter, only one product was isolated and this in 83% yield. We wish now to report an investigation of the structure and configuration of this nitrile.

Reduction of the presumed 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl cyanide (II) with lithium aluminum hydride afforded a crystalline product with the elementary composition of an amino-anhydro-deoxyheptitol. The substance was further characterized through the preparation of a variety of crystalline derivatives: the hydrochloride, a salt with *p*-toluenesulfonic acid, an *N*-2,4-dinitrophenyl derivative, a pentaacetyl, and a hexaacetyl derivative. Periodate oxidation of the *N*-2,4-dinitrophenyl derivative indicated the presence of a 2,6-anhydro-ring; the optical rotation of the oxidized solution was quite close to that obtained in a parallel experiment with 2,6-anhydro-1-deoxy-1-(2,4-dinitrophenylamino)-D-glycero-D-gulo-heptitol,¹ suggesting that the two substances had identical configurations at C-2 and C-6.



However, the amino-anhydro-deoxyheptitol, in agreement with the results obtained previously¹ for the periodate oxidation of 1-amino-2,6-anhydro-1-deoxy-D-glycero-D-gulo-heptitol, underwent an anoma-

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