Addition Reactions of Allenes. III.[1,2] 2,4-Dinitrobenzenesulfenyl Chloride and Bromine[3]

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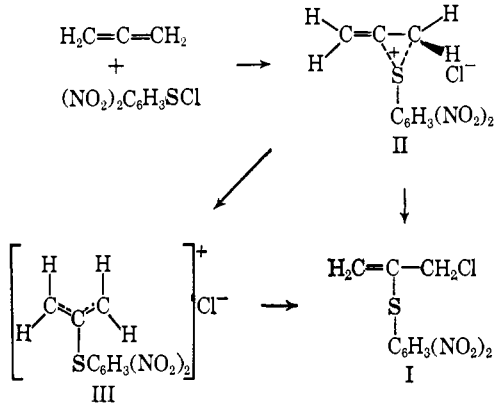
Abstract: Addition of 2,4-dinitrobenzenesulfenyl chloride to optically active 2,2-dimethyl-3,4-hexadien-1-ol (VII) occurred with participation of the hydroxyl group to yield optically active 3-(2,4-dinitrophenylthio)-1,5,5-trimethyl-Δ^3-dihydropyran (Xb). Addition of bromine to VII gave the corresponding 3-bromodihydropyran Xa with complete loss of activity. No method deemed satisfactory for application to the optically active isomers was found for conversion of VII or the corresponding aldehyde VIII to the allenic hydrocarbon XI.

It has been observed that the orientation in the ionic addition of hydrogen chloride to allene involved attachment of hydrogen to the terminal position in the allenic system.[1] Addition of 2,4-dinitrobenzenesulfenyl chloride to allene showed the opposite orientation: the negative fragment of the addend became attached to the terminal position forming I (Scheme I).

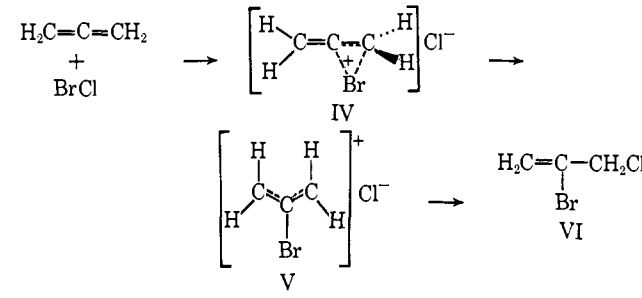
Scheme I



The difference was attributed to formation of a sulfonium intermediate II which might be attacked by chloride ion to form I.

More recently Peer[4] studied addition of bromine, chlorine, and bromine monochloride to allene; orientation of the last of these was similar to that observed with 2,4-dinitrobenzenesulfenyl chloride. It was suggested that the reaction involved initial formation of a π complex (or bromonium ion) IV which opened to an allylic carbonium ion V which reacted with chloride ion to give VI (Scheme II). Addition of chlorine or bromine monochloride to allene in acetic acid gave 3-acetoxy-2-chloropropene or 3-acetoxy-2-bromopropene; a similar mechanism was suggested. Addition of 2,4-dinitrobenzenesulfenyl chloride may be formulated the same way, as shown by III.

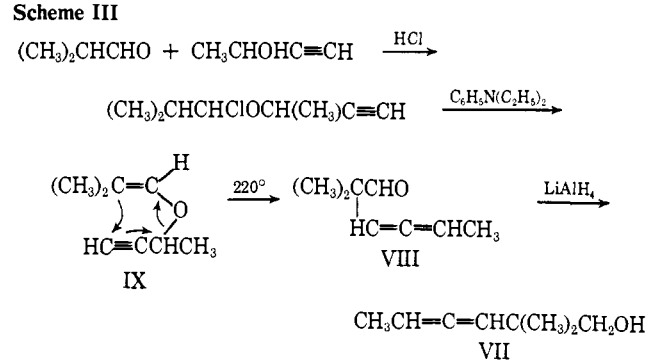
Scheme II



It should be possible to distinguish between these reaction mechanisms by examining additions to optically active allenes. If direct attack on suitably substituted intermediates like II and IV is involved, the products would be expected to be optically active; if these intermediates open to allylic carbonium ions related to III and V, the products would be racemic. Experiments of this nature have now been carried out with 2,2-dimethyl-3,4-hexadien-1-ol (VII).

Synthesis of VII was accomplished by reduction of the corresponding aldehyde, VIII, which was prepared by the Cope rearrangement of 2-methyl-1-propenyl 1-methyl-2-propynyl ether (IX) as summarized in Scheme III. This synthesis was reported earlier.[5] Our synthesis of the α-chloro ether was different from that reported.[5] Compound VIII has also been prepared by pyrolysis of the acetal.[6]

Scheme III



In the earlier work,[6] optically active aldehyde VIII was obtained from active 3-butyn-2-ol and its absolute configuration determined by relating this alcohol to

(1) Paper I: T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).

(2) Paper II: T. L. Jacobs and G. E. Illingworth, Jr., *J. Org. Chem.*, **28**, 2692 (1963).

(3) This research was supported by grants from the National Science Foundation. Preliminary work on the problem was carried out by D. Zunker under Grant GP-724. Most of the experimental work was done by R. Macomber who received support both from a National Science Foundation Undergraduate Research Participation Grant and from Grant GP-5530.

(4) H. G. Peer, *Rec. Trav. Chim.*, **81**, 113 (1962).

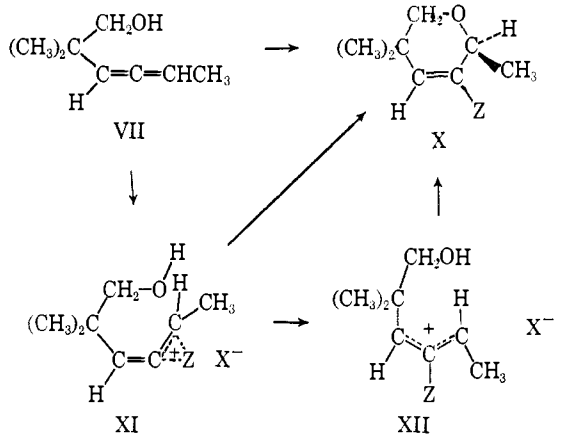
(5) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 5225, 6784 (1965).

(6) E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 180 (1960).

3-buten-2-ol and 2-butanol; (*R*)-2,2-dimethyl-3,4-hexadienal was found to be levorotatory. We chose instead to resolve racemic VII. The hydrogen phthalate of VII was obtained in 80% yield and resolved through the brucine salt. The less soluble brucine diastereomer gave hydrogen phthalate of $[\alpha]^{25}D$ −5.4°; saponification of this produced VII, $[\alpha]^{25}D$ +9.3°.

All addition reactions were carried out first on racemic VII and then on active VII. Addition of bromine in carbon tetrachloride at 0° gave dihydropyran Xa in 48% yield; the rest of the product was an unstable oil. Compound Xa was also obtained in 70% yield from reaction of VII with N-bromosuccinimide in refluxing carbon tetrachloride. When active VII was used, addition products were completely inactive (Scheme IV).

Scheme IV



a, X = Z = Br
b, X = Cl, Z = $SC_6H_3(NO_2)_2$

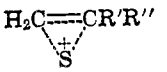
Addition of 2,4-dinitrobenzenesulfenyl chloride to VII in ethanol at 25° gave a similar dihydropyran, Xb, in 80% yield. Compound Xb was also obtained in methylene chloride, but the yield was lower. Active VII gave active Xb, $[\alpha]D$ +36°.

Kharasch[7] first suggested that the reaction of arylsulfenyl chlorides with olefins involves an episulfonium ion intermediate such as II, and all subsequent research has supported this mechanism.[8,9] A recent attempt[8] to show that an open carbonium ion could not explain the stereochemistry of the addition was only partially successful because the stereospecificity is so high. Addition of *p*-chlorobenzenesulfenyl chloride to *cis*-2-butene gave only 0.05% of *dl-erythro*-3-chloro-2-butyl-*p*-chlorobenzene sulfide. No change in the *erythro*/*threo* ratio was observed over a 180° temperature range.

$$L = \frac{([erythro]/[threo])_{T_1}}{([erythro]/[threo])_{T_2}}$$

It was calculated that the ratio *L* would be 5 if the activation energies for the rotation of the carbonium ion to the other rotamer and reaction of charged intermediate with chloride ion differ by only 2 kcal/mole. However, when one is determining such small [*erythro*]/[*threo*] ratios as 0.0005, a change to 0.0001 would probably not be detectable by glpc. Certainly formation of the episulfonium intermediate followed by SN2 ring opening is a more attractive explanation for such high stereospecificities, but the open carbonium ion mechanism has not been rigorously excluded.

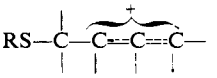
All of the research cited above has addressed itself to the question of whether an open carbonium ion or an episulfonium ion is the intermediate in this addition reaction, but many of the results apply also to the question of whether the episulfonium ion, if formed, might open to the carbonium ion before chloride ion attacks. Demonstration[9] that methane- and benzenesulfenyl chlorides add to simple aliphatic olefins to give initially anti-Markovnikov products which then rearrange to products of Markovnikov orientation is excellent evidence that in this case SN2 attack by chloride ion on an episulfonium ion is the actual reaction course; on a purely steric basis, one would expect a more rapid SN2 attack on the primary position of



rather than on the secondary or tertiary position. Correlation of rates of addition of 4-substituted 2-nitrobenzenesulfenyl chlorides to cyclohexene with σ^+ rather than σ is further evidence against an open carbonium ion intermediate even when Markovnikov orientation is observed.[10]

One would expect that the most likely systems in which one might encounter an open carbonium ion mechanism for additions of sulfenyl chlorides to olefinic bonds would be those in which the incipient carbonium ion is of increased stability. Additions to conjugated dienes and to allenyl systems are examples of such cases.

Conjugated dienes were examined recently;[11] 1,2 adducts were formed initially and these rearranged to the more stable 1,4 adducts on standing. This observation does not exclude the possibility that an open carbonium ion (either formed initially or as a result of opening of an episulfonium ion intermediate) is involved in the reaction. One has only to assume that the rate of attack at the 2 position of the allylic carbonium ion



is greater than the rate of attack at the 4 position by a sufficient factor so that the 1,4 adduct formed is below the detection level. It is not uncommon for a less stable product to be formed more rapidly in such systems. The allenyl system reported in the present paper might also give an open carbonium ion, XIIb, in the initial step of the addition; but if allylic stabilization is involved, this requires rotation of the end carbon and groups attached to it by a sufficient amount to permit orbital overlap by the time the transition state is reached. The alternative suggestion that an episulfonium ion forms first but opens to the carbonium ion (VII → XIb → XIIb) seemed to us more probable.

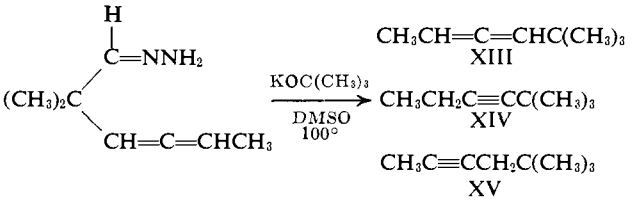
Preservation of optical activity for VII → Xb excludes a symmetrical allylic carbonium ion (XIIb) to

(7) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).
(8) G. H. Schmidt and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).
(9) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966); see this and ref 8 for a number of earlier references.
(10) C. Brown and D. R. Hogg, *Chem. Commun.*, 375 (1965).
(11) W. H. Mueller and P. E. Butler, *ibid.*, 646 (1966).

the extent that the reaction is truly stereospecific. The extent of stereospecificity can be determined if optically pure starting allene and adduct are available but VII may be unsuitable for this purpose because it is a liquid and because *d* and *l* forms of Xb have the same melting point as racemic Xb, suggesting that they form a racemic solid solution. Compound VII used in our experiments was not a pure enantiomer. Other allenyl systems are being examined and will be reported later. Incomplete results obtained so far are reported at this time because the field is so active and because they establish that a stereospecific route, which cannot involve the open carbonium ion, is the mechanism for some and probably most of the addition of 2,4-dinitrobenzenesulfenyl chloride to VII.

Addition of bromine to VII must involve a symmetrical intermediate or transition state and the formulation suggested by Peer[4] is reasonable. It is not surprising that this difference exists between additions of bromine and sulfenyl halides. One would expect a cyclic sulfonium intermediate (*e.g.*, II) to be more stable than IV and rearrangement of the former to an allylic carbonium ion correspondingly less facile. A parallel difference appears to exist for additions to norbornene.[12] The anchimeric assistance to solvolysis given by β substituents involves formation of intermediates similar to those postulated in these addition reactions, although solvolysis of β-substituted allylic compounds which would produce intermediates most like those believed present in our reactions appear not to have been studied. The assistance given by sulfur-containing groups in solvolysis of compounds such as $RSCH_2CH_2Cl$ appears to be much greater than the assistance from bromine in similar bromo compounds.

It would be of interest to examine these addition reactions with optically active allenic hydrocarbons in which participation by an internal atom is not involved. To this end several attempts were made to remove the hydroxyl group from VII or the carbonyl from VIII, but no procedure deemed suitable for application to the optically active allenes was found. Compound VII was readily converted into the tosylate but reduction with lithium aluminum hydride in tetrahydrofuran or with sodium borohydride in aqueous diglyme[13] failed. Reaction of VII with thionyl chloride gave what appeared to be a chlorosulfenate as expected by analogy with neopentyl alcohol.[14] The chloride could not be obtained from this. It seemed surprising, however, that the triethylsilanoxy derivative of VII could not be converted into the corresponding bromide or chloride since triethyl neopentoxysilane gives neopentyl halides in good yield.[15] Reduction of the tosylhydrazone of VIII with lithium aluminum hydride[16] was unsuccessful but partial success was attained by application of the Cram modification[17] of the Wolff–Kishner reduction to the hydrazone of VIII; an 82% yield of hydrocarbons was realized, but in addition to 5,5-dimethyl-2,3-hexadiene (XIII) two acetylenic isomers, XIV and XV, were formed by prototropic rearrangement. The proportions of XIII:XIV:XV were 12:1:6. Separation of



these isomers was accomplished by glpc, but the procedure did not appear suitable for preparation of optically active XIII. Other means are being sought for preparation of an optically active allenic hydrocarbon suitable for this study.

Experimental Section

Unless otherwise noted, vapor phase chromatography was performed on a Perkin-Elmer Model 800 gas chromatograph fitted with a 5 ft × 1/8 in. column containing 12% silicone oil 550 on 80–100 Chromosorb (conditions 86/121–30 are to be interpreted: column temp, 86°; injection temp, 121°; carrier gas flow rate, 30 cc/min). Infrared spectra were recorded on a Perkin-Elmer Infracord 137, with 0.42-mm cells, in carbon tetrachloride solution. Pmr spectra were run at ambient temperature on a Varian A-60. The integrations reported were within ±5%. Melting points were taken in capillary tubes; Anschutz thermometers were used but values are otherwise uncorrected. Boiling points and pressures are uncorrected. Unless otherwise noted, optical rotations were measured on a Hilger standard polarimeter fitted with sodium vapor lamp; a 4.00-dm cell was used and measurements were at room temperature in methanol (*c* 1.0).

2-Methyl-1-propenyl 1-Methyl-2-propynyl Ether (IX). Over a period of 40 min 120 g of dry gaseous hydrogen chloride was passed into a mixture of 105 g (1.5 moles) of 3-butyn-2-ol[18] and 144 g (2.0 moles) of isobutyraldehyde in a flask at 0°. Although water is produced in this reaction, it is important that all reagents are carefully dried and that the reaction mixtures be dried as indicated below. The lower brown aqueous phase was removed by pipet, diluted with an equal volume of water, and extracted with a total of 100 ml of ether. The extracts were returned to the organic phase (still at 0°) and the resulting solution was flushed with dry nitrogen for 40 min. The ethereal solution was dried overnight at 0° over molecular sieves, filtered, and added dropwise with mechanical stirring to 450 g (3.0 moles) of N,N-diethylaniline at 75°. In our hands this base gave better results than N,N-dimethylaniline or than trimethylamine.[5] The mixture was stirred for an additional 24 hr at 75°, then allowed to cool for 1 hr. The hydrochloride salts were removed by suction filtration, washed with 400 ml of ether, and the filtrate and washings were combined and dried over molecular sieves. The solution was rotary evaporated at 60° and 50 mm to remove most of the diethyl ether, then distilled under reduced pressure through a 24-in. Vigreux column to yield 116 g (62.5%) of a mixture of IX and VIII in the ratio of 15:1, bp 47–65° (22 mm). (These two components can be separated by careful fractionation, but this is unnecessary, as the next step gives exclusively aldehyde VIII.) The boiling point of IX is 46–49° (26 mm): infrared (cm^{-1}), 3250 (C≡C—H), 2100 (C≡C), 1690 (C=C). Glpc (86/121–30) showed one major peak at 2.4 min. A peak at 3.5 min is always observed due to aldehyde VIII, which is formed by rearrangement on the glpc column.

2,2-Dimethyl-3,4-hexadienal (VIII). Crude IX (116 g, 0.94 mole) was passed in a stream of dry nitrogen through a 16 × 0.75 in. glass tube packed with glass wool and heated electrically to 220°. Compound IX was introduced into the nitrogen stream dropwise (1 cc/min) and the nitrogen flow was maintained at 100 cc/min. The product was collected in a trap cooled with ice water and the flow of nitrogen was continued overnight. The product was distilled under reduced pressure to yield 110 g (95%) of VIII; bp 56–59° (22 mm); pmr (neat, internal TMS); τ 0.75 (singlet,

(12) H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, **76**, 4072 (1954); H. Kwart and R. K. Miller, *ibid.*, 78, 5678 (1956). Other references are listed in these papers.

(13) H. M. Bell and H. C. Brown, *ibid.*, **88**, 1473 (1966).

(14) W. Gerrard, A. Nechvatal, and B. M. Wilson, *J. Chem. Soc.*, 2088 (1950).

(15) L. H. Sommer, H. D. Blankman, and P. C. Miller, *J. Am. Chem. Soc.*, 73, 3542 (1951).

(16) L. Caglioti and M. Magi, *Tetrahedron*, **19**, 1127 (1963).

(17) D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J. Am. Chem. Soc.*, **84**, 1734 (1962).

(18) We wish to thank Professor A. Steinhofer and Dr. F. Ebel of the Haupt-laboratorium, Badische-Anilin und Soda-Fabrik, for sending us a generous sample of this alcohol.

1 proton), 4.9 (multiplet, 2 protons), 8.4 (multiplet, 3 protons), 8.88 (singlet, 6 protons); infrared (cm^{-1}), 1950 (C=C=C), 1710 (C=O); glc (86/121–30) showed a single peak at 3.5 min.

Anal. Calcd for $C_8H_{12}O$: C, 77.42; H, 9.68. Found: C, 77.51; H, 9.82.

A 2,4-dinitrophenylhydrazone was prepared, mp 115.0–115.1°.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: C, 55.26; H, 5.30. Found: C, 55.63; H, 5.56.

2,2-Dimethyl-3,4-hexadienol (VII). Aldehyde VIII (57 g, 0.46 mole) in 150 ml of dry ether was added over a period of 5 hr to a suspension of 5.6 g (0.16 mole) of lithium aluminum hydride in 250 ml of dry ether stirred magnetically. The reaction mixture was stirred overnight, then carefully hydrolyzed with water and enough 3 *N* sulfuric acid to dissolve the basic solids. The ether phase was separated and the aqueous phase extracted with a total of 75 ml of ether. The combined ether solutions were dried, rotary evaporated to remove solvent, and the residue distilled through a Vigreux column yielding 53 g (92%) of VII: bp 65–69° (13 mm); pmr (neat, internal TMS), 4.9 (multiplet, 2 protons), 5.70 (singlet, 1 proton), 6.70 (singlet, 2 protons), 8.4 (multiplet, 3 protons), 9.01 (singlet, 6 protons); infrared (cm^{-1}), 3500 (OH) and 1950 (C=C=C). Glpc (86/121–30) gave a single peak at 5.4 min.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.04; H, 11.17.

2,2-Dimethyl-3,4-hexadienyl Acid Phthalate. A solution of 37.8 g (0.30 mole) of VII, 46.1 g (0.31 mole) of phthalic anhydride (recrystallized from chloroform), and 50 g of dry pyridine was heated at 70–75° for 30 hr with occasional agitation. While still warm the solution was poured with stirring onto 250 g of crushed ice containing 130 ml of concentrated hydrochloric acid. Stirring was continued until the ice melted and the solution was extracted with a total of 350 ml of ether, which in turn was extracted with a total of 500 ml of 1 *N* sodium hydroxide. The basic solution was immediately acidified with concentrated hydrochloric acid and extracted with 300 ml of ether. This solution was dried and the solvent removed, leaving a viscous, pale yellow oil. The oil was dissolved in 300 ml of boiling hexane, which was then carefully cooled to −78°. The hardened ester was collected on a filter, washed with cold hexane, and air dried, yielding 67 g (80%) of the phthalate as white powdery crystals; mp 39–41°; pmr (carbon tetrachloride solution, internal TMS), 2.1–2.7 (multiplet, 4 protons), 5. (multiplet, 2 protons), 5.97 (singlet, 2 protons), 8.4 (multiplet, 3 protons), 8.92 (singlet, 6 protons).

Resolution of the Acid Phthalate and Formation of Active VII. Three optically active bases were tried for the resolution: strychnine, dehydroabietylamine,[19] and brucine. The last of these gave the best results.

To a warm solution of 54.8 g (0.200 mole) of the phthalate ester in 350 ml of acetone was added with stirring 78.8 g (0.200 mole) of brucine. Warming was continued until the solids had completely dissolved and the solution was allowed to stand at −18° for 48 hr. Crop I (115 g) was filtered, washed liberally with cold acetone, and air dried. (Filtrates from this and later crystallizations were saved.) Crop I was recrystallized twice, yielding 31 g of crystals, $[\alpha]$ −5.4°. Although the rotation had not reached a constant value, decomposition was carried out at this point because the amount of alcohol which would have been obtained after further recrystallization would have been insufficient and would have been difficult to isolate. Melting points of the brucine salts were not sharp; softening was observed at about 80°, but complete melting had not occurred up to 120°. These crystals were dissolved in a minimum amount of warm acetone and poured with stirring into 200 ml of ice water containing 30 ml of concentrated hydrochloric acid. The active phthalate was extracted with a total of 300 ml of chloroform which, after drying and removal of solvent, left 13 g of the ester as an oil. The oil was refluxed over steam with 13 g of sodium hydroxide in 60 ml of water for 15 hr. Extraction of the basic solution with ether, drying, and evaporation left 5 g of impure active VII which, on short-path distillation, yielded 4 g of clear, colorless VII, $[\alpha]^{25}D$ +9.3°. The properties of the active alcohol were identical with those of the inactive compound.

2,2-Dimethyl-3,4-hexadienyl Tosylate. To a cold solution of 16.8 g (0.088 mole) of tosyl chloride in 90 g of dry pyridine was added 10.0 g (0.080 mole) of VII. After several minutes of agitation, the solution was allowed to stand at −2° for 72 hr. The resulting solution containing crystals of pyridine hydrochloride was poured into 100 g of ice water with stirring and the suspension was extracted with a total of 175 ml of petroleum ether (bp 20–40°). This solution, in turn, was extracted twice with 1 *N* hydrochloric acid, then twice with dilute sodium bicarbonate solution, and finally with water. Drying and evaporation of solvent left 18 g (80%) of a clear colorless oil: infrared 1975 cm^{-1}; pmr (carbon tetrachloride solution, internal TMS), 2.25 (doublet, J = 8 cps, 2 protons), 2.70 (doublet, J = 8 cps, 2 protons), 5.0 (multiplet, 2 protons), 6.33 (singlet, 2 protons), 7.57 (singlet, 3 protons), 8.4 (doublet of doublets, 3 protons), 9.0 (singlet, 6 protons).

Anal. Calcd for $C_{15}H_{20}SO_3$: C, 64.26; H, 7.19. Found: C, 64.40; H, 7.18.

2,2-Dimethyl-3,4-hexadienal Hydrazone. A solution of 13.0 g (0.41 mole) of anhydrous hydrazine, 12.2 g (0.10 mole) of VIII, and 6.0 g of glacial acetic acid in 35 ml of dry ethanol was refluxed on a steam bath for 24 hr. The solvent was carefully removed and the hydrazone taken up in 40 ml of ether. The ethereal solution was washed with 0.1 *N* sodium hydroxide–saturated sodium chloride solution, then with saturated sodium chloride solution, dried, and evaporated, yielding 11.8 g (82%) of a yellow liquid (not distilled): pmr (carbon tetrachloride solution, internal TMS), 3.38 (singlet, 1 proton), 4.85–5.30 (multiplet, 4 protons, –HC=C=CH– and NH_2), 8.5 (multiplet, 3 protons), 9.10 (singlet, 6 protons).

Wolff–Kishner Reduction of the Hydrazone. To a solution of 5.6 g (0.050 mole) of potassium *t*-butoxide in 35 ml of dry DMSO was added 9.3 g (0.067 mole) of the hydrazone by injections of small portions over a period of 12 hr. The solution soon became red and nitrogen was evolved. Distillation of the crude reaction mixture afforded 6.5 g of a clear liquid, bp 46–48° (87 mm). The distillate was separated by glpc on a Loenco Prep-Matic employing a 10 ft × 3/8 in. column containing 20% didecyl phthalate on 30–60 Chromosorb W (column temperature, 105°; injection temperature, 117°; detector and collector 110°; flow rate 280 ml/min). The retention times of the products were *t*-butyl alcohol, 7.5 min; XII, 12.5 min; XI, 15 min; XIII, 21 min. The pmr data (neat, external TMS) of the products are as follows: XI, 5.3 (multiplet, 2 protons), 8.7 (multiplet, 3 protons), 9.30 (singlet, 9 protons); XII, 8.05 (quartet, J = 8 cps, 2 protons), 8.95 (singlet, 9 protons), 9.1 (complex triplet, J = 8 cps, 3 protons); XIII, 8.25 (quartet, J = 2.5 cps, 2 protons), 8.45 (triplet, J = 2.5 cps, 3 protons), 9.25 (singlet, 9 protons).

Anal. Calcd for C_8H_{14}: C, 87.20; H, 12.80. Found for XI: C, 87.02; H, 12.80. Found for XIII: C, 87.06; H, 13.00.

Reaction of VII with Bromine. To a solution of 5.0 g (0.04 mole) of VII in 20 ml of carbon tetrachloride, cooled in an ice bath, was added with magnetic stirring during 15 min a solution of 6.4 g (0.04 mole) of bromine in 20 ml of carbon tetrachloride. When active VII was used, activity was measured at this point and found to be 0.0°. The pale yellow solution was evaporated and the residue distilled in a short-path apparatus to yield 4 g (48%) of a straw liquid, bp 90–100° (1 mm), which had a terpenoid odor. This liquid was stable indefinitely when stored at 0°, but decomposed slowly at room temperature unless rigorously dried. The pot residue from the distillation was an intractable tar; the amount of the residue could be lowered if even lower pressures and distillation temperatures were attained. Glpc of the distillate (97/158–30) showed only one major peak at 10 min: infrared (cm^{-1}), 1650 (C=C), 1100 (C—O), no OH, no C=C=C; pmr (carbon tetrachloride solution, external TMS); 4.1 (doublet J = 2 cps, 1 proton), 5.9 (quartet of doublets, J = 2, 7 cps, 1 proton), 6.6 (AB quartet, J = 11, 5, 11 cps, 2 protons), 8.7 (doublet, J = 7 cps, 3 protons), 8.95 and 9.05 (singlets, 3 protons each).

Anal. Calcd for $C_8H_{13}BrO$: C, 46.83; H, 6.34. Found: C, 47.07; H, 6.52.

Reaction of VII with N-Bromosuccinimide. To 1.26 g (0.01 mole) of VII in 13 ml of carbon tetrachloride was added 3.1 g (0.017 mole) of NBS. The solution was refluxed on a steam bath for 17 hr, cooled, filtered, and the solvent removed. The oily product was the same as the product from bromine addition (yield on distillation, 70%). When active VII was employed the rotation of the product was 0.0°.

Reaction of VII with 2,4-Dinitrobenzenesulfenyl Chloride. To a solution of 1.18 g (0.005 mole) of the chloride in 10 ml of methylene chloride cooled to −5° was added 0.63 g (0.005 mole) of VII. A drying tube was fitted to the flask and the solution was allowed to stand at ambient temperature for 2.5 hr. Removal of solvent *in vacuo* left a yellow oil which was recrystallized from methanol–carbon tetrachloride to give 0.9 g (50%) of Xb, mp 91–92°.

(19) W. J. Gottstein and L. C. Cheney, *J. Org. Chem.*, 30, 2072 (1965). We wish to thank Dr. Richard F. Heck of the Hercules Research Center for sending us a generous sample of amine D from which the pure base was prepared.

A mixture of 2.30 g (0.01 mole) of the chloride and 1.30 g (0.01 mole) of VII in 25 ml of anhydrous ethanol[20] was shaken at ambient temperature for 48 hr. Anhydrous ethanol (100 ml) was added and the mixture was gently warmed until all crystalline material had dissolved; 25 ml of water was added and the product was allowed to crystallize slowly at 0°. The bright yellow needles of Xb (2.6 g, 80%) were filtered, washed, and dried, mp 90–92.5°.

When active alcohol VII was used, the product had the same melting point range but showed $[\alpha]D$ +36°, (*c* 0.1, chloroform). A mixture melting point of the active and inactive Xb showed the same melting point range. The pmr data (chloroform solution, internal TMS) were as follows: 1.50 (doublet, J = 2.5 cps, 1 proton), 1.6 (doublet of doublets, J = 2.5, 9 cps, 1 proton), 2.3 (doublet, J = 9 cps, 1 proton), 3.52 (doublet, J = 2 cps, 1 proton), 5.75 (quartet of doublets, J = 2,7 cps, 1 proton), 6.4 (AB quartet, J = 8, 4, 8 cps, 2 protons), 8.65 (doublet, J = 7 cps, 3 protons), 8.84 (singlet, 6 protons).

Anal. Calcd for $C_{14}H_{16}SN_2O_5$: C, 51.84; H, 4.97. Found: C, 51.76; H, 5.03.

(20) One of the referees has questioned the choice of ethanol as solvent because solvolysis of the 2,4-dinitrobenzenesulfenyl chloride would be expected. We chose this solvent because it gave better yields of the crystalline adduct. Other solvents tried included carbon tetrachloride (16 hr, 25°) and ethylene dichloride containing about 5% of acetic acid (3 hr, 25°); both experiments gave oils which were not successfully crystallized, but which contained mainly Xb on the basis of pmr spectra.

In all of these experiments, hydrogen chloride was detected as a reaction product. However, when 2,4-dinitrobenzenesulfenyl chloride was allowed to stand in ethanol at ambient temperature for 24 hr, no acid fumes were given off. It was not established whether or not some hydrolysis of the chloride occurred, but at least it would appear to be slow compared with the addition.

1-Methylphenylhydrazine Oxidation of Sugars. The Alkazones[1]

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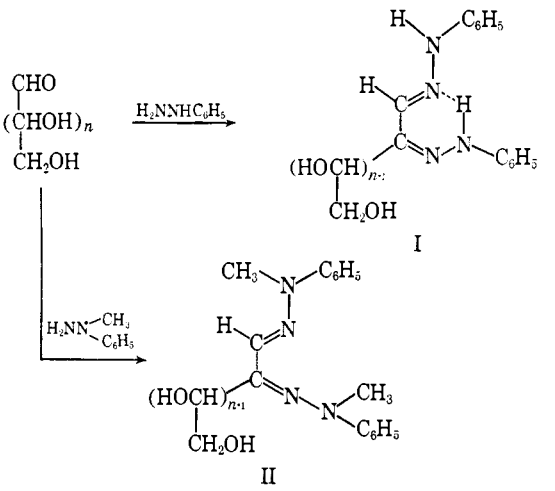
Abstract: Oxidation of 1,3-dihydroxyacetone, erythrose, arabinose, xylose, and fructose is shown to oxidize all hydroxyl functions in the chain in each case giving rise to a new class of compounds for which the name alkazone is suggested. The yield of the alkazone decreases with increasing chain length. In each case a single crystalline alkazone is obtained. The same alkazone is obtained from the stereoisomeric sugars arabinose and xylose. The observed oxidation is consistent with but does not require the Fieser hypothesis that chelate formation is the factor which limits phenylhydrazine oxidation of sugars to osazone formation. Arguments are presented which suggest that chelate formation may not be the factor which limits phenylhydrazine oxidation of sugars.

Fischer's classic study[3] of the phenylhydrazine oxidation of sugars demonstrated that oxidation was limited to osazone formation, *i.e.*, only the hydroxyl function adjacent the carbonyl function was oxidized. It has been suggested[4] that the failure of phenylhydrazine to oxidize sugars further down the chain is associated with chelate formation in the osazone (I). This suggestion has been widely quoted and generally accepted in organic chemistry text books. If chelate formation is the factor responsible for preventing further oxidation, 1-alkylphenylhydrazines would be expected to oxidize down the chain since chelate formation is not possible with alkylphenylosazones (II). This is an obvious corollary of the Fieser chelate hypothesis, but no mention is made of it in discussions of this topic. This omission takes on significance when one reviews the literature of 1-alkylphenylhydrazine oxidation of simple sugars. Only alkylphenylosazones are reported. Furthermore, the logical inconsistency between the explanation given for limitation of phenylhydrazine oxidation and the observation of similarly limited oxidation of sugars by 1-methylphenylhydrazine does not seem to have attracted attention. This inconsistency prompted the present investigation of 1-methylphenylhydrazine oxidation of simple sugars.



I

II

Examination of the literature reveals reports of two methylphenylosazones from 1,3-dihydroxyacetone (or its isomer glyceraldehyde) and one methylphenylosazone each from erythrose, arabinose, xylose, and fructose.[5] The report of two methylphenylosazones (mp

(1) A preliminary account of this work has been published: O. L. Chapman, W. J. Welstead, Jr., T. J. Murphy, and R. W. King, *J. Am. Chem. Soc.*, **86**, 732 (1964).

(2) National Institutes of Health Predoctoral Fellow, 1965–1967.

(3) E. Fischer, *Ber.*, **17**, 579 (1884); **20**, 821 (1887).

(4) L. F. Fieser and M. Fieser, "Organic Chemistry," 2nd ed, D. C. Heath and Co., Boston, Mass., 1950, pp 369–372.

(5) Other methylphenylosazones are known. These are mentioned because the oxidation of each of these by 1-methylphenylhydrazine has been studied in the present work.