lime, concentrated sulfuric acid, and water was then bubbled through the BLMB reaction mixture for 2 min. The flask, carefully covered with aluminum foil, was mounted deep in the water bath at 50.0 ± 0.1°. Aliquots were removed at intervals and diluted with 0.500 *M* sulfuric acid to bring the measured absorbance into the 0.3–0.8 range, where the absorbance-to-concentration dependence was known. The absorbance was determined without delay.

After the first-order logarithmic plot was made, the set of points falling on the straight-line part of the curve was determined, and the slope was found by a least-squares calculation.

Acknowledgment.—We wish to thank The National Cash Register Company, Dayton, Ohio, for grants that supported this work and for help in many ways.

Kinetics and Substituent Effects in Electrophilic Aromatic Substitution. II.[1] Tritylation of Catechol and its Monoethers[2,3]

NÉSTOR BARROETA, GABRIEL CHUCHANI, AND JACOB ZABICKY

Department of Chemistry, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas, Venezuela

Received October 4, 1965

The kinetics of the reaction of trityl perchlorate with catechol, guaiacol, 2-ethoxyphenol, and 2-isopropoxyphenol were followed dilatometrically in nitromethane solvent. Substitution took place by a bimolecular mechanism always at the *para* position relative to a hydroxy group. The monoethers showed an inductive order of activation: $OCH_3 < OC_2H_5 < OCH(CH_3)_2$. The rate of reaction of catechol was always larger than that of guaiacol but comparable with those of the other two ethers. The hydroxyl group has the ability of forming hydrogen bonds both with the solvent and the adjacent group; thus, in spite of not being the most activating when it is alone in the benzene ring (see part I), it can acquire the orientational control of the process. Catechol is faster than guaiacol probably because it can form two hydrogen bonds. Intramolecular hydrogen bonds are believed to be extensive in this series and to constitute the main factor in the orientational control. When no hydrogen bonding is possible, as in the case of 1-ethoxy-2-methoxybenzene, the reaction yields a mixture of the compounds tritylated at positions 4 and 5.

In part I[1] the behavior of phenol and some of its alkyl ethers was studied kinetically on tritylation with trityl perchlorate. In the present work catechol and some of its alkyl ethers were subject to the same reaction and under the same conditions, in order to estimate kinetically both the activation caused by the introduction of two "activating" groups toward electrophilic substitution, and the competition among these groups for orientational control of the process.

The tritylation reaction with trityl perchlorate in nitromethane presented several advantages and disadvantages for the kinetic study of aromatic substitution, which were mentioned and reviewed before.[1] Here it will be added that catechol,[4] guaiacol,[5] and veratrole[5] were tritylated by other authors with triphenylmethanol in the presence of sulfuric acid, according to the Baeyer–Villiger method,[6] and in all three substitution took place at position 4.[7,8]

Results

The rate constants k in Table I represent the average values of second-order initial rate constants, of 9–16 runs, carried out on mixtures in which both reagents were present in concentrations ranging from 0.02 to 0.08 *M*. Being the experimental values "dilatometric rate constants," in units of milliliters liters mole^{-2} hour^{-1}, these had to be divided by 18.69 ml mole^{-1}, which was the average contraction found for the system when 1 mole reacted. The estimates of k allow one to compare the results in this work with those in part I. The kinetic results were sufficiently accurate (about 6% standard deviation) as to enable the appreciation of substituent effects, but not of Arrhenius activation energies, which are shown in Table II. In this table the relative rates of phenol[1] and the substrates studied here compared with that of guaiacol are also shown.

TABLE I

SECOND-ORDER INITIAL RATE CONSTANTS,[a] k, OF THE REACTION OF TRITYL PERCHLORATE WITH AROMATIC SUBSTRATES OF THE TYPE o-$C_6H_4(OH)X$, IN NITROMETHANE SOLVENT

X	30°	40°	50°	60°
OH	0.1332	0.3439	0.5185	1.0080
OCH_3	0.0901	0.2381	0.3992	0.8084
OC_2H_5	0.1164	0.2772	0.5615	1.0801
$OCH(CH_3)_2$	0.1492	0.3199	0.5569	*b*

[a] Units of k, liters mole^{-1} hour^{-1}, estimated from $k_{\text{dilatometric}}$ values in this table. [b] Could not be determined owing to decomposition.

1-Ethoxy-2-methoxybenzene was tritylated under Baeyer–Villiger conditions[6] yielding a mixture of products tritylated at positions 4 and 5.

The tritylation product of 2-ethoxyphenol, with trityl perchlorate in nitromethane or under Baeyer–Villiger conditions, was shown to be 3-ethoxy-4-hydroxytetraphenylmethane, both from its infrared spectrum in the 800–900-cm^{-1} region showing absorption bands typical

(1) Part I: G. Chuchani, H. Díaz, and J. Zabicky, *J. Org. Chem.*, **31**, 1573 (1966).

(2) Presented in part at the Third Caribbean Chemical Symposium, Caracas, Jan 1965.

(3) Abstracted in N. Barroeta, H. Díaz, G. Chuchani, and J. Zabicky, *Acta Cient. Venezolana*, **15**, 248 (1964).

(4) T. Zincke and E. Wugk, *Ann. Chem.*, **363**, 284 (1908).

(5) D. V. N. Hardy, *J. Chem. Soc.*, **1929**, 1000.

(6) A. Baeyer and V. Villiger, *Chem. Ber.*, **35**, 3013 (1902).

(7) Hardy[5] reports a mixture of 4- and 5-tritylated guaiacols under similar conditions. Chuchani[3] prepared the 4 isomer by hydrolysis of the diazonium salt of 4-amino-3-methoxytetraphenylmethane and found it to be identical with the Baeyer–Villiger derivative of guaiacol. This was also found in the present work.

(8) A chemical proof of the position of the trityl group can be deduced from ref 5 and the following papers: F. Sachs and R. Thonet, *Chem. Ber.*, **37**, 3327 (1904); M. Gomberg and G. C. Forrester, *J. Am. Chem. Soc.*, **47**, 2379 (1925); T. R. Lea and R. R. Robinson, *J. Chem. Soc.*, 2351 (1926); G. Chuchani, *ibid.*, 1753 (1959).

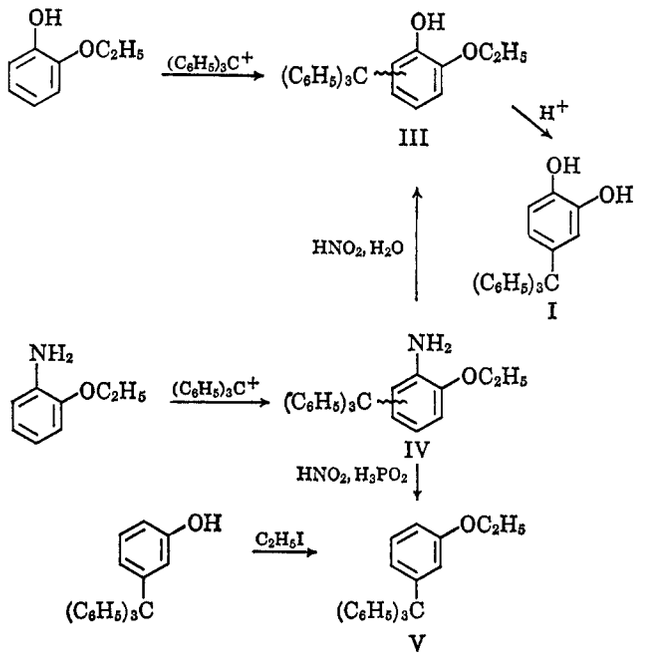


Figure 1.—Tritylation of 2-ethoxyphenol, and elucidation of structure.

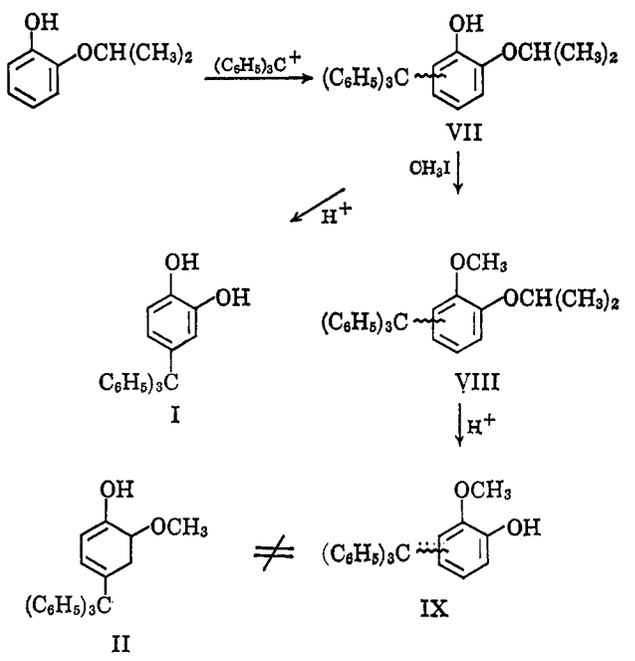


Figure 2.—Tritylation of 2-isopropoxyphenol, and elucidation of structure.

TABLE II

RELATIVE RATES AND ARRHENIUS ACTIVATION ENERGIES[a] OF THE REACTION OF TRITYL PERCHLORATE AND AROMATIC SUBSTRATES, IN NITROMETHANE SOLVENT

Substrate	Relative rates 30°	40°	50°	60°	E_a
Phenol[b]	46	41	45	49	14.4 ± 2.8
Catechol	148	144	130	125	12.7 ± 3.4
Guaiacol	100	100	100	100	11.9 ± 2.3
2-Ethoxyphenol	129	116	141	134	14.6 ± 3.0
2-Isopropoxyphenol	166	134	140	*c*	12.5 ± 0.6

[a] In units of kcal mole^{-1}; standard deviation calculated according to L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press Inc., London, 1963, p 8. [b] Calculated from values in ref 1. [c] Could not be determined owing to decomposition.

of 1,2,4-trisubstituted benzenes,[9] and from the series of reactions in Figure 1.

The tritylation product of 2-isopropoxyphenol, under the two sets of conditions, was shown to be 4-hydroxy-3-isopropoxytetraphenylmethane, both from its infrared spectrum in the 800–900-cm^{-1} region[9] and from the set of reactions in Figure 2.

Attempts to tritylate *o*-phenoxyphenol yielded only amorphous, possibly polymeric, products.

Discussion

When the rate of bromination of phenol[10] is compared with those of the alkoxybenzenes,[11] the former being between one and two orders of magnitude larger than the latter, the control of orientation in electrophilic substitution in the series of *o*-alkoxyphenols could be expected to belong to the hydroxy groups. The same conclusion could however be hardly drawn from the rates observed for phenol and its alkyl ethers on tritylation with trityl perchlorate in nitromethane,[1] the first being larger than that of anisole but smaller than those of phenethole and isopropoxybenzene, and all having their relative rates within a factor of 3. The discrepancy of behavior of the same series of aromatic substrates under various sets of conditions was attributed to the different extents of the electromeric effect when the substrate molecule is in the presence of a bromonium ion or of a trityl carbonium ion, the latter being most stable and probably the less polarizing.

In the case of the *o*-alkoxyphenols it was observed that the hydroxy group controls the orientation to position 4, despite of the rates obtained in part I for the various substituents involved. The control of orientation by the hydroxy group is probably due to its ability to establish hydrogen bonds both with the solvent and intramolecularly with the group in the *ortho* position. When the hydroxy group is hydrogen bonded to the neighboring group an increase of its mesomeric and inductive electron release toward the *para* position relative to it could be expected, as well as a decrease of the same release by the neighboring group to its own *para* position. This would explain both the orientation and the activation series observed for the *o*-alkoxyphenols: The larger the positive inductive effect (basicity)[12] of the alkoxy group, the stronger internal hydrogen bond will be formed and the more reactive the 4 position will be.

Catechol and the *o*-alkoxyphenols were shown to hydrogen bond intramolecularly: the infrared spectra in chloroform and carbon tetrachloride show for catechol two OH stretching bands, one for the bonded and one for the unbonded hydroxy group,[13] and for guaiacol,[14] and *o*-ethoxyphenol[15] only one band, appreciably shifted

(9) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 27.
(10) P. B. D. de la Mare, *Tetrahedron*, **5**, 107 (1959).
(11) G. Baddely, N. H. P. Smith, and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).
(12) W. Gerrard and E. D. Macklen, *Chem. Rev.*, **59**, 1105 (1959); E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).
(13) L. Pauling, *ibid.*, **58**, 94 (1936).
(14) O. R. Wulf, U. Liddel, and S. B. Hendricks, *ibid.*, **58**, 2287 (1936); R. Mecke and A. Reuter, *Z. Naturforsch.*, **4a**, 368 (1949).
(15) M. S. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957).

to frequencies lower than in phenol, indicating extensive intramolecular bonding.

The fact that in 1-ethoxy-2-methoxybenzene the tritylation reaction yielded the mixture of the 4- and 5-trityl derivatives, which could be expected from the results of part I and of Allan and Robinson,[16] while in the case of the *o*-alkoxyphenols orientation was exclusively to position 4, irrespectively of the activations found for the groups in part I, also points at hydrogen bonding being a most important factor in the orientation ability of *o*-alkoxyphenols.

Experimental Section

Materials.—Nitromethane was the commercial solvent purified as previously described.[1] Catechol, guaiacol, and 2-ethoxyphenol were the commercial reagents purified by recrystallizations or distillations under vacuum. 2-Isopropoxyphenol[17] was prepared by the reaction of catechol with 2-iodopropane, and 1-ethoxy-2-methoxybenzene by the reaction of ethyl iodide with guaiacol, according to the general method of etherification described below. 2-Phenoxyphenol was prepared by the demethylation[18] of 1-methoxy-2-phenoxybenzene.[19] Trityl perchlorate and trityl (*^{14}C, uniformly labeled in one ring*) perchlorate were prepared as described before.[1]

General Method of Etherification of Phenols.—The phenolic compound dissolved in 50 times its weight of ethanol was treated with a slight excess of ethanolic sodium ethoxide solution and 1 equiv of the corresponding alkyl iodide, and refluxed for 2 hr. A 10% sodium hydroxide solution (about one-tenth of the volume of the reaction mixture) was then added and the reflux continued for another 4 hr. After the solution was concentrated the ether precipitated on cooling.

3,4-Dihydroxytetraphenylmethane (I).—This was prepared according to Zincke and Wugk.[4]

4-Hydroxy-3-methoxytetraphenylmethane (II).—This was prepared according to Chuchani.[8]

3-Ethoxy-4-hydroxytetraphenylmethane (III).—2-Ethoxyphenol (0.05 mole), triphenylmethanol (0.05 mole), glacial acetic acid (100 ml), and concentrated sulfuric acid (10 ml) were heated at 50° for 2 days. The solid product was recrystallized from ethanol (61%) and had mp 192–193°.

Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 84.91; H, 6.16.

4-Amino-3-ethoxytetraphenylmethane (IV).—*o*-Phenetidine was tritylated with triphenylmethanol in the presence of hydrochloric acid, according to the method of Chuchani.[8] The solid was recrystallized from ethanol–water (72%) and had mp 210°. Attempts to prepare this compound by other methods yielded its N-tritylated derivative (see next synthesis).

Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64; N, 3.69. Found: C, 85.89; H, 6.76; N, 3.83.

3-Ethoxy-4-(N-triphenylmethylamino)tetraphenylmethane. Method 1.—*o*-Phenetidine (20 ml) was added to chlorotriphenylmethane (28 g) and heated at 130–150° for 6 hr. The solid mass was treated with 10% sodium hydroxide solution, filtered off, and washed with ethanol. The product was recrystallized from acetic acid (12 g, 19%) and had mp 253–255°.

Method 2.—Triphenylmethanol (26 g), *o*-phenetidine (13.7 g), glacial acetic acid (500 ml), and concentrated sulfuric acid (20 ml) were heated at 80° for 22 hr. The reaction mixture was diluted with water and treated with excess sodium hydroxide solution. The product was recrystallized from acetic acid (16 g, 25.8%) and had mp 250°, not depressed on admixture with product obtained by method 1. The infrared spectra of the products obtained by both methods were identical.

Anal. Calcd for $C_{46}H_{39}NO$: C, 88.88; H, 6.29; N, 2.25; mol wt, 621. Found: C, 88.87; H, 6.35; N, 2.78; mol wt (Rast), 598.

On refluxing a solution of this compound in the presence of a mineral acid it detritylated to yield IV.

3-Ethoxy-4-hydroxytetraphenylmethane (III) from 4-Amino-3-ethoxytetraphenylmethane (IV).—Compound IV (1.0 g) dissolved in acetone (100 ml) and water (5 ml) was cooled to 0°. Concentrated sulfuric acid (1.5 ml) and a slight excess of sodium nitrite were added, and the mixture was allowed to stand at the same temperature for 1 hr. After adding water (30 ml) and evaporating the acetone, the mixture was treated with concentrated sulfuric acid (3 ml) and refluxed for 2 hr. The resulting product, on recrystallization from acetic acid (0.48 g, 47.9%), had mp 191°, which showed no depression on admixture with the product obtained by direct tritylation of 2-ethoxyphenol (III). Both samples had identical infrared spectra.

3-Ethoxytetraphenylmethane (V) from 4-Amino-3-ethoxytetraphenylmethane (IV).—Compound IV (1.0 g), dissolved in a mixture of acetone (50 ml), 50% hypophosphorous acid (50 ml), and concentrated sulfuric acid (15 ml), was cooled to 0° and then treated with a slight excess of sodium nitrite. The reaction mixture was kept overnight in the refrigerator. The recovered solid, after recrystallization from ethanol (0.4 g, 41.7%), had mp 145°, and showed no depression on admixture with the product (mp 145°, lit.[20] 139–140°) prepared by etherification with ethyl iodide of 3-hydroxytetraphenylmethane (VI).[20] The infrared spectra of both samples were identical.

4-Hydroxy-3-isopropoxytetraphenylmethane (VII).—2-Isopropoxyphenol was tritylated in the conditions described above for the tritylation of 2-ethoxyphenol. The recovered product, after recrystallization from ethanol (70%), had mp 183°.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.29; H, 6.60. Found: C, 85.49; H, 6.64.

This compound (0.5 g), dissolved in glacial acetic acid (20 ml) and concentrated sulfuric acid (0.2 ml), was refluxed for 3 hr, then water (5 ml) was added, and it was allowed to cool. The solid on recrystallization with acetone (0.48 g), had mp 271°, which was not depressed on admixture with a sample of 3,4-dihydroxytetraphenylmethane (I).[4] The infrared spectra of both samples were identical.

3-Isopropoxy-4-methoxytetraphenylmethane (VIII).—Compound VII was etherified with methyl iodide according to the general method described above. The product (87%) had mp 162°.

Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.29; H, 6.87. Found: C, 85.05; H, 6.72.

3-Hydroxy-4-methoxytetraphenylmethane (IX).—The diether VIII (0.070 g), dissolved in glacial acetic acid (20 ml) and concentrated sulfuric acid (0.2 ml), was refluxed for 3.5 hr, then water (5 ml) was added, and the mixture slowly cooled. The product (0.050 g, 71%), after two sublimations, had mp 223°.

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.25; H, 6.02. Found: C, 85.38; H, 5.96.

This product was shown to be different from the tritylation derivative of guaiacol (Chuchani)[8] by their melting points and infrared spectra.

Compound $C_{41}H_{32}$. Method 1.—Triphenylmethanol (9.4 g) and either 2-isopropoxyphenol (5.5 g) or 1,2-diisopropoxybenzene (see below, 7.0 g), dissolved in glacial acetic acid (125 ml) and 100% sulfuric acid (6 ml), were refluxed for 12 hr and then cooled slowly. The recovered solid (1.5 g) had mp 260°.

Method 2.—From the reaction mixtures of trityl perchlorate and 2-isopropoxyphenol used in the kinetic runs, when left in the water bath for several days at 50–60°.

Method 3.—As a by-product of the direct tritylation of isopropoxybenzene previously described.[1]

The mass spectrum[21] of the hydrocarbon showed the parent peak at 524.25 corresponding to the condensed formula $C_{41}H_{32}$.

Anal. Calcd for $C_{41}H_{32}$: C, 93.89; H, 6.11. Found: C, 93.96; H, 6.26.

1,2-Diisopropoxybenzene.—A mixture of catechol (115.6 g) and 2-iodopropane dissolved in ethanol (200 ml) was refluxed with dropwise addition of a 25% potassium hydroxide solution (472 ml) for a period of 6 hr, after which it was refluxed for another 7 hr and the solvent was distilled off. The remanent was treated with more potassium hydroxide solution (500 ml) and steam distilled. The oil (125 g, 61%) had bp 215° (630 mm), $n^{24.8}D$ 1.4844.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.27. Found: C, 73.82; H, 9.18.

(16) J. Allan and R. Robinson, *J. Chem. Soc.*, 376 (1926).
(17) A. J. Birch, *ibid.*, 102 (1947).
(18) H. E. Ungnade and K. T. Zilch, *J. Org. Chem.*, **15**, 1108 (1950).
(19) H. E. Ungnade and E. F. Orwoll, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 566.
(20) R. A. Benkeser and R. B. Gosnell, *J. Org. Chem.*, **22**, 327 (1957).
(21) We thank Professor A. Maccoll of University College London for carrying out the mass spectrum of our sample.

Tritylation of 1-Ethoxy-2-methoxybenzene.—A mixture of this compound (7 g), and triphenylmethanol (12 g), dissolved in glacial acetic acid (200 ml) and concentrated sulfuric acid (9 ml), was heated at 50° for 3 days. The solution was poured into water and the solid, on recrystallization from nitromethane (7 g, 38.6%), had mp 147–149°. The product mixed with triphenylmethanol showed depression of melting point, while on admixture with either 3-ethoxy-4-methoxytetraphenylmethane (X) or 4-ethoxy-3-methoxytetraphenylmethane (XI) the melting point was raised. The infrared spectra of the last two compounds showed that the tritylation product of 1-ethoxy-2-methoxybenzene consisted of a mixture of both.

3-Ethoxy-4-methoxytetraphenylmethane (X).—This was prepared from 3-ethoxy-4-hydroxytetraphenylmethane (III) by etherification with methyl iodide according to the general method described above. The solid (85%), after sublimation under vacuum, had mp 192°.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.29; H, 6.60. Found: C, 84.89; H, 6.77.

4-Ethoxy-3-methoxytetraphenylmethane (XI).—This was prepared from 4-hydroxy-3-methoxytetraphenylmethane (II) by etherification with ethyl iodide according to the general method described above. The solid (78%), after sublimation under vacuum, had mp 159–160°.

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.29; H, 6.60. Found: C, 85.33; H, 6.43.

Product Analysis.—On leaving the most concentrated reaction mixtures used for the kinetic measurements in the water baths for 1 or 2 days, precipitates were recovered which consisted of the pure tritylated derivatives with the trityl group in the position *para* relative to the hydroxy group. The mother liquors yielded only triphenylmethanol and the unreacted substrate. In the case of *o*-isopropoxyphenol, compound $C_{41}H_{32}$ was also recovered after longer stays as described.

Reaction Kinetics.—The dilatometric and radiometric[22] methods followed here were previously described.[1] In this study an average molar contraction for the reaction of 18.69 ± 2.30 ml mole^{-1} was found.

(22) We thank Dr. M. A. Tamers and Mr. A. Carsten for the counting of our radioactive samples.

Protection of the Hydroxyl Group with Vinyl Thioethers

LOUIS A. COHEN AND JOHN A. STEELE

Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014

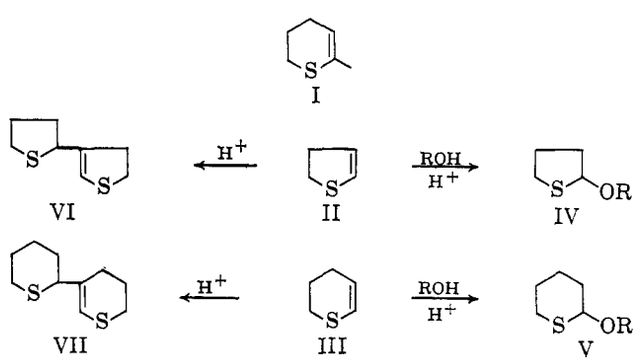
Received February 15, 1966

The cyclic vinyl thioethers, 2,3-dihydrothiophene (II) and 2,3-dihydro-4H-thiopyran (III), react with alcohols, under acid catalysis, by addition to the double bond. The preparation of adducts with cholestanol, cyclopentanol, and 5′-O-acetylthymidine is described. The protective grouping can be removed readily by reaction with silver ion at neutral pH. Implications of the technique for the synthesis of ribonucleotides are discussed.

The intensive efforts which have been devoted to the chemical formation of 3′–5′-interribonucleotide linkages[1] have served to remove a major obstacle from the synthesis of ribonucleic acid chains. An element of prime importance in such a synthesis is the availability of a blocking agent for the 2′-hydroxyl function which can survive a variety of manipulations at other centers and yet be removable under relatively mild conditions. Both these requirements have been met, in previous work, by use of either the tetrahydropyranyl ether[2] or the acetate ester.[3] In the former case, unblocking has sometimes required acid conditions more vigorous than desirable for the total survival of the remaining species; in the latter case, alkaline hydrolysis of the acetate liberates the 2′-hydroxyl which may interact with the neighboring phospho diester function.[1] In either case, the use of acid or alkaline conditions limits the extent to which protective groups may be used for other purposes in other regions of the molecule.

Several years ago, the use of dihydropyran for the protection of sulfhydryl functions in peptide synthesis was explored in this laboratory.[4] It was shown that the adduct obtained with this reagent could survive a variety of chemical treatments and that the blocking group could be ultimately removed by addition of silver or mercuric ions at neutral pH and at low temperatures. It seemed reasonable to suppose that the same reaction, by interchange of the respective hetero atoms, could be applied to the synthesis of ribonucleotides by protection of an hydroxyl function with a sulfur analog of dihydropyran.

The most readily available reagent for this purpose, 2,3-dihydro-6-methyl-4H-thiopyran (I),[5] failed to form a stable adduct with simple alcohols, most likely because of a facile acid-catalyzed reversibility at the tertiary reaction center.



The simpler vinyl thioethers, 2,3-dihydrothiophene (II)[6] and 2,3-dihydro-4H-thiopyran (III),[7,8] behaved as expected, forming the adducts IV and V, respectively. These vinyl thioethers differ from their oxygen analogs by their ease of polymerization in the presence of traces of acid, occasionally with explosive rapidity. Since the addition of an hydroxyl function to the olefinic bond itself requires acid catalysis, it became necessary

(1) For an extensive bibliography, see D. Söll and H. G. Khorana, *J. Am. Chem. Soc.*, **87**, 350, 360 (1965).

(2) M. Smith, D. H. Rammler, I. H. Goldberg, and H. G. Khorana, *ibid.*, **84**, 430 (1962); D. H. Rammler and H. G. Khorana, *ibid.*, **84**, 3112 (1962).

(3) D. H. Rammler, Y. Lapidot, and H. G. Khorana, *ibid.*, **85**, 1989 (1963).

(4) G. F. Holland and L. A. Cohen, *ibid.*, **80**, 3765 (1958).

(5) L. Bateman and R. W. Glazebrook, *J. Chem. Soc.*, 2834 (1958).

(6) G. Sosnovsky, *J. Org. Chem.*, **26**, 281 (1961); *Tetrahedron*, **18**, 15, 903 (1962).

(7) For an alternative method of preparation, *cf.* W. E. Parham, L. Christensen, S. H. Gruen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

(8) Alternatively, 3,4-dihydro-2H-thiopyran.