

TABLE VII

MASS SPECTRAL DATA^a FOR (CH₃)₃N (A.P.I. CATALOG AND OUR DATA) AND FOR TRIMETHYLAMINE FROM DEUTERATED CHOLINE CHLORIDE

Mass (<i>m/e</i>)	(CH ₃) ₃ N		Trimethylamine from deuterated choline chlorides ^c		
	A.P.I.	Ours ^b	≥NCD ₂ - CH ₂ OH	≥NCH ₂ - CD ₂ OH	≥NCH ₂ - CH ₂ OD
14	6.3	5.4	6.8	4.9	5.4
15	33.7	45.5	43.0	37.1	35.0
16	0.5	0.6	1.1	0.6	0.7
57	7.4	8.5	7.5	7.5	6.5
58	100.0	100.0	100.0	100.0	100.0
59	38.7	44.3	43.7	46.9	45.0
60	1.3	1.5	1.6	1.8	1.3

^a Relative peak heights. ^b Trimethylamine, from the radiolysis of ordinary choline chloride, after G.L.C. purification on dimethylsulfolane. ^c Representative data only—either two or three experiments were done on each deuterated choline. For each compound, the separate determinations of trimethylamine mass spectra were in good agreement.

decomposition of crystalline choline chloride. Unfortunately, however, we still have no understanding of *why* choline chloride is so sensitive to ionizing radiation. What we now further know about the mechanism, as a result of the present work, is:

(1) The carbon atoms of the ethanol moiety maintain their identities during the mechanism leading to the production of acetaldehyde—*i.e.*, the oxygen atom

remains attached to the same carbon, and there is no symmetrical intermediate.

(2) None of the hydrogen atoms of the three methyl groups of choline chloride appear in the radiolytically-produced acetaldehyde.

(3) The five hydrogen atoms of the ethanol moiety show considerable mobility during the radiolysis. It is difficult to give quantitative values for these hydrogen transfers, particularly since H-D isotope effects are involved, but the following intramolecular processes do occur:

(a) Unexpectedly, protons (sometimes both) may be lost from the N-methylene group during its transition to the methyl group of the acetaldehyde. Hydrogen from this group may appear in the CHO group of the acetaldehyde. Far more often (10–20 times) an N-CH₂ hydrogen is simply eliminated from the ethanol moiety and appears as HCl.

(b) O-Methylene hydrogens appear to have about equal probabilities of elimination and of appearance in the acetaldehyde methyl group.

(c) Hydroxyl hydrogens usually are eliminated, but their elimination probability is only about twice that of their appearance in the acetaldehyde methyl group. This latter appearance is, in turn, about ten times as probable as appearance in the acetaldehyde CHO group.

(4) Although they are only minor processes, intermolecular hydrogen transfers do take place. Transfers to another molecule occur in the cases of the N-methylene and hydroxyl hydrogens, but do not involve O-methylene hydrogens.

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Bond Angle Calculations in Aromatic Nitrogen-containing Heterocycles¹

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RECEIVED DECEMBER 11, 1962

A calculation is performed of the bond angles in pyridine, pyrazine, pyridazine, pyrimidine, *s*-triazine and *s*-tetrazine by considering interactions between the σ -electrons only. First the approximate molecular energies are determined as functions of the various bond angles which are then obtained by a subsequent minimalization of the energy. The agreement between theory and experiment is reasonable for pyrazine, *s*-triazine and *s*-tetrazine and poor for pyridine and pyrimidine. The possible significance of this trend is discussed.

I. Introduction

Recently one of us reported a rather naïve calculation of the internal bond angles of the triazine molecule.^{2,3} This calculation was based on the assumption that the lone pair electrons on the nitrogens are sp²-hybridized. By performing an approximate calculation of the molecular energy as a function of the internal C-N-C and N-C-N bond angles and by subsequently minimizing this expression it was found that the C-N-C angles should be 110°, which agrees reasonably well with the experimental value⁴ of 113°. Recently we reconsidered this calculation and found a minor error in one of the integrals involved. We also noticed that the repulsion between the σ - and π -electrons had erroneously been omitted. If we correct for these two effects the theoretical value becomes 114°, as will be shown later, and the agreement with experiment

becomes almost perfect. However, it is easily shown that this good agreement cannot be anything but fortuitous. For this purpose we draw a comparison with the results of much more exact and complete calculations, for example the work of Ellison and Shull⁵ on the water molecule. These authors found that the theoretical H-O-H angle is about 120°, which differs by 15° from the experimental value of 105°. Since this calculation, which is much more reliable than our work on *s*-triazine, gives such a large difference between the theoretical and experimental bond angles, we are forced to conclude that the excellent agreement that we obtain for *s*-triazine must be coincidental.

However, it is important to speculate about the nature of the coincidence: Is the good agreement between theory and experiment only a freakish occurrence, limited to the triazine molecule only, or is it caused by the fact that in stating our basic assumptions we fortunately derived a general method to perform a reliable calculation of the part of the molecular energy that depends on the bond angles? One way of finding the answer to this question is to perform a complete calculation of the molecular energy of triazine, but this would be such a difficult problem that we do not even wish to

(1) This study is in part a contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency. The work was also supported by a grant from the U. S. Army Research Office (Durham) to the University of Pennsylvania.

(2) H. F. Hameka and A. M. Liquori, *J. Chem. Phys.*, **24**, 1262 (1956).

(3) H. F. Hameka and A. M. Liquori, *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B*, **59**, 242 (1956).

(4) P. J. Wheatley, *Acta Cryst.*, **8**, 224 (1955).

(5) F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955).

try. There is a second, less rigorous, but more practical way to arrive at an answer. Here we perform the same calculation on a series of different molecules. If the agreement between theory and experiment is satisfactory for all molecules that we have considered, we may claim that we have accidentally derived a reliable theoretical description for the phenomenon that we are studying. If the agreement is good for some molecules, but poor for others, we may try to correlate the agreement with some chemical properties of the molecules that have been considered and thus try to predict for which additional molecules our theoretical description might give reasonable results. This procedure may almost be called the experimental approach to theoretical chemistry; it has been widely applied, especially to larger conjugated organic molecules. For example, the Hückel MO description of π -electron systems and many of its refinements fall in this category.

In this paper we wish to apply this experimental-theoretical approach to a study of the internal bond angles of six-membered aromatic ring systems, composed of carbon and nitrogen atoms. Calculations are performed on pyridine, pyrazine, pyridazine, pyrimidine, *s*-triazine and *s*-tetrazine. An inspection of the available experimental values of the internal bond angles in these molecules shows that the C-N-C, C-N-N and N-N-N bond angles are consistently smaller than 120° , whereas the C-C-C, C-C-N and N-C-N angles are generally, but not always, larger than 120° ; the deviations are always less than 10° . We wish to investigate the possibility that these variations in the bond angles may be explained assuming an sp^2 -hybridization of the lone pair electrons on the nitrogens and by considering the energy of the σ -electrons only. This approach is based on the belief that the effect of the π -electron distribution on the molecular dimensions is negligible in this case.

The theoretical results are obtained by calculating and minimizing the molecular energy as a function of the bond angles. An essential condition for the applicability of the theory is that the bonds are not bent; that is, that the hybridized atomic orbitals point exactly in the directions of the corresponding adjacent nuclei.

Let us now consider the details of the energy calculations. In previous work on the *s*-triazine molecule^{2,3} the part of the energy that depends on the bond angles was taken as a sum of three contributions: (1) the repulsion energy between electrons in the various adjacent bonds and lone pairs; (2) the energy of the C-H and C-N bonds; and (3) the energy necessary to bring the atoms to their valence states, which depends on the promotion energy—that is, the energy required to promote an electron from a $2s$ - to a $2p$ -state. We discovered that there is a fourth comparable contribution to the molecular energy which may influence the calculation of bond angles, namely the Coulomb repulsions between the π - and σ -electrons. In addition, we discovered a minor error in one of the integrals that occur in the calculations; we plan to correct for this.

Apart from the many approximations that are inherent in our proposed model, we will introduce some additional simplifications. In evaluating the interactions between the electrons, only the Coulomb terms are considered and all exchange integrals are neglected. Furthermore, all overlap charges are not explicitly considered and only short range interactions are taken into account.

Apparently we cannot even attempt to estimate the possible errors due to our approximations. All that we can say is that the approximations are consistent with one another. Therefore the significance of our approach depends completely on the accuracy of our

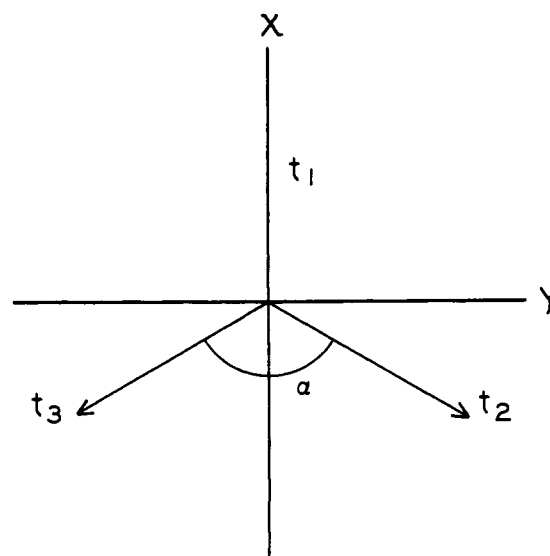


Fig. 1.—Hybridized atomic bonding and lone pair orbitals of nitrogen.

results; if the agreement between theory and experiment is good, we may conclude that we have derived a reasonable theory, even if it lacks a proper foundation; otherwise our method is obviously not practical. It should be pointed out that the same criteria should be applied to Hückel MO calculations on organic conjugated molecules.

II. Energy Calculations

A detailed account of the calculation of the molecular energy as a function of the bond angles along the lines indicated in section I may be found in previous work.³ It may be helpful to repeat the main points of the argument.

Before calculating the energy we must construct the molecular wave function. Since we intend to neglect exchange terms, this function may be represented as a single product with each factor containing one or more hybridized atomic orbitals. Each hybridized atomic σ -orbital will be constructed from atomic Slater orbitals s , p_x and p_y , where we take the z -axis perpendicular to the plane of the molecule. The atomic Slater orbital p_z is taken to participate in the formation of the π -bonds. If we take the direction of the lone pair on a nitrogen atom as the x -axis then we obtain the following hybridized orthonormal orbitals (see Fig. 1)

$$\begin{aligned} t_1 &= a s_N + (1 - a^2)^{1/2} p_{xN} \\ t_2 &= 1/2 \sqrt{2}(1 - a^2)^{1/2} s_N - 1/2 \sqrt{2} a p_{xN} + 1/2 \sqrt{2} p_{yN} \\ t_3 &= 1/2 \sqrt{2}(1 - a^2)^{1/2} s_N - 1/2 \sqrt{2} a p_{xN} - 1/2 \sqrt{2} p_{yN} \end{aligned} \quad (1)$$

where the bond angle α between the bonding orbitals t_2 and t_3 is given by

$$a = \cotg 1/2\alpha \quad (2)$$

Similarly, we have for a carbon atom the hybridized orbitals

$$\begin{aligned} u_1 &= b s_C + (1 - b^2)^{1/2} p_{xC} \\ u_2 &= 1/2 \sqrt{2}(1 - b^2)^{1/2} s_C - 1/2 \sqrt{2} b p_{xC} + 1/2 \sqrt{2} p_{yC} \\ u_3 &= 1/2 \sqrt{2}(1 - b^2)^{1/2} s_C - 1/2 \sqrt{2} b p_{xC} - 1/2 \sqrt{2} p_{yC} \end{aligned} \quad (3)$$

if we take the x -axis here along the C-N bond. The bond angle β between the orbitals u_2 and u_3 is determined by

$$b = \cotg 1/2\beta \quad (4)$$

Each hybridized σ -orbital contains an unknown parameter a or b , which may be directly connected with the bond angle on the corresponding atom through eq. 2 or 4. It may be helpful to observe that in the

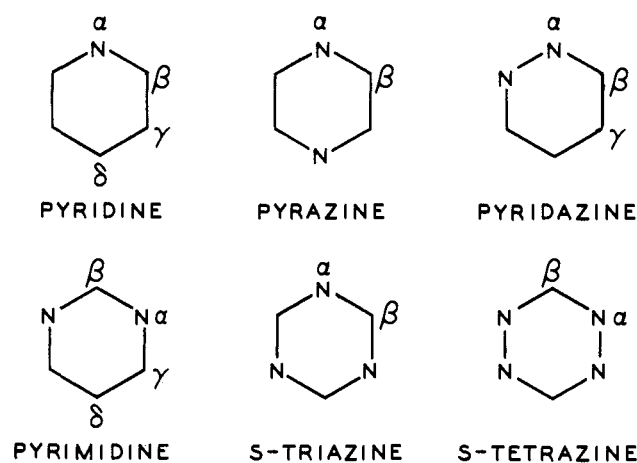


Fig. 2.—Molecules and definitions of bond angles that are calculated.

case of three equivalent sp^2 -hybridized orbitals the hybridization parameter is $3^{-1/2}$ and the bond angles are all 120° . If a or b become smaller than $3^{-1/2}$ the angles α or β become larger than 120° and *vice versa*.

Since we plan to neglect the exchange integrals in evaluating the molecular energy we will represent the molecular wave function of the σ -electrons as a product of one-electron functions, where each one-electron function corresponds to either a σ -bond or lone pair and may be derived from the functions defined in eq. 1 and 3. This molecular wave function will be used as a basis to calculate the various contributions to the molecular energy that were mentioned in section I as a function of the various parameters a and b .

We first consider the Coulomb repulsions between the σ and lone pair electrons centered on one particular nitrogen atom or between the σ -electrons on one particular carbon. If we neglect the exchange integrals, the variations in electronegativity and the overlap charges we may approximate these energies by

$$\begin{aligned} E_C &= 2U_{1,2} + U_{2,3} \\ E_N' &= T_{1,1} + 4T_{1,2} + T_{2,3} \end{aligned} \quad (5)$$

where

$$\begin{aligned} U_{n,m} &= \langle u_n(1)u_m(2) | (e^2/r_{12}) | u_n(1)u_m(2) \rangle \\ T_{n,m} &= \langle t_n(1)t_m(2) | (e^2/r_{12}) | t_n(1)t_m(2) \rangle \end{aligned} \quad (6)$$

By substituting eq. 1 and 3 we may express the energies in terms of the integrals I and J , whose definitions and numerical values are reported in Table I.

TABLE I
DEFINITIONS AND VALUES OF THE ATOMIC INTEGRALS I_k FOR NITROGEN^a

Integral	Definition	Value
I_1	$\langle p_{xN}(1) p_{xN}(2) (e^2/r_{12}) p_{xN}(1) p_{xN}(2) \rangle$	100.2
I_2	$\langle s_N(1) s_N(2) (e^2/r_{12}) s_N(1) s_N(2) \rangle$	93.0
I_3	$\langle p_{xN}(1) p_{yN}(2) (e^2/r_{12}) p_{xN}(1) p_{yN}(2) \rangle$	89.4
I_4	$\langle s_N(1) p_{xN}(2) (e^2/r_{12}) s_N(1) p_{xN}(2) \rangle$	93.0
I_5	$\langle p_{xN}(1) p_{yN}(2) (e^2/r_{12}) p_{yN}(1) p_{xN}(2) \rangle$	5.4
I_6	$\langle s_N(1) p_{xN}(2) (e^2/r_{12}) p_{xN}(1) s_N(2) \rangle$	20.6

^a The energies are expressed in terms of $Q_N = (q_N e^2 / 512a_0)$, where q_N is the effective nuclear charge of the nitrogen Slater orbitals. The corresponding integrals J_k for carbon are similarly defined; they have the same values if they are expressed in terms of $Q_C = (q_C e^2 / 512a_0)$.

$$\begin{aligned} E_C &= \frac{3}{4}(-J_1 + J_4 + 4J_6)b^4 + \frac{1}{2}(2J_1 + J_2 - J_3 - 2J_4 - 2J_5 - 4J_6)b^2 + \text{const.} \\ E_N' &= \frac{3}{4}(-I_1 - I_2 + 2I_4 + 4I_6)a^4 - \frac{1}{2}(3I_2 - 3I_3 - 2I_5 - 4I_6)a^2 + \text{const.} \end{aligned} \quad (7)$$

We should also consider the Coulomb repulsions between the π -electron centered on the nitrogen and the corresponding σ -electrons (the analogous term for the carbons does not depend on the hybridization parameter). This energy term is given by

$$E_N'' = (I_4 - I_3)a^2 + \text{const.} \quad (8)$$

and the sum E_N of E_N' and E_N'' is

$$E_N = \frac{3}{4}(-I_1 - I_2 + 2I_4 + 4I_6)a^4 - \frac{1}{2}(3I_2 - 5I_3 + 2I_4 - 2I_5 - 4I_6)a^2 + \text{const.} \quad (9)$$

Substitution of the values of Table I yields

$$\begin{aligned} E_C &= 18.8Q_C(3b^4 - 2b^2) + \text{const.} \\ E_N &= 18.8Q_N(3a^4 - 2a^2) + \text{const.} \end{aligned} \quad (10)$$

where $Q_C = (q_C e^2 / 512a_0)$ and $Q_N = (q_N e^2 / 512a_0)$. The quantities q_C and q_N are the orbital exponents for the carbon and nitrogen Slater orbitals; their values will be taken as 3.18 and 3.90, respectively.

The various bond energies may all be calculated from the formula

$$E_{XY} = -S_{XY}(1 + S_{XY})^{-1}(I_X I_Y)^{1/2} \quad (11)$$

which was first proposed by Mulliken.⁶ Here E_{XY} is the energy of bond XY, I_X and I_Y are the ionization potentials of atoms X and Y, respectively, and S_{XY} is the overlap integral of the hybridized orbitals forming the bond; it will in general depend on the hybridization parameters a or b of the orbitals on atoms X and Y. The numerical values of the overlap integrals may be obtained from the tables of Mulliken, Rieke, Orloff and Orloff.⁷

A final contribution to the molecular energy arises from the orbital energies of the electrons in the various hybridized atomic orbitals. The part of the energy that depends on the hybridization parameters contains only the difference in energy Δ_N between electrons in a 2p- and a 2s-state on a nitrogen. For one nitrogen atom this energy may be approximated by

$$E_N^p = -\Delta_N a^2 \quad (12)$$

We will take Δ_N equal to 5.12 e.v. (see ref. 3).

The part of the total molecular energy that depends on the hybridization parameters may now be represented as

$$E = \Sigma_C(E_C + E_{CH}) + \Sigma_N(E_N + E_N^p) + \Sigma(E_{CC} + E_{CN} + E_{NN}) \quad (13)$$

where we have to sum over all atoms and bonds. This is a function of six hybridization parameters, and consequently a function of the six internal bond angles. We have determined the minimum of this function for a series of six-membered heterocyclic molecules containing carbon and nitrogen atoms by varying all six internal bond angles in each case with the auxiliary restriction that the sum of the bond angles is 720° . The sets of bond angles for which the energy minima occur have been reported in Table II and Fig. 2.

III. Results and Discussion

The calculations were performed for the molecules pyridine, pyrazine, pyridazine, pyrimidine, *s*-triazine and *s*-tetrazine (see Fig. 2). Experimental bond angles are available for pyridine,⁸ pyrazine,⁹ pyrimidine,¹⁰ *s*-triazine⁴ and *s*-tetrazine.¹¹ The root mean square deviation between the theoretical and experimental values is 3.8° ; the deviation is largest for the angle δ

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(7) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(8) B. Bak, L. Hansen and J. Rastrup-Anderson, *ibid.*, **22**, 2013 (1954).

(9) P. J. Wheatley, *Acta Cryst.*, **10**, 182 (1957).

(10) P. J. Wheatley, *ibid.*, **13**, 80 (1960).

(11) F. Bertinotti, G. Giacomello and A. M. Liquori, *ibid.*, **9**, 510 (1956).

TABLE II
CALCULATED BOND ANGLES AND THEIR EXPERIMENTAL VALUES

Molecule	Angle ^a	Calcd.	Exptl.	Ref.
Pyridine	α	110°	117°	8
	β	121	124	
	γ	122	118.5	
	δ	123	118	
Pyrazine	α	112	115	9
	β	124	122.5	
Pyridazine	α	113		
	β	124		
	γ	123		
Pyrimidine	α	111	115	10
	β	124	128	
	γ	125	123	
	δ	124	116	
<i>s</i> -Triazine	α	114	113	4
	β	126	127	
<i>s</i> -Tetrazine	α	115	116	11
	β	130	127	

^a The various angles are defined in Fig. 2.

in pyrimidine where we predict a value larger than 120° and the experimental result is smaller than 120°.

In judging the values in Table II we should bear in mind that we actually calculate the bond angle deviations from 120°. It follows then that the agreement between calculated and experimental values is good for *s*-triazine, reasonable for *s*-tetrazine and pyrazine and poor for pyridine and pyrimidine. It seems that the agreement becomes better as the molecules have higher symmetry.

In section I we already mentioned that our calculations contain so many approximations that it is difficult to judge the accuracy of the results from purely

theoretical arguments. However, we can make some qualitative statements. The concept of sp²-hybridized lone pair orbitals on the nitrogen and the resulting theory tend to favor a decrease of the bond angles on the nitrogens and an increase of the bond angles on the carbons, as follows from the formulas in section II and from previous considerations.³ It seems that the formulas that result from this concept give a reasonable quantitative prediction for these deviations for the more symmetric molecules; whether or not this is fortuitous is still undecided. This gives us some grounds for concluding that for the more asymmetric molecules like pyridine and pyrimidine there may be some additional effects, apart from the sp²-hybridization of the lone pair electrons, that play a role in determining the molecular dimensions; for example, the interaction between the π -electrons, the bending of bonds, etc. We are tempted to believe that the relative importance of these additional effects is less for *s*-triazine, *s*-tetrazine and pyrazine. Whatever the accuracy of our considerations is, they show clearly that serious errors may result if an attempt is made to calculate the molecular dimensions by considering the π -electron interactions only.

Finally, it may be interesting to speculate about the possibility of extending the above method to bond angle calculations in other molecules. In five-membered heterocycles, such as furan, thiophene, etc., it is fairly certain that the bonds are bent. This means that some additional parameters have to be introduced in the energy calculations, namely the angles between the directions of the hybridized orbitals and the corresponding actual bonds. For more complex aromatic molecules, containing more than one ring system, the interactions between the π -electrons probably play a significant role.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY, SOCORRO, N. M.]

A Correlation of Volume of Activation, Solvent Polarity and Reactant Charge Type for Various Organic Reactions

By K. R. BROWER

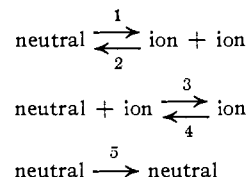
RECEIVED JANUARY 8, 1963

The volumes of activation for organic reactions of various charge types, the partial molar volumes of several organic solutes, and the volume changes of several reactions have been measured for solvents of contrasting polarity. It is found that reactions which involve no change of polarization have essentially the same volume of activation in polar and non-polar solvents, whereas the variation of activation volume for reactions in which ions are created or destroyed amounts to a substantial fraction of the variation of partial molar volumes of electrolytes. A semiquantitative measurement of transition state polarization is thereby provided.

Introduction

It has long been recognized that the volume of activation for reactions in solution reflects not only the intrinsic difference in molecular dimensions of the transition state and reactants, but also the difference in their degrees of solvation.¹ For certain reactions of alkyl and aryl halides with amines the separation of these effects has been attempted by changing the polarity of the solvent and noting the effect on the volume of activation.² This method for diagnosing polarization changes in the activation process appeared sufficiently promising to warrant a test for its reliability for a variety of reactant charge types and solvents. The correlation of reaction rate with solvent polarity for

various charge types has been investigated by Ingold and others,³ and the present study was planned along similar lines. The following set of charge types was selected



An effort was made to restrict the choices to reactions whose mechanism have already been thoroughly studied; thus, type 1 was exemplified by the Menschutkin reaction, 2 by nucleophilic substitution on quaternary ammonium ions and sulfonium ions by phenoxide ion, 3 by nucleophilic substitutions on an alkyl halide

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. VII.

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