pentafluorosulfur (IIb) in 50 ml. of ethyl ether. Evolution of nitrogen continued even after the addition was complete and a total of 5 l. (0.22 mole) was evolved. The solution was distilled to give 10 g. (40%) of (2-azido-2-trifluoromethyl-1-aziridyl)pentafluorosulfur (IVb) as an unstable colorless liquid which on standing slowly loses nitrogen, b.p. 75–76° (150 mm.), $n^{25}D$ 1.3538; infrared maxima (neat) were observed at 4.68 (N_3) and it was transparent in the 6.0-μ region. The F^{19} n.m.r. spectrum showed peaks typical for SF_5 and CF_3 groups and proton n.m.r. (neat) in τ-values at 7.37 and 7.16 (broad peaks, $C{<}^{H_1}_{H_2}$).

Anal. Calcd. for $C_3H_2F_8N_4S$: F, 54.66; N, 20.15; S, 11.53. Found: F, 54.60; N, 19.97; S, 11.57.

On further distillation, there was obtained 3.5 g. of a liquid, b.p. 63–68° (20 mm.). Infrared maxima (neat) were observed at 4.70 (N_3), impurity at 5.9 μ (C=N). F^{19} n.m.r. showed peaks for CF_3 and SF_5, along with unassigned small peaks due to impurities and proton n.m.r. (neat) in τ-values at 7.28 and 7.10 (broad peaks, $C{<}^{H_1}_{H_2}$), 6.10 (singlet, CH_2X). Repeated distillation did not remove the impurities. It is concluded that the major component is (2-azidomethyl-2-trifluoromethyl-1-axiridyl)pentafluoro sulfur (Vb).

1-(3-Azido-2-methylpropenyl)-2,4-dinitrobenzene (IX).—To a dry ethereal diazomethane solution (approximately 0.04 mole) was added 2.0 g. (0.009 mole) of 2-(2,4-dinitrophenyl)-3-methyl-2H-azirine (VIII)[7] in 5 ml. of benzene, and the solution was allowed to stand at 25° for 18 hr. The solvent was evaporated *in vacuo* to give a brown oil which was decolorized by passing it through a column of Woelm neutral alumina using a mixture of 20% benzene–80% petroleum ether (b.p. 00–00°) as eluent. There was obtained 2.0 g. (85%) of 1-(3-azido-2-methylpropenyl)-2,4-dinitrobenzene as a light yellow oil; infrared maxima (neat) were observed at 4.76 (N_3) and 6.06 μ (C=C); ultraviolet maxima in acetonitrile at 245 mμ (ϵ 10,600) and 290 (ϵ 8650); proton n.m.r. in τ-values at 8.9 (singlet CH_3), 6.75 (singlet, CH_2–), 3.97 (singlet, =CH), the aromatic protons being typical for 1,2,4-trisubstituted benzene.

Anal. Calcd. for $C_{10}H_9N_5O_4$: C, 45.63; H, 3.45; N, 26.61. Found: C, 45.72; H, 3.71; N, 26.69.

Acknowledgment.—The author wishes to thank Dr. C. G. Krespan for valuable discussions during the course of this work, Mrs. Adah Richmond for the gas chromatographic analyses, and Mr. C. B. Matthews for the n.m.r. spectra.

Activated Aziridines. I. Reaction of Anilines with O-Ethyl-N,N-Ethyleneurethane. Mechanism and Hammett ρ-Constant

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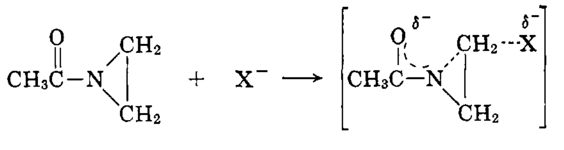
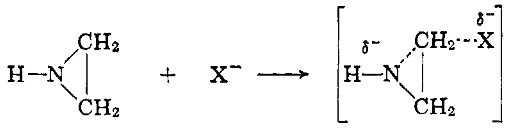
Received February 4, 1964

Classification of N-substituted aziridines into two groups of compounds is proposed. The term "activated" aziridines is suggested for those derivatives which contain substituents capable of stabilizing a negative charge which is formed on the aziridine nitrogen in the transition state when the derivative reacts with a nucleophile. The reaction of aniline or *meta-* or *para*-substituted anilines with the activated aziridine O-ethyl-N,N-ethyleneurethane in anhydrous ethanol at 50° was found to be first order in the aniline derivative and first order in activated aziridine. The reaction gave only a single ring-opened product, O-ethyl-N-(2-anilinoethyl)urethane. Electron-supplying groups in the aniline increased the rate while electron-withdrawing groups caused a decrease. The Hammett ρ-constant under these conditions was found to be -1.47. The data were all consistent with the proposal that the reaction proceeds through a bimolecular displacement by the aniline nitrogen on the aziridine carbon.

Aziridines may be broadly divided into two groups of compounds based on their reactivity toward nucleophilic materials and general properties. These groups are (1) compounds which contain substituents capable of stabilizing a negative charge which is formed on the aziridine nitrogen in the transition state when the compound reacts with a nucleophile, *e.g.*, 1-acetyl aziridine and (2) compounds which contain no such substituent, *e.g.*, ethylenimine, or compounds containing a basic aziridine nitrogen. The ability of the substituent to conjugate with the partial negative charge on the aziridine nitrogen in eq. 1 greatly reduces the activation energy needed to attain this state from that required to attain the transition state 2.[1]


(1)


(2)

The activated aziridines will readily undergo ring-opening reactions with nucleophilic materials in the absence of an acid catalyst as shown by their reaction with amines.[2-5] A number of activated aziridines have also been isomerized or dimerized by heating with nucleophilic ions such as iodide ion.[6] This reaction is presumed to involve nucleophilic attack by the ion on the carbon of the aziridine ring.

Ring-opening reactions involving those compounds in the second group may, in practically all reported cases, be ascribed to the reactivity of the protonated or quaternized aziridine or the Lewis acid adduct of the aziridine. Amines or ammonia react readily with aziridines containing a basic aziridine nitrogen but only

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(1) It should also be noted that such substituents conjugate more readily with nonaziridine nitrogen than with aziridine nitrogen. See H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4551 (1961). Thus much of the lowering of activation energy may be due to increased conjugation of the substituent with the nitrogen as it proceeds from aziridine nitrogen to nonaziridine nitrogen.

(2) Y. Iwakura and A. Nabeya, *J. Org. Chem.*, **25**, 1118 (1960).

(3) D. V. Kashelikar and P. E. Fanta, *ibid.*, **26**, 1841 (1961).

(4) W. Gauss, P. Moser, and G. Schwartzenbach, *Helv. Chim. Acta*, **35**, 2359 (1952).

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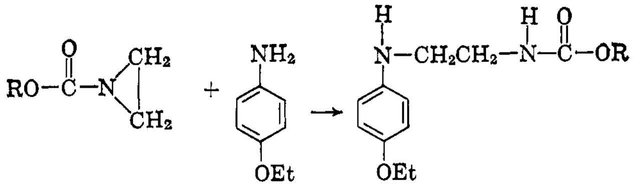
(6) For a review of this isomerization, see H. W. Heine, *Agnew. Chem.* **74**, 772 (1962); *Agnew. Chem., Intern. Ed. Engl.*, **1**, 528 (1962).

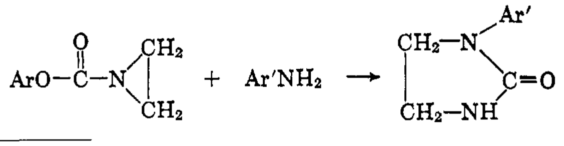
in the presence of acidic catalysts.[7-10] In the absence of acid catalysts no reaction was observed between the basic aziridines and amines even after heating for extended periods.[7,10] Bestian[11] reported that ethylenimine reacts with amines in the absence of acid catalysts but it is probable that minute traces of acidic materials were present in his experiments. Whereas he reported that refluxing anhydrous ethylenimine gently for 28 days caused a 10% conversion to N-(2-aminoethyl)aziridine, it was recently found[12] that a very highly purified sample of ethylenimine could be heated for 8 days at 180° with no greater than 4% conversion to this product.

At the present time there are only a few reports in the literature which give information on the kinetics and mechanism of ring-opening reactions with nucleophilic reagents for the activated aziridines. Although it would seem that such ring-opening reactions should occur analogously to those of aziridines containing a basic aziridine nitrogen (for which kinetic and mechanism studies have been made[13]), we felt it would be of value to offer some information confirming the mechanism.

Several exploratory reactions with O-ethyl-N,N-ethyleneurethane revealed that an apparently clean reaction occurred with aniline. Thus this reaction was chosen for our kinetic work.

The reaction of aniline and substituted anilines with O-alkyl- and aryl-N,N-ethyleneurethanes has been reported by Iwakura and Nabeya.[2] These authors found that O-cyclohexyl-N,N-ethyleneurethane gave, after standing for 2 months with aniline at room temperature, O-cyclohexyl-N-2-anilinoethylurethane in 30% yield, while O-ethyl- or O-n-butyl-N,N-ethyleneurethane failed to give such a product under the same conditions even after 1 year. However, these three O-alkyl derivatives reacted with p-phenetidine to give the corresponding ring-opened products within 1 week at room temperature. When O-aryl-N,N-ethyleneurethanes were treated with anilines the products formed were 1-aryl-2-imidazolidones. Evidence was given to show that the imidazolidones resulted from first ring-opening reaction by the aniline and then ring closure with elimination of the aryloxy group as the phenol.





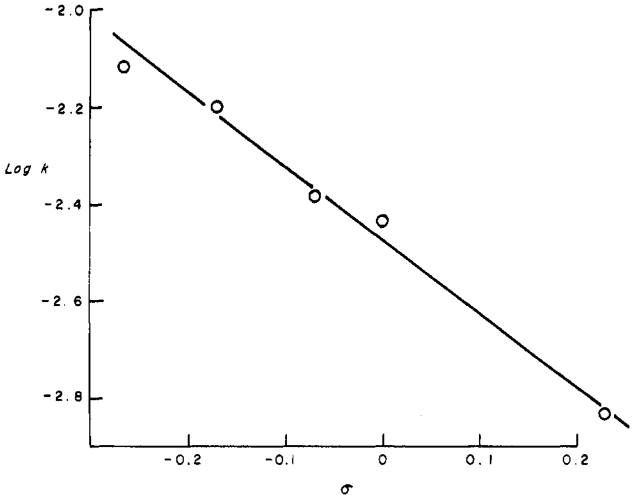
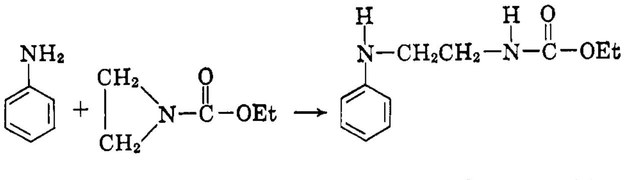
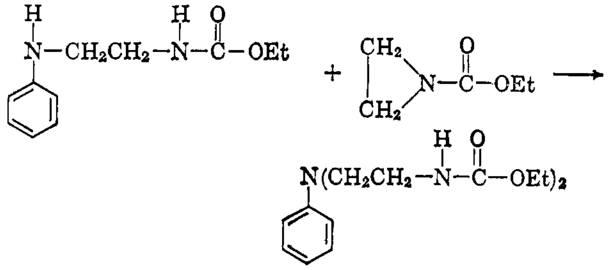


Fig. 1.—Hammett plot for reaction of anilines with O-ethyl-N,N-ethyleneurethane in ethanol at 50°.

In contrast to the results reported by Iwakura and Nabeya, it was found that aniline reacted smoothly and completely with O-ethyl-N,N-ethyleneurethane in ethanol solvent at 50° within 3 days to give the ring-opened product.



The reaction was found to be first order in aniline, first order in O-ethyl-N,N-ethyleneurethane. From a reaction mixture containing equimolar amounts of reactants and carried to 100% conversion under essentially the same conditions as the kinetic experiment, the product obtained was shown by infrared analysis to contain no aniline. Thus, the following was not an important side reaction.



Second-order rate constants were measured for reaction of various substituted anilines with O-ethyl-N,N-ethyleneurethane to determine the effect of the substituent upon the rate. These results are shown in Table I. Electron-supplying groups increased the rate of reaction while electron-withdrawing groups decreased the rate. A Hammett plot was made from the data in Table I giving a ρ-constant of -1.47 for this reaction under the indicated conditions. This plot is shown in Fig. 1. This ρ-constant is a smaller numerical value than ρ-constants reported for reactions of anilines with nitro-substituted aryl halides[14]; however, it is identical with the ρ-constant obtained for reaction

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(11) H. Bestian, *Ann.*, **566**, 210 (1950).

(12) The author is indebted to D. L. Childress, Texas Organic Research Laboratory, The Dow Chemical Co., Freeport, Texas, for this experiment.

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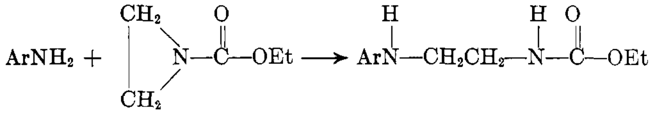
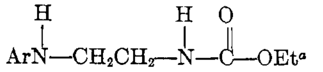
TABLE I

REACTION RATES OF SUBSTITUTED ANILINES WITH O-ETHYL-N,N-ETHYLENEURETHANE IN ETHANOL AT 50°



Ar	10^3k, l. mole^{-1} min.$^{-1}$
p-Methoxyphenyl	7.67
p-Methylphenyl	6.33
m-Methylphenyl	4.11
Phenyl	3.58
p-Chlorophenyl	1.47

TABLE II



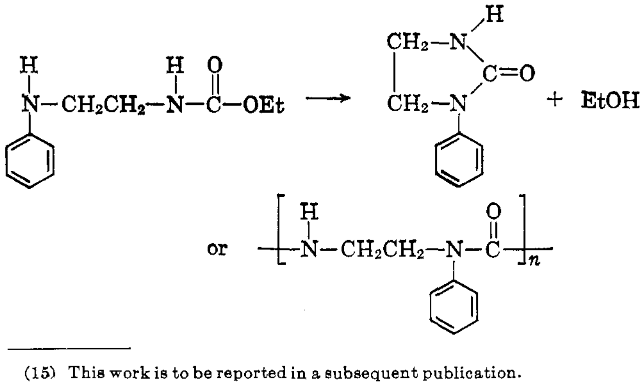
$$\mathrm{ArNH{-}CH_2CH_2{-}NH{-}C(=O){-}OEt}^{a}$$

Ar	n^{20}_{D}	d_{20}	Calcd. % C	Calcd. % H	Calcd. % N	Calcd. MD	Calcd. Neut. equiv.	Found % C	Found % H	Found % N	Found MD	Found Neut. equiv.[b]
Phenyl[c]	1.5440	1.105	63.44	7.74	13.45	59.11	208	63.06	7.69	13.55	59.50	207
p-Methylphenyl	1.5400	1.100	64.84	8.16	12.60	63.73	222	64.28	8.30	12.76	63.40	216
m-Methylphenyl	1.5412	1.104	64.84	8.16	12.60	63.73	222	65.13	8.24	12.86	63.29	216
p-Methoxyphenyl			60.49	7.61	11.77		238	60.39	7.63	12.32		232
p-Chlorophenyl[d]			54.43	6.23	11.54		242	54.35	6.03	12.05		235

[a] Purified only by removal of solvent from reaction mixture of aniline derivative and O-ethyl-N,N-ethyleneurethane. [b] Neutralization equivalent was determined by titration with standard *p*-toluenesulfonic acid in acetic acid solvent to methyl violet end point. [c] B.p 155–159° (0.10 mm.). [d] M.p. 59–61°.

of the anilines with methyl *p*-toluenesulfonate in ethanol at 50°. The value of the ρ-constant for this latter reaction is -1.48.[15]

The kinetic experiments were carried out with an excess of the aniline derivative over O-ethyl-N,N-ethyleneurethane to minimize any reaction of the product with the activated aziridine. A secondary product so formed was isolated in low yield by Iwakura and Nabeya when O-cyclohexyl-N,N-ethyleneurethane was treated with *p*-phenetidine. It was desirable, however, to prepare the ring-opened products under essentially the conditions of the kinetic experiments. This was accomplished by heating at 50° ethanol solutions approximately 1 molar in each reactant for 3 days. In each case removal of the ethanol solvent left a near quantitative yield of the ring-opened product as a clear, slightly colored oil which had an infrared spectrum completely consistent with that expected for the product and which contained none of the starting aniline as determined from the infrared spectra. No further purification was carried out on these products. Analyses are shown in Table II. Attempted distillation of the product obtained from aniline and O-ethyl-N,N-ethyleneurethane resulted in an apparent decomposition reaction which occurred at a pot temperature of about 185°. This decomposition is thought to be due to the preceding reaction. Before significant amounts of decomposition had occurred, a small amount of distillate was obtained with b.p. 155–159° (0.10 mm.). This material had an infrared spectrum identical with that of the product from aniline and O-ethyl-N,N-ethyleneurethane purified only by removal of the ethanol solvent under vacuum.



The second-order kinetics for this reaction, effect of substituent groups in the aniline on the rate, magnitude of the Hammett ρ-constant, and structure of the product isolated are all consistent with the proposal that the reaction proceeds through a bimolecular displacement by the aniline nitrogen on the aziridine carbon.

Experimental

General Procedure for Preparation of the O-Ethyl-N-(2-anilinoethyl)urethanes.—All of these products were prepared exactly according to the procedure shown below for O-ethyl-N-(2-*p*-toluidinoethyl)urethane. Analyses for all of the products are shown in Table II.

p-Toluidine (10.7 g., 0.10 mole) and 11.5 g. (0.10 mole) of O-ethyl-N,N-ethyleneurethane[11] were dissolved in 100 ml. of anhydrous ethanol. The solution was held at 50.0 ± 0.1° by a constant-temperature bath for 3 days. The solvent was then evaporated under reduced pressure (about 1 mm.) at 30° to leave a clear, slightly colored oil. The infrared spectrum of this oil was completely consistent with that expected for O-ethyl-N-(2-*p*-toluidinoethyl)urethane and showed that no unreacted *p*-toluidine was in the product. The weight of product obtained was 21.6 g. (97.4% yield).

Attempted Distillation of O-Ethyl-N-(2-anilinoethyl)urethane.—A distillation was attempted on a sample (13.0 g.) of the product obtained as above from aniline and O-ethyl-N,N-ethyleneurethane. Distillation began at a pot temperature of 175° at 0.10 mm. and a fraction (6.23 g.) was collected with b.p. 155–159° at 0.10 mm. During distillation of this fraction, decomposition began in the pot at a pot temperature of about 185°. As the distillation proceeded and the pot temperature rose, the product in the pot became darker and emitted fumes which were rapidly swept through the distillation apparatus. After collection of the above fraction, distillation ceased and the pot temperature rose to 240°. Infrared analysis of the pot residue indicated the presence of urea linkage. The infrared spectrum of the distillate was identical with that of the original product from aniline and O-ethyl-N,N-ethyleneurethane.

Kinetic Experiments.—All of the kinetic experiments were carried out in exactly the same manner with the exception of one experiment which was carried out at equal molar concentrations of aniline and O-ethyl-N,N-ethyleneurethane to demonstrate that the second-order rate constant was the same as that obtained from an experiment where the aniline concentration was twice that of O-ethyl-N,N-ethyleneurethane. In this manner it was demonstrated that the reaction was first order with respect to both

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(15) This work is to be reported in a subsequent publication.

reactants. The following general procedure was used for the kinetic experiments.

Ten individual samples were prepared which consisted of 5.00 ml. of a 1.00 *M* solution of O-ethyl-N,N-ethyleneurethane in anhydrous ethanol and 5.00 ml. of a 2.00 *M* solution of the aniline derivative in anhydrous ethanol. These samples were then placed in a constant-temperature bath held at 50.0 ± 0.1° and this time recorded as "zero" time. At various time intervals samples were removed and analyzed for unreacted O-ethyl-N,N-ethyleneurethane. This analysis was carried out by adding the sample to 20.0 ml. of a solution of concentrated hydrochloric acid in pyridine which was approximately 0.25 *M* HCl. The pyridine solution was then refluxed for 30 min., cooled, diluted with water, and titrated to a phenolphthalein end point with 0.100 *N* NaOH solution. A blank sample (20.0 ml. of pyridine-HCl solution) was treated in the same manner and the difference in titer for the two samples corresponded to the amount of HCl consumed. The HCl consumed corresponds to the amount of O-ethyl-N,N-ethyleneurethane present in the sample. This method of analysis has been shown to be accurate and reproducible for a number of the activated aziridines.[16]

The rate constants, k, given in Table I were determined from the slope of the line obtained by plotting $[1/(a - b)] \ln [a(b - x)/b(a - x)]$ *vs.* time in minutes, where a is the initial concentration of O-ethyl-N,N-ethyleneurethane, b is the initial concentration of aniline derivative, and x is the amount of O-ethyl-N,N-ethyleneurethane consumed in the reaction at each time. The ρ-constant for the reaction was determined by the method of least squares from a plot of the accepted σ-values[14] for the various substituents *vs.* log k. The standard deviation for the points from the line obtained in this plot was 0.10.

Acknowledgment.—The author gratefully acknowledges the able assistance of Mr. S. A. Sims and Miss Jane Stevens. Infrared spectra of the products were obtained and interpreted by Mr. H. L. Spell.

[16] L. Levine, unpublished results.

Reactions of Aliphatic Methanesulfonates. I. Syntheses of Long-Chain Glyceryl-(1) Ethers[1]

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University of Minnesota, The Hormel Institute, Austin, Minnesota

Received May 15, 1964

Methanesulfonates of saturated and unsaturated long-chain alcohols were prepared and used for syntheses of alkyl glyceryl-(1) ethers (3-alkoxy-1,2-propanediols) by reaction with 1,2-O-isopropylideneglycerol (2,2-dimethyl-1,3-dioxalane-4-methanol).

The use of halides and *p*-toluenesulfonates (tosylates) of unsaturated, long-chain alcohols as alkylating agents has been limited by great difficulties in their isolation[2,3] and purification and by the formation of *trans* isomers.[4] Esters of methanesulfonic acid (mesylates), as described in the present communication, can be easily synthesized without isomerization of double bonds. The mesylates offer additional advantages over tosylates such as simplicity of preparation, lower tendency to form emulsions, better crystallizing properties, and higher stability which recommend their application as alkylating agents. Mesylates of unsaturated, long-chain alcohols have not been described previously, whereas some saturated analogues are known.[5-7] A simple method for the preparation of saturated and unsaturated long-chain mesylates is presented here. The characteristic data and yields of the crystallized and highly purified products are quoted in Table I.

Alkyl glycerol-(1) ethers are ubiquitous constituents of human,[8] animal,[9] and plant[10] tissues. Hexadecyl,[11] octadecyl,[11] and 9-octadecenyl[12] glyceryl-(1) ethers, the most abundant members of this class of compounds, have been synthesized and so have the short-chain homologs up to C-11.[13] Syntheses of other saturated and unsaturated glyceryl-(1) ethers have not been reported, although it is known that these compounds occur naturally.[14]

Reboul[15] has described the first synthesis of a glyceryl-(1) ether in 1860. The procedure, however, starting from epichlorohydrin and sodium ethoxide, has been found unsuitable for the preparation of long-chain homologues.[11] Therefore, Davis, *et al.*,[11] have developed a method for oxidation of allyl alkyl ethers by means of hydrogen peroxide, which has been improved upon later.[16] In the present study additional methods have been investigated using sodium[17] or potassium salts[3,18] of 1,2-O-isopropylideneglycerol[19] and alkyl halides[18] or tosylates,[3,17] and were compared with results obtained from the reaction of metal alkoxides and various alkylating glycerol derivatives.[12,15]

Thin layer adsorption chromatography (t.l.c.) was employed for analyzing the reaction mixtures of a series of experiments. It was found that the use of 1,2-O-isopropylideneglyceryl tosylate as alkylating agent, as suggested by Baer, *et al.*,[12] for the synthesis of glyceryl-(1) ethers, leads invariably to formation of sub-

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