[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Selenium Dehydrogenation of Guaiol and Related Compounds. Selenium as a Hydrogen Transfer Agent

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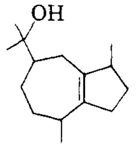
Selenium dehydrogenation of guaiene, two isomeric dihydroguaienes, tetrahydroguaiene and guaiol in *m*-terphenyl as solvent for relatively short reaction times resulted in mixtures of S-guaiazulene (1,4-dimethyl-7-iso-propylazulene) and Se-guaiazulene (2,4-dimethyl-7-iso-propylazulene). The S-guaiazulene appears to be formed first, and then is isomerized to Se-guaiazulene. In experiments with guaiene, it was shown that considerably more guaiazulene was obtained than could be accounted for by the sum of the selenium which disappeared from the solid phase and the hydrogen selenide evolved. The formation of guaiazulene does not result from a stoichiometric reaction with selenium but principally from a disproportionation in which selenium functions as a hydrogen transfer agent. By use of a suitable hydrogen acceptor, the yield of guaiazulene can be improved.

Introduction

Although selenium has long been used as a dehydrogenating agent in the determination of the structures of natural products and often in a final aromatization step in complex syntheses, very little work has been done to investigate possible mechanisms for hydrogen removal by selenium. The dehydrogenation of the naturally-occurring sesquiterpene alcohol, guaiol (I) and related compounds to the interesting guaiazulene aromatics has been reported previously.[1] Preliminary experiments in our laboratory indicated that, during the selenium dehydrogenation, compounds more highly hydrogenated than the starting compound were formed during the dehydrogenation. Furthermore, it has been shown previously[2] that allylic hydrogens are fairly susceptible to selenium attack. For these reasons it was decided to attempt to obtain information on the yields of guaiazulene under comparable conditions from the compounds related to guaiol and having structures II–V.



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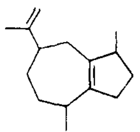

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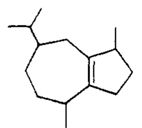

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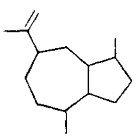

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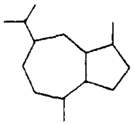

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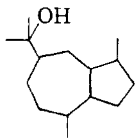

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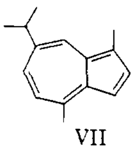

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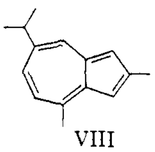

VIII

Reproducible results could not be secured when the compounds were simply heated with selenium, but this difficulty was avoided by carrying out the dehydrogenations in *m*-terphenyl as solvent. The pure *m*-terphenyl did not react with elemental selenium.

Experimental

The selenium employed in all the dehydrogenation reactions was the commercial gray, powdered metallic variety (reagent grade) obtained from Fisher Scientific Co.

Guaiol (I) was isolated from guaiac wood oil (Fritzsche Brothers) by dissolving the oil in acetone and cooling to −10° in an ice–salt–water-bath. The precipitated guaiol was filtered and washed with cold acetone. Three recrystallizations from acetone gave white platelets, m.p. 93°. About 50–60 g. of pure guaiol could be obtained from one pound of the oil. The infrared absorption spectrum of guaiol (mull) showed no absorption in the 1660–1640 cm.$^{-1}$ range although there is a double bond in the molecule. This is not unusual[3] with highly substituted double bonds because of symmetry considerations.

Guaiene (1,4-dimethyl-7-isopropylidene-1,2,3,4,5,6,7,8-octahydroazulene, II) was prepared by dehydration of guaiol (I) with potassium bisulfate. A typical procedure follows. A mixture of 45 g. of guaiol and 22 g. of previously fused and pulverized potassium bisulfate was added to a distilling flask and heated in an oil-bath at 150–160° for about one hour under atmospheric pressure. The product was distilled *in vacuo* to give 20 g. of crude guaiene. The same procedure was carried out on the whole guaiac wood oil, without isolation of the guaiol, and 120 g. of the oil yielded 60 g. of crude guaiene. Infrared spectra of the two crude products were identical. Redistillation yielded a colorless liquid, b.p. 128–130° (12 mm.), $n^{25}\text{D}$ 1.5005, d^{25}_{4} 0.910; literature[4] 119–120° (8 mm.), $n^{20}\text{D}$ 1.5069, $d^{20}{}_{4}$ 0.9035.

Although guaiene is a mixture of isomers, the strong absorptions in the infrared at 1640 and 888 cm.$^{-1}$ would seem to indicate that the isomer represented by II is the principal isomer. This is consistent with the results obtained by O'-Brien and co-workers[5] in the pyrolysis of the phenylazophenylurethan of guaiol.

e-Dihydroguaiene (1,4-dimethyl-7-isopropyl-1,2,3,4,5,-6,7,8-octahydroazulene, III; the prefix *e* is used to denote the isomer which results from the hydrogenation of the external double bond of guaiene) was prepared by partial hydrogenation of II. The internal double bond is rather difficult to saturate[6] and, thus, the external double bond can be preferentially hydrogenated with Raney nickel at low pressure. To 20 g. of guaiene in 150 ml. of 95% ethanol, 5 g. of Raney nickel[7] was added and the mixture was hydrogenated in a Parr apparatus at room temperature. One mole of hydrogen per mole of guaiene was absorbed. After removal of the nickel, the solvent was evaporated and the product distilled. Redistillation gave 15 g. of a colorless liquid, *e*-dihydroguaiene, b.p. 123–124° (11 mm.), $n^{25}\text{D}$ 1.4887, $d^{25}{}_{4}$ 0.891. The infrared spectrum of *e*-dihydroguaiene showed no bands at 1640 and 888 cm.$^{-1}$, both of which were present in guaiene.

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[1] *E. g.*, L. Ruzicka and A. J. Haagen-Smit, *Helv. Chim. Acta*, **14**, 1104 (1931).

[2] J. D. Fitzpatrick and Milton Orchin, THIS JOURNAL, **79**, 4765 (1957).

[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 34.

[4] J. Pliva and F. Sorm, *Coll. Czech. Chem. Comm.*, **14**, 274 (1949).

[5] K. G. O'Brien, A. R. Penfold, N. D. Sutherland and R. L. Werner, *Austral. J. Chem.*, **7**, 298 (1954).

[6] Pl. A. Plattner and L. Lemay, *Helv. Chim. Acta*, **23**, 897 (1940).

[7] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc. New York, N. Y., p. 181.

Dihydroguaiol (VI), m.p. 78–79°, was prepared by hydrogenation of guaiol with Raney nickel[7] under 1500 p.s.i. of hydrogen at 100°, according to the method of Plattner and Lemay.[6]

i-Dihydroguaiene (1,4-dimethyl-7-isopropylidene-1,2,3,-3a,4,5,6,7,8,8a-decahydroazulene, IV; the prefix denotes the isomer which results from the hydrogenation of the internal double bond of guaiene) was prepared by dehydration of VI with potassium bisulfate in the same manner as described above for the dehydration of guaiol. Redistillation of the product gave a colorless liquid, *i*-dihydroguaiene, b.p. 123–124° (11 mm.), $n^{25}\text{D}$ 1.4887, $d^{25}{}_4$ 0.890. The infrared spectrum of *i*-dihydroguaiene showed absorption at 1640 and 888 cm.$^{-1}$ which indicates that IV is the principal isomer.

Tetrahydroguaiene (1,4-dimethyl-7-isopropyl-1,2,3,3a,-4,5,6,7,8,8a-decahydroazulene (V) commonly called guaiane) was prepared by hydrogenation of IV with Raney nickel[7] under low pressure at room temperature in the same manner as described above for the preparation of *e*-dihydroguaiene from guaiene. Redistillation of the product gave a colorless liquid, tetrahydroguaiene, b.p. 118–119° (7 mm.), $n^{25}\text{D}$ 1.4780, $d^{25}{}_4$ 0.880; literature[4] 118° (8 mm.), $n^{20}\text{D}$ 1.4779, $d^{20}{}_4$ 0.8801. The infrared spectrum of tetrahydroguaiene showed no bands at 1640 and 888 cm.$^{-1}$. There are, of course, stereochemically different guaianes, but no attempt was made to discriminate among these.

S-Guaiazulene (VII).—Five grams of guaiene (II) and 1.2 g. of sulfur were heated for two hours at 220°. The hydrogen sulfide was trapped in a lead acetate solution. The reaction mixture was taken up in petroleum ether, filtered to remove unreacted sulfur and, after the solvent was evaporated, the residue was distilled under reduced pressure. The deep blue distillate was again taken up in petroleum ether and extracted with 85% phosphoric acid. The blue color disappeared from the petroleum ether layer and the phosphoric acid layer became dark brown. The phosphoric acid layer was separated, diluted with water, and extracted with ether, the blue color returning to the organic phase. Evaporation of the ether gave 0.562 g. of S-guaiazulene, trinitrobenzene complex, needles, m.p. 154–155° (lit.[8] 151.5°). The trinitrotoluene complex, m.p. 89° (lit.[8] 89°), was prepared in the same way and crystallized as black needles.

The ultraviolet absorption spectrum of S-guaiazulene in 95% ethanol showed maxima at 244, 285, 289 and 304.5 μ with log ε of 4.477 at 244 mμ and 4.633 at 288.5 mμ.

Se-Guaiazulene (VIII).—Four grams of guaiene and 4 g. of selenium were heated for 16 hours at 300–320°. The hydrogen selenide was trapped in a lead acetate solution. The product was worked up in the same manner as described above for S-guaiazulene and 0.106 g. of Se-guaiazulene was obtained. The molecular complex was prepared with trinitrobenzene in the usual way; it crystallized in dark violet needles, m.p. 149–150° (lit.[9] 153°). A mixed melting point of the trinitrobenzene complexes of S guaiazulene and Se-guaiazulene gave a melting range of 138–140°. The ultraviolet absorption spectrum of Se-guaiazulene in 95% ethanol showed maxima at 244, 279.5, 288.5 and 305.5 mμ, with log ε of 4.350 at 244 mμ and 4.730 at 288.5 mμ. The visible spectrum agreed with that in the literature.[9] Dilute solutions of S-guaiazulene are blue, whereas dilute solutions of Se-guaiazulene are violet.

Dehydrogenation Reactions.—The apparatus consisted of a test-tube reactor equipped with a stirrer and two side-arms. Nitrogen was passed through the reactor during the reaction to provide an inert atmosphere and to sweep out the hydrogen selenide into a lead acetate solution. During reaction the reactor was immersed in a constant temperature salt-bath. The heating mantle for the bath was controlled by a powerstat whose voltage was set to maintain the temperature of the bath three or four degrees below the desired temperature. An immersion heater, controlled through a Thermocap Relay, provided auxiliary heat. The temperature was constant to within ±0.5° at 290°. The sample to be dehydrogenated, the selenium and the solvent (when it was used) were heated in the reactor under a stream of nitrogen for the desired reaction time and then allowed to cool. The amount of lead selenide, the amount of unreacted selenium and the amount of guaiazulene formed were determined. After a reaction was complete the reaction mixture was taken up in petroleum ether and the unreacted selenium was filtered and weighed. After removal of the selenium, the petroleum ether solution of the reaction mixture was extracted with 85% phosphoric acid as described under the preparation of S-guaiazulene (VII). After regeneration of the guaiazulene and extraction with petroleum ether, the petroleum ether solution was diluted to 100 ml. An aliquot of this solution was diluted to 100 ml. with 95% ethanol and analyzed spectrophotometrically. The absorptions at 244 and 288.5 mμ were used to calculate the quantity of S-guaiazulene and Se-guaiazulene and the total guaiazulene present was also checked from the absorbance values at the isoabsorptive point[10] at 268.5 mμ. Analysis of mixtures of known concentration by this method gave excellent agreement with theory.

Heating of Selenium and *p*-Terphenyl.—When 0.107 g. of selenium was heated with 0.833 g. of *p*-terphenyl [11] at 270° for 16 hours, no hydrogen selenide was evolved, and the selenium was recovered quantitatively. Some of the selenium did dissolve, forming a red solution, but on cooling was precipitated and recovered.

Isomerization of S-Guaiazulene (VII).—Pure S-guaiazulene (14 mg.) heated in 1 g. of *m*-terphenyl for one hour at 290°. The ultraviolet absorption spectrum of the guaiazulene isolated from this mixture corresponded exactly to pure S-guaiazulene, indicating that there was no thermal isomerization at 290°. However, when 14 mg. of pure S-guaiazulene was heated with 5 mg. of selenium in 1 g. of *m*-terphenyl for only 5 minutes at 290°, the ultraviolet absorption spectrum of the isolated guaiazulene indicated that one-sixth of the S-guaiazulene had been isomerized to Se-guaiazulene.

Results and Discussion

Evidence for S-Guaiazulene as an Intermediate in the Formation of Se-Guaiazulene.—According to the literature,[1,8,12] dehydrogenation of guaiene (II) with sulfur gives S-guaiazulene (VII), whereas dehydrogenation with selenium gives Se-guaiazulene (VIII). Birrell[13] appeared to have obtained VII by selenium dehydrogenation, but did not give experimental details.

In the present work, selenium dehydrogenation of compounds II–V for relatively short reaction times led to mixtures of the two isomeric azulenes. Qualitative evidence was obtained that S-guaiazulene would isomerize to Se-guaiazulene at 290° in the presence of selenium and without hydrogen selenide evolution. The isomerization did not occur in the absence of selenium, although it has been reported[14] that 1-phenylazulene is isomerized thermally to 2-phenylazulene at 330°.

The present study also showed that lowering the selenium dehydrogenation temperature (*m*-terphenyl solvent, 1 hour) from 290 to 270° gave a fivefold lowering of the ratio of VIII/VII, even though the total guaiazulene formed was approximately the same at both temperatures. Furthermore, in experiments at 290°, the ratio of VIII/VII rose from about 5 after one hour to almost 18 after 5 hours even though again the total yield of guaiazulene remained approximately the same.

Discussion of Reaction Sequence.—The experimental evidence may be used to postulate a se-

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[8] A. St. Pfau and Pl. Plattner, *Helv. Chim. Acta*, **19**, 858 (1936).

[9] M. Gordon, *Chem. Revs.*, **50**, 174 (1950).

[10] M. Ish-Shalom, J. D. Fitzpatrick and M. Orchin, *J. Chem. Ed.*, **34**, 496 (1957).

[11] This isomer was employed in some of the early experiments but the *m*-isomer is preferred.

[12] L. Ruzicka and E. A. Randolph, *Helv. Chim. Acta*, **9**, 118 (1936).

[13] K. S. Birrell, THIS JOURNAL, **56**, 1248 (1934).

[14] Pl. Plattner, A. Forst, M. Gordon and K. Zimmerman, *Helv. Chim. Acta*, **33**, 1910 (1950).

quence of reactions which consists of (a) attack of selenium at an allylic position of the substrate, (b) incorporation of the selenium to form an organoselenium compound, (c) disproportionation of the intermediate seleno compounds (or radicals generated therefrom) to produce material more highly saturated than the original as well as aromatic material. It will also be evident that selenium does not function as a stoichiometric reagent to simultaneously abstract two hydrogen atoms with the elimination of hydrogen selenide. Evidence bearing on each of these points is outlined below.

The results of dehydrogenation experiments with compounds II–V under identical conditions are shown in Table I. The decreasing order of yields (based on weight of starting material) is the expected order if the double bond and the number of available allylic hydrogens play important roles as has been proposed earlier.[2]

TABLE I

YIELDS OF GUAIAZULENE FROM DEHYDROGENATION

Conditions: temperature 290°, 1 hr., 2.70×10^{-3} mole of starting compound, 4.05×10^{-3} g. atom of selenium,[a] 2.5 g. of *m*-terphenyl, flow rate 60 ml. N_2/min.

Compound	Recovd. selenium, % As H_2Se	As Se[b]	Yield of guaiazulene, % Based on starting cmpd.	Based on H_2Se[c]
II	1.7 ± 0.1	66.5 ± 0.4	14 ± 1	1600 ± 70
IV	1.8 ± .1	91.2 ± .4	4.9 ± 0.2	540 ± 20
III	2.2 ± .2	91.5 ± .4	2.5 ± .2	420 ± 20
V	3.5 ± .3	93.2 ± .4	0.27 ± .02	27 ± 1

[a] This is one-half the stoichiometric amount of selenium for the reaction: Guaiene + 3Se → guaiazulene + $3H_2Se$. [b] Recovered elemental selenium. [c] Calcd. on basis of one mole of guaiazulene for 3 moles of H_2Se.

The experiments recorded in Table I were performed in *m*-terphenyl solvent. In a series of dehydrogenation experiments using guaiene in the absence of solvent, it was noted that in each reaction the rate of evolution of hydrogen selenide at first increased, reached a maximum and then decreased. This behavior is typical for reactions which proceed through an intermediate which then decomposes to the final product. It is considered here as good evidence for the formation of some intermediate in the production and evolution of hydrogen selenide. If the hydrogen selenide were formed as a result of a direct reaction between the selenium and the hydrocarbon, the maximum rate of evolution would occur at the start of the reaction. The incorporation of selenium was shown in a further experiment in which 3 g. of guaiol was heated with 3.2 g. of selenium for 20 hours at 220°, a temperature which was considerably below the usual dehydrogenation temperature of 290–300°. A trace of hydrogen selenide was liberated during this period. The reaction mixture was taken up in petroleum ether and the unchanged selenium recovered and weighed. The loss in weight indicated that 0.078 g. of selenium had been incorporated. The recovered substrate was returned to the reactor and heated alone for 6 hours at 280°. During this period the evolved hydrogen selenide (0.136 g. of PbSe) corresponded to 48% of the selenium which had been incorporated. Apparently the organoselenium compounds formed at 220° decompose at higher temperatures.

It is apparent from the yields of guaiazulene based on H_2Se evolution shown in the last column of Table I (and Table II) that much more hydrogen is lost in the aromatization of the starting compounds than appears as H_2Se. After one of the dehydrogenations of guaiene in the absence of solvent, the non-aromatic material was recovered. The infrared spectrum of this material differed considerably from that of the starting guaiene. The absorption bands at 1640 and 888 cm.^{-1} were absent indicating that the external double bond of guaiene had disappeared during the reaction, probably due to hydrogenation. The conclusion that a hydrogen transfer reaction is involved in the dehydrogenation is consistent with the early work on the formation of hydrindenes[15a] and chlorestanone from cholesterol[15b] as well as with the recent work of Teeter, Bell, and Danzig[16] in which it was shown that methyl linoleate when heated to 250° with selenium was partially cyclized and aromatized and also was partially hydrogenated to methyl octadecanoates.

If disproportionation, or hydrogen transfer, is the main route to the formation of guaiazulene, it might be expected that carrying out the reaction in a solvent which could act as a hydrogen acceptor would result in an increased yield of guaiazulene. When 5 g. of oleic acid was used in place of the 2.5 g. of *m*-terphenyl in the first reaction in Table I, the yield of guaiazulene was more than doubled and stearic acid could be isolated. These results suggest that the yields of aromatized materials in selenium dehydrogenations of natural products (or intermediates in aromatic syntheses) might be greatly improved by the use of good hydrogen acceptors. Such studies are in progress in this Laboratory.

The results obtained in the selenium dehydrogenation of guaiene with various starting weights of guaiene and selenium are shown in Table II. These data show that the yield of guaiazulene is essentially independent over a wide range of the relative concentration of the reactants. The yields of guaiazulene based on H_2Se evolution again show the non-stoichiometric character of the reaction and the probability of hydrogen transfer reactions. Such hydrogen transfer reactions obvi-

TABLE II

DEHYDROGENATION OF GUAIENE

Conditions: temperature 290°, 1 hr., 2.5 g. of *m*-terphenyl, flow rate 60 ml. of N_2/min.

Starting materials			Yield of guaiazulene, %	
Guaiene, mg.	Se, mg.	Moles guaiene/g. atoms Se	Based on guaiene	Based on H_2Se
552	320[a]	0.68	14 ± 1	1600 ± 60
552	50	4.35	13 ± 1	1500 ± 70
1104	50	8.7	14 ± 1	2000 ± 80
1104	25	17.4	10.5 ± 0.5	1900 ± 80

[a] This is one-half the stoichiometric amount of selenium for the reaction: guaiene + 3Se → guaiazulene + $3H_2Se$.

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(15) (a) L. Ruzicka and E. Peyer, *Helv. Chim. Acta*, **18**, 676 (1935); (b) Doree and Petrow, *J. Chem. Soc.*, 1391 (1935); Yokoyama and Kotake, *Bull. Chem. Soc. Japan*, **10**, 138 (1935).

(16) H. M. Teeter, E. W. Bell and M. J. Danzig, *J. Org. Chem.*, **23**, 1156 (1958).

ously do not occur on the surface of the selenium as they do in the case of platinum and palladium because reducing the amount of selenium did not affect the yield. In fact in the last experiment in Table II all the selenium was in "solution" and the reaction mixture was homogeneous.

Although these studies are not far enough advanced as yet to warrant speculation regarding mechanism, it does appear probable that in many respects selenium attack is analogous to oxygen attack. Reactions involving formation of hydroperselenides and diselenides and cleavage of these to form radical intermediates appear to be important steps.

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CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE HOUDRY LABORATORIES, HOUDRY PROCESS CORP.]

The Catalytic Effects of 1,4-Diaza[2.2.2]bicyclooöctane for Isocyanate Reactions

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The reaction of phenyl isocyanate with either water or 2-ethylhexanol is of the first order with respect to the catalyst concentration, the isocyanate concentration and the water or alcohol concentration. When the 2-ethylhexanol is present in large excess over the phenyl isocyanate, the catalytic effect of triethylenediamine decreases with increasing alcohol concentration while the rate of the uncatalyzed reaction increases. In a solvent-free system the catalytic effect disappears entirely. When either dioxane or benzene is used as a solvent, the reaction of phenyl isocyanate with 2-ethylhexanol is about three times greater than with water. The kinetics of the catalyzed reaction is compatible with the mechanism postulated by Baker and co-workers, but there are other possible mechanisms that cannot be excluded. Comparison of the catalytic activity of triethylenediamine with triethylamine, N,N'-dimethylpiperazine and N-ethylmorpholine shows that it is, respectively, 4.3, 5.3 and 17.3 times greater for the reaction between phenyl isocyanate and 2-ethylhexanol in benzene and 2.7, 2.8 and 5.5 times greater for the reaction between phenyl isocyanate and water in 1,4-dioxane.

The two main reactions of isocyanate group involved in the production of polyurethan foams are the reactions of the isocyanate groups with organic hydroxyl groups and water. The first of these reactions is responsible for chain growth, while the second causes chain extension and provides the carbon dioxide necessary for the foaming.

The kinetics of the reaction with hydroxyl group in the presence of a variety of tertiary amine catalysts has been studied by Baker, Bailey, Dyer, Ephraim and others.[1-7] However, there is very little information on the reaction of isocyanates with water.

In practical tests, it was found that 1,4-diaza-(2.2.2)bicyclooöctane, also called triethylenediamine, is an excellent catalyst in the preparation of polyurethan foams[8,9] and therefore it appeared of interest to collect quantitative data on the activity of this tertiary amine for catalyzing isocyanate reactions in the model system phenyl isocyanate–2-ethylhexanol–water.

The purpose of this paper is to show that triethylenediamine has an unusually high catalytic effect on the reactions in this system.

Experimental

Materials.—Phenyl isocyanate (Fisher certified reagents) and 2-ethylhexanol-1 (Eastman Kodak Co., practical) were fractionally distilled under reduced pressure prior to use. Spectro grade benzene (Eastman Kodak Co.) was refluxed, distilled and stored over calcium hydride. 1,4-Dioxane (Union Carbide Chemicals Co.) was refluxed with sodium until the metal became shiny, doubly distilled from sodium and stored over calcium hydride. A peroxide test on the pure material proved to be negative. DABCO-grade diazabicyclooöctane of the Houdry Process Corp. was purified by sublimation. The product used was of 99.8% purity. The other tertiary bases used, triethylamine (Pennsalt Chemical Corp.), N,N'-dimethylpiperazine and N-ethylmorpholine (Union Carbide Chemicals Co.) were fractionally distilled prior to use.

Procedure.—Stock solutions were prepared by weighing out the correct amount of material and diluting to the proper level using volumetric flasks. Whenever possible, a dry-box was used in effecting transfers.

Reaction mixtures were prepared by adding the desired amount of tertiary base and alcohol to a flask, diluting with solvent short of the calibration mark and adding the proper amount of phenyl isocyanate solution to make up to the mark.

The reaction flasks were stoppered with rubber caps so that samples could be withdrawn at the proper time interval with a hypodermic syringe. The reaction flasks were thermostated with a water-bath at 23°. A few experiments were also carried out at 47°.

A Perkin-Elmer, model 12, infrared spectrometer was used to measure the optical density of the isocyanate peak. Samples withdrawn from the reaction flask were placed in a cell, and the spectrum was scanned in the $4.5\ \mu$ region.[5] When the isocyanate peak was reached the time was noted.

Calibration data showed an almost linear correlation between optical density at $4.33\ \mu$ and isocyanate concentration. None of the solvents or reaction products was found to interfere with isocyanate analysis.

Calculation of the Rate Constants.—The rate constants (k_0 and k_2 for the catalyzed and uncatalyzed reactions, respectively) were calculated on the basis of simple second-order kinetics. In the case of the reaction with water, it was assumed that the rate is controlled by the reaction of phenyl isocyanate with one mole of water to form phenyl-

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(1) J. W. Baker and J. Gaunt, *J. Chem. Soc.*, 9, 19, 27 (1949).

(2) J. W. Baker and J. B. Holdsworth, *ibid.*, 713 (1947).

(3) J. Burkus and C. F. Eckert, THIS JOURNAL, **80**, 5948 (1958).

(4) J. W. Baker, M. M. Davies and J. Gaunt, *J. Chem. Soc.*, 24 (1949).

(5) M. E. Bailey, V. Kirss and R. G. Spaunburgh, *Ind. Eng. Chem.*, **8**, 794 (1956).

(6) E. Dyer, H. A. Taylor, S. J. Mason and J. Samson, THIS JOURNAL, **71**, 4106 (1949).

(7) S. Ephraim, A. E. Woodward and R. B. Mesrobian, *ibid.*, **80**, 1326 (1958).

(8) W. E. Erner, A. Farkas and P. W. Hill, in the course of publication.

(9) R. D. Aylesworth, R. H. Boehringer, D. T. Moore and M. H. Smith, *Modern Plastics*, 145 May (1958).