Anal. Found for copolymer: C, 89.72; H, 7.16. This indicates an approximate composition of 19 mole % vinylphenol, and was confirmed by infrared absorption.

For observing the effects of various catalysts, about 1 g. monomer was dissolved in 10 ml. solvent and placed in a test tube with a trace of initiator. With benzoyl peroxide where no solvent was used, the sample was heated at 60° for 24 hr. With boron trifluoride–etherate and aluminum chloride in hexane and tetrachloroethane, respectively, the polymer precipitated immediately on addition of the initiator, and blue color appeared which darkened on standing. Similarly, polymer was obtained by adding a catalytic amount of sulfuric acid to the monomer in hexane and allowing to stand at room temperature. When the monomer was added to a mixture of sulfuric and glacial acetic acids (1:9 volume ratio), an immediate exothermic reaction occurred. The solution became purple in color, darkened on standing, and increased markedly in viscosity. All of the polymers formed except this one were soluble in ethanol and reprecipitated from water. This polymer was also insoluble in dioxane, acetone, and dimethylformamide, although swellable, and was isolated by pouring the reaction mixture into water.

PLASTICS BASIC RESEARCH LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICH.

The Nitration of Acenaphthene with $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$

J. R. LACHER, KEITH ENSLEY, ANNE TENGE, AND J. D. PARK

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While investigating the behavior of UO_3 in red fuming nitric acid, the compound $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ was prepared. This material has been previously made by Gibson and Katz[1] by reaction of liquid N_2O_4 with hydrated uranium trioxide. The compound shows interesting chemical properties. It reacts violently with aniline and similar substances to produce immediate combustion. It dissolves in many common organic solvents being similar in this respect to uranyl nitrate hexahydrate. With ethyl alcohol and ether it dissolves liberating a colorless gas; in glacial acetic acid it dissolved without gas evolution indicating that this would be a good solvent. A glacial acetic acid solution reacted at room temperature with acenaphthene to give the 5-nitro derivative, while an acetic anhydride solution reacted in the cold to give 5,6-dinitroacenaphthene.

The nitrating ability of the compound could be explained in the manner proposed for $BF_3 \cdot N_2O_4$ by Bachman *et al.*[2,3] The uranyl nitrate exhibits electronegative properties similar to those of BF_3 and thus it might have the ability to distort the N_2O_4 in the following manner: $H_2O \cdot UO_2(NO_3)_2 + O_2N \vdots 1NO_2 = (H_2O \cdot UO_2(NO_3)_2 \leftarrow NO_2)^{-}NO_2^{+}$. This distortion produces a nitronium ion which according to present theory is necessary for nitration.

EXPERIMENTAL

The presence of N_2O_4 in the compound was established by treating it with ether and collecting the colorless gas evolved in an inverted test tube filled with ether. The test tube was stoppered and cooled in a dry ice–cellosolve bath and a colorless liquid was obtained. When a small fragment of ice was added to the liquid, a deep blue color was obtained, indicating the presence of N_2O_4 by formation of N_2O_3.[4] The liquid was warmed and the presence of NO_2 determined by odor and color. An analysis of compound gave 56.7% uranium oxide and 10.9% nitrogen (Du Pont Nitrometer). Theoretical for $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ is 56.7% UO_3 and 11.1% N.

The procedure used in the nitration of acenaphthene was similar to the method employed by Sacks and Mosebach[5] in the preparation of 5 nitroacenaphthene but replacing nitric acid as the nitration agent with $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$. Two g. of acenaphthene were suspended in 16 ml. of glacial acetic acid. A solution containing 7.56 g. of $UO_2(NO_3)_2 \cdot H_2O.N_2O_4$ dissolved in glacial acetic acid was slowly added to the acenaphthene suspension at room temperature. After most of the nitrating reagent had been added, the material present suddenly dissolved and was immediately followed by the formation of a yellow precipitate. This yellow crystalline product after two recrystallizations with glacial acetic acid gave a melting point of 100–102°. The melting point previously reported for the nitroacenaphthene was 101–102°.

In an attempted preparation of 3-nitroacenaphthene the method of Morgan and Harrison[6] was employed. The reaction was carried out in acetic anhydride below 0°. Again the uranium compound replaced the nitric acid as a nitrating agent. Two g. of acenaphthene were dissolved in 135 ml. of acetic anhydride and cooled to −5°; 7.56 g. of $UO_2(NO_3)_2 \cdot H_2O \cdot N_2O_4$ were dissolved in a small amount of acetic anhydride and the resulting solution added slowly to the acenaphthene solution. About 1 hr. was required for the addition of nitrating mixture. The reacting mixture was stirred continuously at a temperature near −7°. When only a small amount of the nitrating solution remained to be added, the temperature suddenly rose to 10° and changed from a yellow color to brownish green. The mixture was then cooled again and a yellow-green color was observed. The resulting mixture was added to cold water in order to dissolve the uranyl nitrate and precipitate the nitrated compound. The crude product (1.5 g.) was obtained while the theoretical yield for mononitroacenaphthene is 1.3 g. and 1.6 g. for the dinitroacenaphthene. After recrystallization twice with acetic acid a melting point of 175.5–177° was obtained. After recrystallization a third time followed by drying for 8 hr. under a vacuum, a melting point of 203–205° was observed. This melting point corresponds closely to the 5,6-dinitroacenaphthene whose melting point has been recorded as 210–212.[7] Chemical analysis of the nitro product obtained was as follows: C, 59.39%; H, 3.5%, N, 11.23%; and by difference 0, 25.79%. The theoretical per cents for the dinitroacenaphthene are: C, 59.02%; H, 3.30%; N, 11.47% and 0, 26.20%. The infrared spectra of the compound prepared here were identical to that given by a known sample of 5,6-dinitroacenaphthene. It has been reported[8] that nitrogen

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tetroxide reacts with acenaphthene to give 5,6-dinitroacenaphthene.

The nitro derivatives gave the correct color tests with concentrated H_2SO_4 as described by ref. 6.

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CHEMISTRY LABORATORIES
UNIVERSITY OF COLORADO
BOULDER, COLO.

Quaternary Ammonium Salts of 1,4-Diazabicyclo[2.2.2]octane

SHIGERU OAE, BERT HOVARTH,
CLYDE ZALUT, AND ROBERT HARRIS

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The interesting pharmacologic properties of quaternary ammonium derivatives of piperidine[1] prompted us to synthesize a number of "bicyclic" quaternary ammonium derivatives of 1,4-diazabicyclo[2.2.2]octane, which has recently become commercially available.[2] All the compounds, listed in Table I, were prepared by a simple substitution reaction (S_N2) in a suitable solvent.

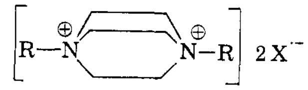
We have tried the substitution with secondary bromides, such as 2-bromobutane and isopropyl bromide. The reaction product in these two cases was monoalkylated quaternary ammonium dibromide. Apparently both elimination and substitution reactions took place simultaneously, changing half of the starting alkyl bromides to the corresponding olefins. With 2-bromoacetate and 4-bromo-pentan-1-ol, the main reaction was elimination, giving 1,4-diazabicyclo[2.2.2]octane dihydrogen dibromide as the only isolable crystalline products, even when the reaction mixture was kept at room temperature. A few typical runs are described in the Experimental.

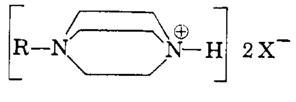
EXPERIMENTAL

1,4-Dialkyl-1,4-diazabicyclo[2.2.2]octane diiodide. 1,4-Diazabicyclo[2.2.2]octane (0.05 mole) was dissolved in 50 ml. of methanol. To this solution, 0.1 mole of alkyl iodide was added and the mixture was refluxed for 1 to 2 hr. On standing at room temperature overnight, after removing about half of the solvent, crystalline product formed. Crystals were collected and recrystallized 2 or 3 times from methanol. Yields were almost quantitative.

1,4-Dialkyl-1,4-diazabicyclo[2.2.2]octane dibromide. 1,4-Diazabicyclo[2.2.2]octane (0.025 mole) was dissolved in 100 ml. of warm carbon tetrachloride. To this solution 0.05 mole of alkyl bromide was added at once and the mixture was refluxed for 1 to 16 hr. depending on starting compound.

TABLE I



R	X	Reaction Medium	Refluxing Time 3 Hr.	M.P., °C. (with decomposition)	Formula	Yield	Calcd.		Found	
							C, %	H, %	C, %	H, %
CH_3—	I	Ethanol	1	260	$C_8H_{18}N_2I_2$	90	24.25	4.55	24.27	4.57
C_2H_5—	I	Methanol	2	248	$C_{10}H_{22}N_2I_2$	96	28.31	5.19	28.34	5.27
n-C_4H_9	I	Methanol	2	220	$C_{14}H_{30}N_2I_2$	90	35.01	6.25	34.95	6.41
n-$C_{11}H_{23}$—	Br	CCl_4	6	194	$C_{28}H_{58}N_2Br_2$	87	57.60	9.95	57.67	9.88
n-$C_{14}H_{29}$—	Br	Acetone	6	282	$C_{34}H_{70}N_2Br_2$	92	61.28	10.51	61.11	10.54
n-$C_{16}H_{33}$—	Br	CCl_4	6	285	$C_{38}H_{78}N_2Br_2$	83	63.17	10.81	63.35	10.86
Benzyl-	Cl	Ethanol	3	295	$C_{20}H_{26}N_2Cl_2$	93	65.70	7.20	65.75	7.47
HO—CH_2CH_2—	Br	Ethanol	16	208	$C_{10}H_{22}N_2Cl_2O_2$	52	33.20	6.14	32.21	6.13
$C_2H_5O{-}\overset{O}{\overset{\Vert}{C}}{-}CH_2$	Br	CCl_4	1	193	$C_{14}H_{26}N_2Br_2O_4$	75	37.60	5.90	37.53	5.95
HOOC—CH_2CH_2—	Br	CCl_4	1	345	$C_{12}H_{22}N_2Br_2O_4$	85	34.50	4.31	33.65	5.41
										
iso-C_3H_7—	Br	CCl_4	2	228	$C_9H_{23}N_2Br_2$	66	34.20	6.40	34.0	6.60
s-C_4H_9	Br	MeOH	3	340	$C_{10}H_{25}N_2Br_2$	58	36.10	7.60	36.05	6.65

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