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

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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.

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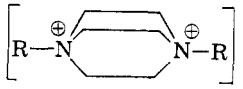
EXPERIMENTAL

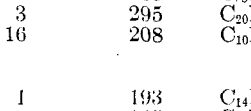
1,4-Dialkyl-1,4-diazabicyclo[2.2.2]octane diiodide. 1,4-Diazabicyclo[2.2.2]octane (0.05 mole) was dissolved in 50 ml. of methanol. To this solution, 0.1 mole of alkyl iodide was added and the mixture was refluxed for 1 to 2 hr. On standing at room temperature overnight, after removing about half of the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

1,4-Dialkyl-1,/-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.

(2) Houdry Process Corp., Philadelphia 2, Pa.

TABLE I



R	X	Reaction Medium	Refluxing Time 3 Hr.	M.P., °C. (with decomposition)	Formula	Yield	Calcd. C, %	Calcd. H, %	Found C, %	Found 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—C(=O)—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

On standing for 48 hr. at room temperature, clusters of colorless crystals formed. The product was collected and recrystallized from hot ethanol.

The same reaction condition was applied for bromide and 2-bromobutane. Evolution of olefinic gas was detected in both cases and when cooled a large quantity of colorless crystals formed. Recrystallization from aqueous acetone and ether gave colorless crystals of m.p. 228°.

Both 2-bromoethylacetate and 4-bromopentan-1-ol were reacted in the same way in methanol solution. After methanol was removed, colorless hygroscopic crystals were obtained in large quantity. This was recrystallized from ethanol, m.p. 319° with decomposition. Mixed melting point with authentic sample of 1,4-dihydro-1,4-diazabicyclo[2.2.2]octane dibromide of m.p. 319° did not show depression.

Anal. Calcd. for $C_6H_{14}N_2Br_2$ C, 26.4; H, 5.15. Found: C, 26.63; H, 5.41.

The results of physiological tests indicate that 1,4-diazabicyclo[2.2.2]octane bis(hexadecylbromide) has some activity against microorganisms while 1,4-diazabicylo[2.2.2]-octane bis(tetradecylbromide) shows a little CNS depressant activity in mice.

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Reaction of Triphenylsilyllithium and of Triphenylsilylpotassium with Benzaldehyde

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It has been reported recently that silyllithium compounds add to the carbonyl group of aliphatic ketones to give α-silylcarbinols.[1] From the reaction of triphenylsilylpotassium and −lithium with aromatic ketones, however, "abnormal" addition products resulted, in which the silicon atom is bonded to oxygen.[2,3] Two reactions show that silylmetallic compounds add in a "normal" manner to aliphatic aldehydes. Triphenylsilylmethanol was obtained from the reaction of triphenylsilylpotassium with formaldehyde,[4] and 1-(triphenylsilyl)-ethanol was synthesized from acetaldehyde and the corresponding silyllithium reagent.[5] In an extension of these studies, the reaction of triphenylsilyllithium and of triphenylsilylpotassium with benzaldehyde has been investigated.

Rapid addition of one equivalent of benzaldehyde (II) to triphenylsilyllithium (I) at −60° yielded benzyloxytriphenylsilane (V) in fair yield. Prior to hydrolysis, the reaction mixture gave a strongly positive Color Test I.[6] When a second equivalent of benzaldehyde was added, Color Test I was negative, and no benzyloxytriphenylsilane was isolated. Instead, the monotriphenylsilyl ether of 1,2-dihydroxy-1,2-diphenylethane (VI, with hydrogen replacing lithium) was obtained as a mixture of isomers. At room temperature, using a slow rate of addition, triphenylsilyllithium reacted further with the alkoxysilane-type intermediate VI to give hexaphenyldisilane and 1,2-dihydroxy-1,2-diphenylethane, the latter compound as a mixture of its stereoisomers.

Whereas benzyl ethers, the carbon analogs of V, rearrange upon treatment with phenyllithium to give the corresponding carbinols,[7] Brook, in

$$C_6H_5CH_2OR \xrightarrow{C_6H_5Li} C_6H_5CH(Li)OR \longrightarrow C_6H_5CH(R)OLi$$

some attractive studies, observed that phenyl-substituted α-silylcarbinols in the presence of catalytic amounts of base undergo the reverse rearrangement to give the corresponding alkoxysilanes.[8] Diphenyl(triphenylsilyl)methanol was shown to form triphenyl(diphenylmethoxy)silane by rearrangement,[8] and, similarly, phenyl(triphenylsilyl)methanol yielded benzyloxytriphenylsilane.[9]

$$(C_6H_5)_3Si{-}CH(OH){-}C_6H_5 \longrightarrow (C_6H_5)_3Si{-}O{-}CH_2{-}C_6H_5$$

The course of the reaction of I with II might therefore be explained by assuming that in the first step a "normal" addition takes place to give III, which immediately rearranges with the formation of IV. The organometallic reagent IV yields benzyloxytriphenylsilane (V) on hydrolysis, while treatment with another equivalent of benzaldehyde gives VI. Since alkoxytriphenylsilanes are reported[10] to react with triphenylsilylmetallic compounds with the formation of hexaphenyldisilane, the isolation of large amounts of the latter can be easily explained from the reaction of I and VI. To our surprise, large amounts of hexaphenyldisi-

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