EXPERIMENTAL

The n-heptane solvent was freed from olefinic contaminant by passage through a silica gel chromatographic column and then dried by distillation from sodium metal. The dioxane solvent was purified according to the method of Fieser.[6]

Dipole moment study. The dipole moment of 2-bromocyclooctanone in n-heptane and dioxane solution was determined at 25°. The data were treated by the method of Halverstadt and Kumler,[7] and the actual calculations were performed by applying automatic computing methods with an IBM 650 computer as described earlier.[8]

The molar refractivity was calculated from standard values of atomic refractivities[9] and had the value 44.720 cc. Atomic polarization was neglected. The data are summarized in Table III.

TABLE III

DIPOLE MOMENT DATA FOR 2-BROMOCYCLOOCTANONE AT 25°

N_2	d_{12}	ϵ_{12}
Dioxane Solvent		
0.0071283	1.031228	2.3191
0.0041682	1.029428	2.2697
0.0027629	1.028583	2.2465
0.0016669	1.027949	2.2283
0.0008651	1.027463	2.2143
0.0000000	1.026897	2.2013
$\alpha = 16.5874$	$\beta = 0.6039$	$\epsilon_1 = 2.2007$
$d_1 = 1.026921$	$P_{2\infty} = 284.60$	$\mu = 3.426$D
n-Heptane Solvent		
0.0079180	0.683125	1.9706
0.0059871	0.681701	1.9547
0.0041774	0.680434	1.9409
0.0024350	0.679182	1.9261
0.0012521	0.678316	1.9174
0.0000000	0.677423	1.9069
$\alpha = 8.0093$	$\beta = 0.7188$	$\epsilon_1 = 1.9070$
$d_1 = 0.677422$	$P_{2\infty} = 266.67$	$\mu = 3.295$D

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N-Bromocaprolactam

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In the course of investigating the halogenation of caprolactam we had occasion to prepare the heretofore unknown *N*-bromocaprolactam. We have found that *N*-bromocaprolactam is useful as a brominating agent in much the same manner as *N*-bromosuccinimide,[1] *N*-bromophthalimide[2] and *N*-bromo-5,5-dimethylhydantoin.[3] We have also found that the new *N*-bromo derivative functions in many instances as an oxidizing agent in the same manner as *N*-bromoacetamide.[4] Whereas the known *N*-bromo-derivatives usually require a peroxide catalyst and/or actinic light to initiate bromination, *N*-bromocaprolactam can be employed without the aid of a catalyst.

The *N*-bromocaprolactam can be prepared following the procedure of Oliveto[5] for the synthesis of *N*-bromoacetamide. However, the product obtained by this method is usually difficult to crystallize, and in most cases can be purified only after several recrystallizations from water. We have found that a relatively pure *N*-bromocaprolactam can be obtained by a modified procedure, which involves adding liquid bromine to an aqueous solution of caprolactam followed by the addition of 50% aqueous potassium or sodium hydroxide until the bromine color is discharged, and treating the resultant solution with common salt to precipitate the *N*-bromocaprolactam, which after several ice water washes, melts at 64–66°.

EXPERIMENTAL

N-Bromocaprolactam. Into a flask equipped with an agitator, thermometer, and dropping funnel was placed a mixture of 271.2 g. (2.4 mol.) of caprolactam and 90 ml. of water. The reaction mixture was cooled to about 0° by an ice-salt bath, following which 320 g. (2.0 mol.) of liquid bromine was added dropwise over a 30-min. period. After the addition was complete, 270 ml. of a 50% aqueous potassium hydroxide solution (previously cooled to 10°) was added dropwise maintaining the temperature of the reaction mixture below 10° throughout the addition. The resultant yellow solution was stirred at ice temperatures for an additional 2 hr., following which 80 g. of sodium chloride was added, effecting precipitation of the *N*-bromocaprolactam. The product was filtered, washed thoroughly with ice water, and dried at room temperature *in vacuo*. There was obtained 288 g. (75%) of *N*-bromocaprolactam; m.p. 64–66°.

Anal. Calcd. for $C_6H_{10}NOBr$: Br, 41.6; N, 7.3. Found: Br, 41.2; N, 7.0.

4-Bromoacetanilide. Into a flask equipped with an agitator and reflux condenser was placed a solution of 13.5 g. (0.1 mol.) of acetanilide in 100 ml. of chloroform. Then while stirring, 19.2 g. (0.1 mol.) of *N*-bromocaprolactam was added all at once. After a short induction period (*ca.* 15 min.), the reaction mixture began to reflux, after which the solution was stirred at room temperature for 2 hr. The solid residue obtained after evaporating the solvent was washed with cold water to remove the caprolactam formed during

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the reaction. There was obtained 18 g. (84%) of 4-bromoacetanilide; m.p. 165°; lit.[6a] 167°.

5-Bromoisatin. A suspension of 16.2 g. (0.11 mol.) of isatin in 100 ml. of carbon tetrachloride was treated with 21.2 g. (0.11 mol.) of *N*-bromocaprolactam. The reaction mixture was heated to reflux to initiate bromination, following which it was stirred at room temperature overnight. The insoluble product was filtered, washed with carbon tetrachloride to insure the removal of residual caprolactam, and finally dried. There was obtained 19 g. (77%) of 5-bromoisatin; m.p. 254–256°; lit.[7] m.p. 255–256°.

Cyclohexanone. Into a flask equipped with a stirrer and reflux condenser were placed 5 g. (0.05 mol.) cyclohexanol, 75 ml. benzene, and 10 ml. pyridine. While agitating, 9.6 g. (0.05 mol.) of *N*-bromocaprolactam was added all at once. After a short induction period (*ca.* 15 min.), an exothermic reaction occurred, causing the benzene to reflux. The mixture was then allowed to stir without further application of heat for 18 hr. The solid pyridine hydrobromide was filtered. The filtrate was washed with a dilute aqueous solution of sodium hydrosulfite to decompose any unreacted *N*-bromocaprolactam, following which the organic layer was washed successively with two 50-ml. portions of 2*N* sulfuric acid, two 50-ml. portions of distilled water, and finally dried over anhydrous sodium sulfate. After removing the benzene by distillation, there was obtained 4 g. (82%) of cyclohexanone. The ketone was identified by converting it to its 2,4-dinitrophenylhydrazone; m.p. 159°; lit.[6b] 162°.

Benzophenone. To a solution of 9.2 g. (0.05 mol.) of benzhydrol in 75 ml. of benzene was added 10 ml. of pyridine, following which 9.6 g. (0.05 mol.) of *N*-bromocaprolactam was added all at once. The solution was refluxed for 1 hr. to initiate the reaction, following which the mixture was stirred at room temperature for 18 hr.

The product was isolated as in the previous experiment. There was obtained 8 g. (88%) of benzophenone; 2,4-dinitrophenylhydrazone; m.p. 239–240°; lit.[6c] 239°.

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Oxidation of Hindered Phenols. Preparation of Bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadiene-4-one) Peroxide

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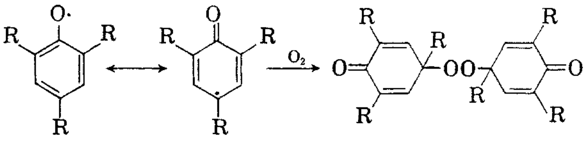
Cook and Woodworth[1] have reported the quantitative preparation of the stable 2,4,6-tri-butylphenoxy radical (I) by oxidation of 2,4,6-tri-*t*-butylphenol (II) with alkaline ferricyanide. Moreover, they found that I could be converted to bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadiene-4-one) peroxide (III) if the oxidation of II were carried out in the presence of air or oxygen. In this manner they were able to prepare III in a crude yield of 81% utilizing a reaction time of a few hours. We have found that III can be prepared quickly in a state of high purity and in essentially quantitative yield by oxidizing II with silver oxide in the presence of oxygen. Interestingly enough, although the yield of III is nearly quantitative, the solutions never absorb the theoretical amount of oxygen. Thus, in a typical experiment, when 0.01 mol. of II was oxidized in 100 ml. of benzene with 0.022 mole of silver oxide, 0.0035 mol. of oxygen was absorbed. This corresponds to only 70% of the theoretical quantity of oxygen, although 0.0049 mol. (98%) of III was isolated. This finding suggests that some of the oxygen which ultimately ends up in the peroxide must come directly from the silver oxide.



I R = *t*-butyl III

Silver oxide is known to undergo a rather facile thermal decomposition to silver metal and oxygen although the reaction is very slow below 160°.[2] However, as the decomposition is catalyzed by light as well as by silver metal itself, it is perhaps not unreasonable that some of the oxygen does come from the oxide. Moreover, as silver metal is a catalyst for the decomposition, it may not be unreasonable to suggest that I can also function as a catalyst for this decomposition. In this connection, Witsiepe[3] has recently investigated the use of silver oxide in preparing stable phenoxy radicals, including I. He found that II could be converted quantitatively to I only when freshly prepared silver oxide was employed under rather special conditions. Most of the present work was carried out utilizing a sample of commercial silver oxide. However, the same results were also obtained when we employed a sample of silver oxide freshly prepared according to Witsiepe's directions. In view of these results we would suggest that silver oxide is a poor choice as a reagent when the object is to prepare I itself. Along these same lines Müller and co-workers[4] found that when II was oxidized with lead dioxide, the yield of I was not quantitative, apparently because of reaction of I with the lead dioxide. In view of the present results it would seem likely that here too there is a direct reaction

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