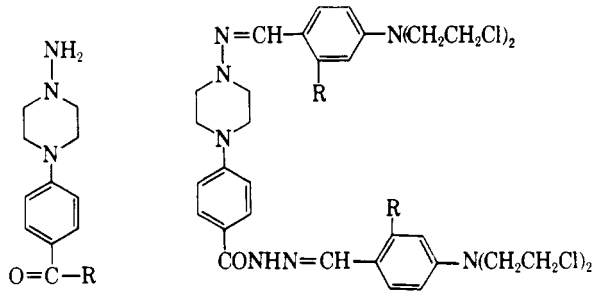
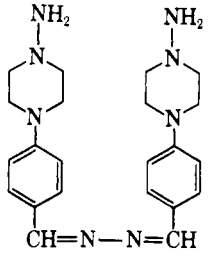
was shown by the reaction of I with two moles of aldehydes to give compounds II and III.



I. R = $NHNH_2$ II. R = H
IV. R = OH III. R = CH_3



V

In a similar manner *p*-[N,N-bis(2-chloroethyl)amino]benzoic acid and 95% hydrazine gave compound IV which was also then reacted with an aldehyde. Both *p*-[N,N-bis(2-chloroethyl)amino]benzaldehyde and its azine[3] also reacted with hydrazine to give compound V.

These results are of interest in that they indicate that caution should be used in attempts to treat hydrazine with some function in a molecule which also contains the bis(2-chloroethyl)amino grouping. The sequence may also be a convenient route to 1-amino-4-substituted piperazines which have generally been prepared by nitrosation and reduction of an N-monosubstituted piperazine.[6]

Experimental[7]

Reaction of Ethyl *p*-[N,N-Bis(2-chloroethyl)amino]benzoate with Hydrazine.—A mixture of 9.1 g. (0.031 mole) of ethyl *p*-[N,N-bis(2-chloroethyl)amino]benzoate and 50 ml. of 95% hydrazine was heated for 2 hr. on a steam bath. After cooling, 6.75 g. (91%) of solid, m.p. 204–206°, was obtained. Recrystallization from a large volume of absolute ethanol[8] gave I, m.p. 203–205°.

Anal. Calcd. for $C_{11}H_{17}N_5O$: C, 56.15; H, 7.28; N, 29.77. Found: C, 56.54, 56.28; H, 7.48, 7.39; N, 29.46; Cl, 0.

Refluxing a suspension of I in absolute ethanol with an absolute ethanol solution of a slight excess of *p*-[N,N-bis(2-chloroethyl)-amino]benzaldehyde gave on cooling an 89% yield of II, m.p. 209–211°.[8]

Anal. Calcd. for $C_{33}H_{39}N_7Cl_4O$: C, 57.31; H, 5.68; N, 14.19; Cl, 20.51. Found: C, 57.45; H, 5.67; N, 13.78; Cl, 20.30.

Similarly I and 4-[N,N-bis(2-chloroethyl)amino]-2-methylbenzaldehyde gave a 97% yield of III, m.p. 188–189°.[8]

Anal. Calcd. for $C_{35}H_{43}N_7Cl_4O$: C, 58.42; H, 6.02; N, 13.63; Cl, 19.71. Found: C, 58.47; H, 5.91; N, 13.61; Cl, 20.12.

Reaction of *p*-[N,N-Bis(2-chloroethyl)amino]benzoic Acid with Hydrazine.—As described for the preparation of I, 4 g. (0.015 mole) of the acid and 25 ml. of 95% hydrazine on heating for 2 hr. gave 3.19 g. (96%) of IV, m.p. 262–266° dec.[8]

Anal. Calcd. for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83. Found: C, 59.33; H, 6.87.

Refluxing IV with *p*-[N,N-bis(2-chloroethyl)amino]benzaldehyde gave an 81% yield of the hydrazone, m.p. 240–245°.[8]

Anal. Calcd. for $C_{22}H_{26}N_4Cl_2O_2$: C, 58.80; H, 5.83; N, 12.47; Cl, 15.78. Found: C, 58.65, 58.93; H, 6.02, 6.17; N, 12.37; Cl, 16.05.

Reaction of *p*-[N,N-Bis(2-chloroethyl)amino]benzaldehyde with Hydrazine.—As described for the preparation of I, 3 g. (0.012 mole) of the aldehyde and 25 ml. of 95% hydrazine on heating for 1.5 hr. gave 1.6 g. (33%) of V, m.p. >330°.[8]

Anal. Calcd. for $C_{22}H_{30}N_8$: C, 65.00; H, 7.44; N, 27.57. Found: C, 64.80, 64.79; H, 7.44, 7.45; N, 27.10.

The same material (V) was obtained in 73% yield from the azine[3] and hydrazine.

(6) See for example: E. A. Conroy, U. S. Patent 2,663,706 (1953); *Chem. Abstr.*, **49**, 4730 (1955).

(7) All melting points are uncorrected. Analysis by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Drs. Weiler and Strauss, Oxford, England.

(8) All compounds described were purified in this manner.

The Reaction of Eneamines with Benzoyl Peroxide[1]

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The versatility of the eneamine as an important intermediate in organic synthesis has been well established.[2] The reactions of this class of compounds have one thing in common—nucleophilic attack on the other reagent involved. It was therefore reasoned that such attack would also occur on the peroxy oxygen of benzoyl peroxide to give, after hydrolysis, 2-benzoyloxy ketones, thus providing a useful route to various types of 2-oxygenated ketones.

This postulate was shown to be correct by the reaction of 1-morpholinocyclohexene (Ia) with benzoyl peroxide at room temperature to give a 30% yield of 2-benzoyloxycyclohexanone (IIa). A 25% yield of 2-benzoyloxycyclopentanone (IIc) was also realized on reaction of the morpholine eneamine of cyclopentanone (Ic) with benzoyl peroxide. Use of the pyrrolidineeneamine (Ib) did not improve the yield, nor did running the reaction at 0° instead of at room temperature.

It was hoped that this reaction could be used on the eneamines of 1-methyl-2 (Id) or 1-benzoyl-4-piperidones[3] (Ie,f) to give products of possible psychotomimetic properties (IId,e).[4] Unfortunately, only intractible material could be obtained on reactions with either the morpholine or pyrrolidine eneamines of these ketones at room temperature or at 0°.

Experimental

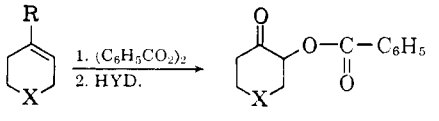
2-Benzoyloxy Ketones.—To 0.07 mole of the eneamine[2,3] in 75 ml. of purified dioxane was added dropwise, with stirring, 17.0 g. (0.07 mole) of benzoyl peroxide in 125 ml. of purified dioxane over a period of 1 hr. The resulting solution became warm and turned a dark amber color. When addition was complete,

(1) Support for this work by the National Institutes of Health through research grant 09696 from the Division of General Medical Sciences, U. S. Public Health Service, is gratefully acknowledged.

(2) See, for example, M. E. Kuehne, *J. Am. Chem. Soc.*, **84**, 837 (1962), and references cited therein.

(3) R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958).

(4) A review of compounds with these properties has recently been published; D. F. Downing, *Quart. Rev.* (London), **XVI**, 133 (1962). See also S. B. Kadin and J. G. Cannon, *J. Org. Chem.*, **27**, 240 (1962).



I II

Ia. X = CH_2; R = N O

b. X = CH_2; R = N

c. X = —; R = N O

d. X = N—CH_3; R = N

e. X = N—COC_6H_5; R = N O

f. X = N—COC_6H_5; R = N

IIa. X = CH_2
c. X = —
d. X = N—CH_3
e. X = N—COC_6H_5

the solution was warmed at 50–70° for 3 hr. After this time 200 ml. of water was added and the resulting solution refluxed overnight. The solution was cooled, poured into an additional 500 ml. of water, and extracted with ether. The ether was washed with 10% hydrochloric acid, saturated aqueous sodium carbonate, and water. The dried ethereal solution was evaporated and the product recrystallized from aqueous ethanol. In some instances the reaction was cooled in an ice bath during the addition, allowed to warm to room temperature for 3 hr. and hydrolyzed by stirring with water at room temperature overnight. These precautions did not appreciably alter the outcome of the reaction.

2-Benzoyloxycyclohexanone (IIa) was formed in 30% yield with a m.p. of 85–86° on recrystallization from aqueous ethanol (reported[5] m.p. 87°).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.46. Found: C, 71.64; H, 6.53.

2-Benzoyloxycyclopentanone (IIc) was formed in 25% yield with a m.p. of 90–91° on recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.57; H, 5.92.

The 2,4-dinitrophenylhydrazone had a m.p. of 128–129° (95% ethanol).

Anal. Calcd. for $C_{18}H_{16}N_4O_6$: C, 56.24; H, 4.19; N, 14.57. Found: C, 56.34; H, 4.26; N, 14.70.

(5) M. Bergmann and M. Greith, *Ann.*, **448**, 48 (1926).

Preparation of Hydrogen Phthalate Derivatives of Tertiary Alcohols

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Interest in this laboratory in low temperature liquid phase pyrolysis of esters has necessitated the development of a good procedure for the preparation of tertiary alcohol ester derivatives which decompose at relatively low temperatures. Zeiss[3] reported that the hydrogen phthalate derivative of 2-phenyl-2-butanol decomposed at its melting point (111°). Although no study was made of the decomposition products, it seemed reasonable to assume that an ordinary ester pyrolysis occurred and at a low temperature. Doering and Zeiss[4] previously reported on the preparation of the hydrogen phthalate derivative of 2,4-dimethylhexan-4-ol. The oil obtained was characterized as the barium salt. The procedure used by these workers involved the conversion of the tertiary alcohol to its potassium salt in boiling benzene followed by the addition of phthalic anhydride.

Fessler and Shriner[5] reported on the preparation of hydrogen phthalate derivatives of six aliphatic tertiary alcohols from tetrachlorophthalic anhydride. The yields range from 36 to 66%. The method involved treatment of the alcohols with ethylmagnesium to obtain the alkoxy magnesium bromide which was then treated with tetrachlorophthalic anhydride. No derivatives of mixed aliphatic–aromatic tertiary alcohols were recorded and all attempts to prepare an acid phthalate of triphenylcarbinol failed.

We have developed a convenient procedure for the preparation of hydrogen phthalate derivatives of aliphatic, mixed aliphatic–aromatic, and aromatic tertiary alcohols. The procedure involves treatment of the alcohol with ethereal triphenylmethylsodium at room temperature. The addition of phthalic anhydride followed by a short period of stirring (1–2 hr.) yields the solid derivative. The method is very convenient both as a characterization and a preparative procedure since the triphenylmethylsodium which has a blood-red color in ether can be titrated rapidly into the colorless ethereal alcohol solution until a red coloration persists. This indicates complete proton removal from the alcohol. As can be seen from the chart, the yields of the acid phthalates are good with the exception of that for triphenylcarbinol (30%). Unlike Shriner's observation, we have found that this procedure yields easily crystallizable hydrogen phthalate derivatives.

It is interesting to note that all of the hydrogen phthalate derivatives of the tertiary aliphatic series have decomposition points between 132–155°. The presence of one or two aromatic rings results in simultaneous melting and decomposition of the derivative. This substitution tends to lower the decomposition point substantially. The derivative from triphenylcarbinol did not decompose at the melting point or even at 300°. In all cases of decomposition, phthalic acid was isolated as the only solid residue. Olefins and olefinic mixtures (where possible) were obtained in yields greater than 85% in those cases which have been studied in detail. A report embodying the results of the pyrolysis of the hydrogen phthalates will appear in a later paper.

Experimental

Alcohols.—Triphenylcarbinol, *t*-amyl alcohol, and *t*-butyl alcohol were obtained from commercial sources. The remaining

(1) Supported by a grant from the Research Council of Ontario, Canada.
(2) Recipient of a National Research Council of Canada Studentship.

(3) H. H. Zeiss, *J. Am. Chem. Soc.*, **73**, 2391 (1951).
(4) W. von E. Doering and H. H. Zeiss, *ibid.*, **72**, 147 (1950).
(5) W. A. Fessler and R. L. Shriner, *ibid.*, **58**, 1384 (1936).