sodium acetate was added and the porphin was re-extracted into benzene (3 × 200 ml.). The benzene solution was distilled to dryness under reduced pressure, the residue redissolved in hot benzene (50 ml.) and purified as previously described.

Anal. Calcd. for $C_{20}H_{14}N_4$: C, 77.5; H, 4.5; N, 18.1. Found: C, 77.5; H, 4.7; N, 18.3.

Acknowledgment. I wish to thank Professor C. Rimington for suggesting this problem and for his interest and encouragement.

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Substituted Aminobenzacridines

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Received May 13, 1959

The preparation of a number of substituted 7-aminobenz[*c*]acridines as potential amoebicides has been reported by Elslager and co-workers[1,2] and by Short and co-workers.[3] The present communication deals with the preparation of a number of substituted 7-aminobenz[*c*]acridines and 12-aminobenz-[*a*]acridines for trials against *Entamoeba histolytica in vitro*.

The compounds were prepared by the interaction of 7-chlorobenz[*c*]acridine and 12-chlorobenz[*a*]-acridine with a slight excess of the appropriate amine in phenol at 120° for 2 hours and isolated as the salicylate as described in an earlier communication by Chatterjee.[4] The compounds were purified by crystallization from 90% ethanol and are shown in Table I.

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(1) E. F. Elslager, A. M. Moore, F. W. Short, M. J. Sullivan, and F. H. Tendick, *J. Am. Chem. Soc.*, **79**, 4699 (1957).

(2) E. F. Elslager, F. W. Short, M. J. Sullivan, and F. H. Tendick, *J. Am. Chem. Soc.*, **80**, 451 (1958).

(3) F. W. Short, E. F. Elslager, A. M. Moore, M. J. Sullivan, and F. H. Tendick, *J. Am. Chem. Soc.*, **80**, 223 (1958).

(4) A. K. Chatterjee, *J. Org. Chem.*, **24**, 856 (1959).

Attempted Preparation of Benzpinacol Carbonate

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Received April 9, 1959

In an endeavor to synthetize benzpinacol carbonate, needed for a kinetic study, two different methods have been attempted: 1) a base-catalyzed ester-interchange between benzpinacol (I) and diethyl carbonate, and 2) the reaction of phosgene with I in presence of antipyrine, according to the method of Ludwig and Piech.[1] Both methods failed to produce the desired cyclic carbonate. Instead, the first method gave a mixture consisting of benzophenone (II), ethyl benzhydryl, and dibenzhydryl carbonates (III and IV), whereas the sec-

(1) B. J. Ludwig and E. C. Piech, *J. Am. Chem. Soc.*, **73**, 5779 (1951).

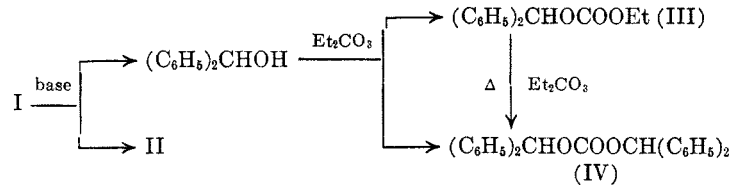
TABLE I[a]

Serial No.	Base	Salt	M.p. of Salt, °C.	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1	7-benzylaminobenz[*c*]acridine	1.5 $C_7H_6O_3$[b]	202	76.52	76.81	4.99	4.98	5.18	5.10
2	12-benzylaminobenz[*a*]acridine	1.5 $C_7H_6O_3$	216	76.52	76.49	4.99	4.80	5.18	5.15
3	7-(2-phenylethyl)aminobenz[*c*]-acridine	1.5 $C_7H_6O_3$	204	76.76	76.55	5.23	4.92	5.05	4.90
4	12-(2-phenylethyl)aminobenz[*a*]-acridine	1.5 $C_7H_6O_3$	203	76.76	76.91	5.23	4.80	5.05	5.15
5	7-(3-phenylpropyl)aminobenz-[*c*] acridine	1.5 $C_7H_6O_3$	187	76.98	77.21	5.45	5.53	4.92	4.75
6	12-(3-phenylpropyl)aminobenz-[*a*]acridine	1.5 $C_7H_6O_3$	194	76.98	77.15	5.45	5.55	4.92	4.70
7	7-(4-phenoxybutyl)aminobenz-[*c*] acridine	$C_7H_6O_3$	174	76.98	77.00	5.66	5.87	5.28	5.19
8	12-(4-phenoxybutyl)aminobenz-[*a*] acridine	$C_7H_6O_3$	172	76.98	76.75	5.66	5.82	5.28	5.20
9	7-*p*-dimethylaminoanilinobenz-[*c*]acridine	1.5 $C_7H_6O_3$	200	74.74	74.50	5.26	5.00	7.37	7.26
10	12-*p*-dimethylaminoanilinobenz-[*a*] acridine	1.5 $C_7H_6O_3$	196	74.74	74.53	5.26	5.13	7.37	7.42

[a] All melting points are uncorrected. [b] $C_7H_6O_3$, salicylic acid.

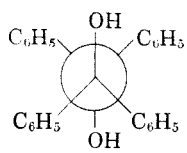
ond one yielded, again, a mixture composed of equimolar quantities of benzpinacolone (V) and tetraphenylethylene oxide (VI) as the only identifiable products.

The reactions involved in the formation of II, III, and IV may be formulated as below:



Accordingly, I first undergoes a base-catalyzed disproportionation into II and benzhydrol, and then the latter produces III and/or IV by ester-interchange with diethyl carbonate.[2] The first stage, involving C—C bond fission, actually represent a reversal of the benzpinacole formation.[3]

The transformation of I into V and VI, is presumably an acid-catalyzed process, which probably proceeds by way suggested by Gebhart and Adams.[4] The above demonstrated ability of phosgene-antipyrine system to cause in I a 1.2-nucleophilic molecular rearrangement paralells that of acetyl chloride–pyridine system,[5] but unlike the former the latter leads only to the formation of V. The action of thionyl chloride-antipyrine on I resembles that of acetyl chloride–pyridine (see experimental). It is worthy to note that unlike the acyl halides, similar treatment of I with acetic anhydride–pyridine resulted only in its cleavage into II and benzhydrol. From the above it is evident that because of the tendency of benzpinacole to undergo easily either molecular rearrangement or a reaction involving C—C bond cleavage, the methods herein described are certainly not applicable for the formation of benzpinacole carbonate. These failures could conceivably be related to conformational factors, as due to the repulsion between the phenyl groups. I most probably tends to exist as the rotational isomer Ia, having the OH groups farther apart, and therefore would not favor the formation of the presumably strained cyclic ester.



Ia

EXPERIMENTAL

Benzpinacol, m.p. 194–195° (from ligroin-benzene) was prepared in 90% yield by the method of Bachmann.[6]

The reaction of benzpinacol with phosgene. A solution containing a mixture of benzpinacol (18.5 g., 0.05 mole) and antipyrine (18 g., 0.1 mole) in dry chloroform (600 ml.) was treated with a 10% solution of phosgene (50 ml.) in toluene in a fashion as described. The reaction mixture was filtered, and from the precipitate 5 g. of crystalline benzpinacolone melting at 172° was obtained, after being thoroughly washed with water. Two recrystallizations, first from chloroform-ethanol, and then from benzene-ligroin, raised the m.p. to 184°. It gave no depression of melting point upon admixture with an authentic sample, prepared according to the method of Bachmann.[7] From the filtrate, 11 g. of residue were obtained after removal of solvents by distillation at reduced pressure. From this residue three identifiable products were isolated upon ether treatment. Two products were obtained from the ether extracted by means of fractional crystallization: (1) 1 g. of benzpinacolone, m.p. 184° (benzene-ligroin), and (2) 1.2 g. of benzpinacole, m.p. 194–195° (benzene-ligroin). From the ether-insoluble residue, 8 g. (46%) of tetraphenylethyleneoxide, a third reaction products, were obtained as colorless needles, melting at 209° (reported[8] m.p. 208°) upon several recrystallizations from ethanol. The yield of analytically pure product was 4 g. (23%).

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.66; H, 5.75. Found: C, 90.11; H, 6.13.

Isolation of ethyl benzhydryl and of dibenzhydryl carbonates (III and IV). In the treatment of benzpinacol (37 g., 0.1 mole) with diethyl carbonate (12 g., 0.1 mole) in the presence of 2 mole % of sodium methoxide, 7 g. (76%) of ethanol, boiling at 78–81°, were liberated after 4 hr. of heating (pot temperature 130°). After removal of unreacted starting materials in the usual way, the residue (42 g.) was subjected to fractional distillation at reduced pressure, whereupon two cuts were obtained: (i) b.p. 112–124° (1 mm.), (20 g.) and (ii) 4 g. of a product boiling at 135–140° (1 mm.), leaving behind 8 g. of a residue (iii) in the distilling flask. Refractionation of fraction (i) gave 12 g. (67%) of benzophenone, b.p. 117° at 1 mm., which solidified upon cooling. Recrystallization from ether gave a crystalline product melting at 47–48°. The infrared spectrum shows bands at 1656 cm.$^{-1}$ (carbonyl), 1631 cm.$^{-1}$, 1580 cm.$^{-1}$

The 2.4 dinitrophenyl hydrazone was crystallized from acetic acid, orange-yellow needles, m.p. 238° (lit.[9] m.p. 238–239°). It gave no depression in mixed melting point with an authentic material. Fraction (ii) was combined with the residue remaining in the distilling flask after redistillation of (i) and the whole was again refractionated. The cut boiling at 140° (1 mm.) was collected yielding on cooling

(2) Since disproportionation of unsummetrical carbonates into symmetrical ones is a possible process [see J. L. R. Williams, D. D. Reynolds, K. R. Dunham, and J. F. Tinker, *J. Org. Chem.*, **24**, 64 (1959)] IV could have well been originated from III by a similar way.

(3) For leading references see, G. W. Wheland "Advanced Organic Chemistry," John Wiley & Sons, Inc., New York, 1949, p. 716–720.

(4) H. J. Gebhart and K. H. Adams, *J. Am. Chem. Soc.*, **76**, 3925 (1954).

(5) W. Thörner and T. Zincke, *Ber.*, **10**, 1475 (1877); see also S. Winstein and R. B. Henderson in Elderfield's "Heterocyclic Compounds," Vol. I, John Wiley & Sons, Inc., New York, 1950, p. 19–20.

(6) W. E. Bachmann, *Org. Syntheses*, **Coll. Vol. II**, 71 (1941).

(7) W. E. Bachmann, *Org. Syntheses*, **Coll. Vol. II**, 73 (1941).

(8) J. F. Norris, R. Thomas and B. M. Brown, *Ber.*, **43**, 2954 (1910).

(9) N. R. Campbell, *Analyst*, **61**, 393 (1936).

4 g. of a solid ethyl benzhydryl carbonate (III). Recrystallization of the latter from ethanol gave white crystals of m.p. 52°. The yield of pure product amounts to 16% of conversion.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.25; saponif. equiv. 256. Found: C, 74.7; H. 5.8; Sapon. equiv., 260. Infrared: (C=O) 1739 cm.$^{-1}$, (C—H) 1376 cm.$^{-1}$, 1460 cm.$^{-1}$, 3030 cm.$^{-1}$, 1587 cm.$^{-1}$ (phenyl).

Identification of IV. For the purpose of identification, fraction (ii) was subjected to alkaline hydrolysis. Thus, 0.81 g. of (ii) were dissolved in 20 ml. of 0.5*N* ethanolic potassium hydroxide and the resulted solution was refluxed for 2 hr. From the cooled acidified solution, crystalline benzhydrol (0.41 g., m.p. 68–68.5°) was recovered by ether extraction and crystallization from aqueous ethanol. No depression in melting point was observed for a mixture with an authentic sample of benzhydrol (reported[10] m.p. 68°).

Fraction (iii) was purified by its crystallization from ethanol giving colorless crystals of melting point 127°. The yield of this product amounted to 41% of conversion.

Anal. Calcd. for $C_{27}H_{22}O_3$: C, 82.2; H, 5.6; mol. wt., 394. Found: C, 82.7; H, 5.5; mol. wt., 380 (Rast).

The infrared spectrum shows bands (cm.$^{-1}$) at 3096, 3067, 3053 (C—H aromatic), 1739 (carbonyl), 1591, 1504, 1460, 1370, 1274.

Identification of (iii). Alkaline hydrolysis of this fraction in a fashion described above again afforded, in 80% yield, colorless needles of benzhydrol (from aqueous ethanol) melting at 68°.

Experiments aimed at converting benzpinacole into tetraphenylethylene oxide by means of a variety of reagents failed. Thus, when benzpinacole was treated with thionyl chloride–antipyrine, phosphor pentoxide in benzene, and polyphosphoric acid (for 1–2 min.), benzpinacoline has invariably been recovered as the only identifiable reaction product.

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(10) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," J. Wiley & Sons, Inc., New York, N. Y., 1941.