an inflection at 234 mμ (ε 420) tailing off to zero at about 300 mμ. The nmr (CCl_4) spectrum consisted of three sharp peaks at δ 2.85, 2.72, and 4.0 with area ratios of 1:3:3, respectively.

Anal. Calcd for $C_6H_7NO_4$: C, 45.86; H, 4.49; N, 8.92. Found: C, 45.7; H, 4.3; N, 8.7.

Registry No.—**7,** 16504-38-4; 9-(1-bromoethylidene)-fluorene, 16504-39-5; **9,** 16504-40-8; **12,** 16504-41-9; **16,** 16504-42-0; **24,** 16504-43-1; **26,** 16520-65-3; 2,3-dicarbomethoxy-2H-azirine, 16504-44-2.

Reactions of Phosphorus Compounds. XV. A General Synthesis of 2H-1-Benzopyrans

EDWARD E. SCHWEIZER, JOACHIM LIEHR, AND DONALD J. MONACO

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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Substituted 2H-1-benzopyrans and 3H-naphtho[2,1-*b*]pyran (IX) have been prepared from vinyltriphenylphosphonium bromide (III), substituted salicylaldehydes, or 2-hydroxy-1-naphthaldehyde, respectively.

In a previous communication in this series, 2H-1-benzopyran[1] was prepared by utilizing the vinylphosphonium salt (III) and salicylaldehyde. In addition to 2H-1-benzopyran, the following series of compounds have been synthesized: pyrrolizines,[2] carbocyclics,[3] olefins,[4a] 1,2-dihydroquinolines,[4b] and 2,5-dihydrofurans[5] from the vinylphosphonium salt (III) and suitable addenda. We now wish to report a general preparation of substituted 2H-1-benzopyrans (VI) and 3H-naphtho[2,1-*b*]pyran (IX) utilizing the vinylphosphonium salt (III) and suitable phenolic aldehydes as shown in Scheme I.

These types of compounds are of interest because of the occurrence of the benzopyran ring system in the active constituents of several plants used as insecticides[6] and natural dyes.[7] Previous preparations have been accomplished in the following manners: (a) by the intramolecular cyclization of phenyl propargyl ether;[8,9] (b) by the slow distillation of a crude mixture of 4- and 6-bromochroman in the presence of alcoholic sodium ethoxide;[10] (c) by dimethyl sulfoxide dehydration of 4-chromanol or a two-step conversion from the 4-chromanol involving a Kraft pyrolysis of 4-chromanyl acetate.[11]

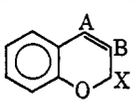
In situ preparation and reaction of the sodium salts of salicylaldehyde (Id), 3-methoxy salicylaldehyde (Ia), or 2-hydroxy-1-naphthaldehyde (VIII) with the vinylphosphonium salt (III) in an acetonitrile–ether solvent system afforded 2H-1-benzopyran (VId), 8-methoxy-2H-1-benzopyran (VIa), and 3H-naphtho[2,1-*b*]pyran (IX) in 71, 57, and 14% yields respectively. 5-Chlorosalicylaldehyde (Ic) was treated in the same way (except that the solvent system used was a N,N-dimethylformamide (DMF)–ether mixture) to give 6-chloro-2H-1-benzopyran (VIc) in 29% yield. Attempted preparation of 6-nitro-1,2-benzopyran (VIb) from 5-nitrosalicylaldehyde (Ib) and the vinylphosphonium salt (III) utilizing the above procedure was unsuccessful. However, preparation and isolation of the sodium salt of 5-nitrosalicylaldehyde followed by pyrolysis with the vinylphosphonium salt (III) *in vacuo* afforded the desired benzopyran (VIb) in 27% yield.

The 2H-1-benzopyrans were characterized by their physical constants, nmr spectra, and absorption in the infrared region of 1200–1260 cm^{-1} which is characteristic for the C–O stretch of aromatic ethers.[12,13]

The nuclear magnetic resonance spectra of the synthesized 2H-1-benzopyrans show patterns which are characteristic for this type of structure. The spectra can be divided into three major parts. (1) The aromatic protons appear as a multiplet. (2) The protons associated with the substituents of the aromatic ring, *i.e.*, the methyl protons of 8-methoxy-2H-1-benzopyran (VIa), exhibit a singlet centered at 3.72 ppm downfield from tetramethylsilane. (3) The protons of the pyran ring system exhibit an ABX_2 system.

The protons of the ABX_2 system exhibit the following splitting characteristics. The protons associated with the carbon α to the oxygen atom (CH_2) appear as a quadruplet (J_{BXCH_2} = 3 cps; J_{AXCH_2} = 2 cps) centered in the range of 4.37–4.96 ppm downfield from tetramethylsilane for 6-chloro-2H-1-benzopyran and 5-nitro-2H-1-benzopyran (VIb), respectively (with the others lying in between). The proton associated with the β-carbon atom appears as a pair of triplets (J_{AB} = 10 cps; J_{BX} = 3 cps) centered in the range of 5.30–5.83 ppm downfield from tetramethylsilane for 6-chloro-2H-1-benzopyran and 5-nitro-2H-1-benzopyran, respectively, at the extremes (Table I). The proton associated with the A-

TABLE I
CENTER OF NMR BANDS ASSOCIATED WITH THE PYRAN RING PROTONS OF VARIOUS 2H-1-BENZOPYRANS IN PARTS PER MILLION FROM TETRAMETHYLSILANE



Compound	X	B	A
2H-1-Benzopyran	4.53	5.38	6.20
8-Methoxy-2H-1-benzopyran	4.75	5.70	6.43
6-Nitro-2H-1-benzopyran	4.96	5.83	6.42
3H-Naphtho[2-1-*b*]pyran	4.65	5.60	6.92
6-Chloro-2H-1-benzopyran	4.37	5.30	6.88

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(3) E. E. Schweizer and G. O'Neill, *ibid.*, **30**, 2082 (1965).
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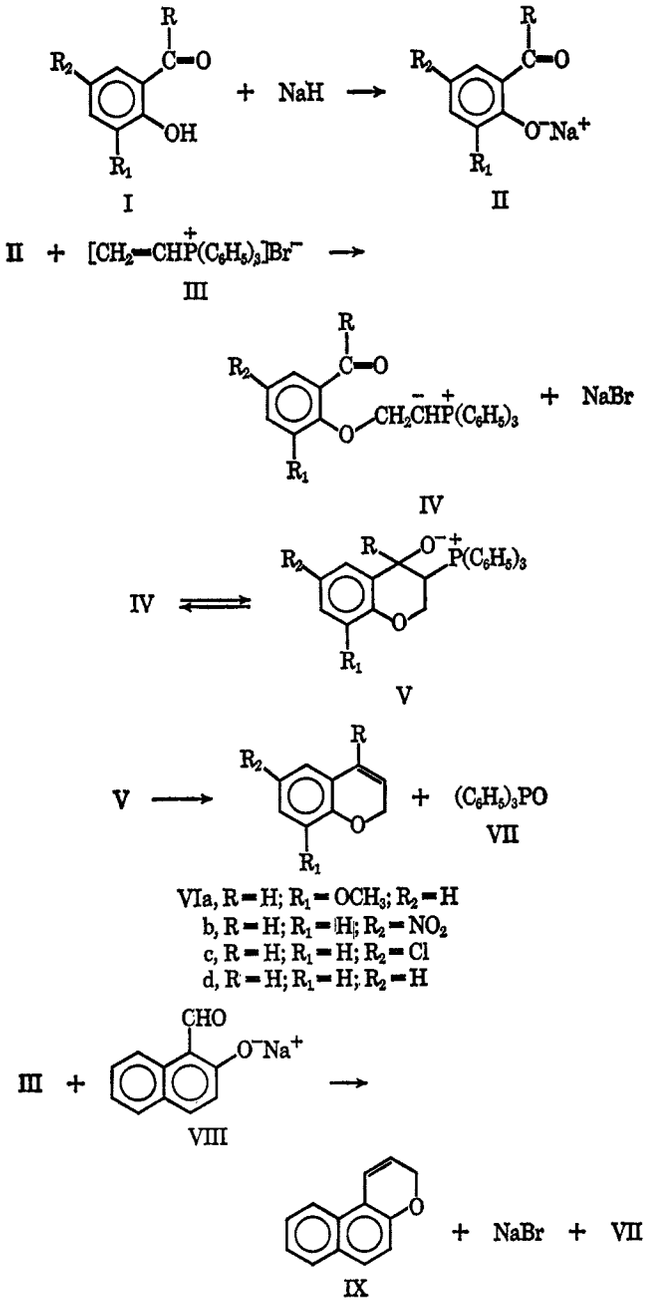
(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd ed, 1958, pp 45–48.
(13) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., p 172.

SCHEME I



carbon atom also appears as a pair of triplets (J_{AB} = 10 cps; J_{AX} = 2 cps) centered in the range of 6.20–6.92 ppm downfield from tetramethylsilane for 2H-1-benzopyran and 3H-naphtho[2,1-*b*]pyran, respectively, as extremes. The above assigned splitting patterns for the vinyl group agree with previously reported results[4] for open-chain vinyl compounds.

The reaction of the sodium salt of *o*-hydroxybenzophenone with the vinyl salt (III) utilizing both solution and pyrolysis techniques did not give the anticipated product, 4-phenyl-2H-1-benzopyran, in sufficient yield for isolation and positive identification. However, its probable formation was demonstrated by infrared spectroscopy and the identification of trace amounts of triphenylphosphine oxide (VII) in the reaction residue. In addition to the above, triphenylphosphine and starting material were also isolated.

In the reaction of *o*-hydroxyacetophenone with the vinylphosphonium salt (III) utilizing both solution and pyrolysis techniques triphenylphosphine oxide was isolated, indicating that a Wittig reaction had taken place; however, none of the anticipated product, 4-methyl-2H-1-benzopyran, could be isolated and only a trace of product could be detected by vapor phase chromatography. In addition to the phosphine oxide, starting material and triphenylphosphine were also isolated.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Infracord 137 and nmr spectra were obtained on a Varian A-60 analytical nmr spectrometer, using tetramethylsilane as standard. All melting points were uncorrected and obtained on a Fischer–Johns melting point apparatus. Analyses were by Micro-Analysis, Inc., Wilmington, Del.

The vinyltriphenylphosphonium bromide[14] and *o*-hydroxybenzophenone[15] were prepared according to reported procedures. The latter may also be bought from the Aldrich Co. The 2-hydroxy-1-naphthaldehyde was obtained from Columbia Organic Chemicals Co., Inc.; the 5-nitrosalicylaldehyde, 5-chlorosalicylaldehyde, and 3-methoxy-2-hydroxybenzaldehyde were obtained from Eastman Kodak Co. Sodium hydride was obtained as an approximately 53% dispersion in mineral oil from Metal Hydrides, Inc., Beverly, Mass. Anhydrous reagent grade solvents were used in all cases. All reactions were carried out under a nitrogen blanket.

General Procedure. The Preparation of 8-Methoxy-2H-1-benzopyran (VIa).—3-Methoxy-2-hydroxybenzaldehyde (10.0 g, 0.072 mol) was added to a stirred mixture of 2.9 g of sodium hydride dispersion in mineral oil (52% NaH, 1.5 g, 0.0625 mol) and 100 ml of ether. After the gas evolution abated, 22.8 g (0.062 mol) of salt III was introduced to the mixture and 100 ml of acetonitrile was added dropwise. The reaction mixture was

TABLE II

Product	Ir bands, cm^{-1}		Nmr data, δ
VIa	1262 (aromatic ether)		3.72 (s, 3, O-CH_3)
	1570 (s)	1070 (s)	4.75 (quad, 2, O-CH_2—)
	1470 (s)	1030 (s)	5.70 (m, 1, O-CH_2-CH=)
	1205 (s)	790 (s)	6.43 (m, 1, C_6H_3-CH=)
	1095 (s)	735 (s)	6.60–6.93 (m, 3, C_6H_3)
VIb	1258 (aromatic ether)		4.96 (quad, 2, O-CH_2—)
	1600 (s)	1025 (s)	5.83 (m, 1, O-CH_2CH=)
	1500 (s)	900 (s)	6.42 (m, 1, C_6H_3-CH=)
	1480 (s)	832 (s)	7.32–7.90 (m, 3, C_6H_3)
	1240 (s)	794 (s)	
	1090 (s)	744 (s)	
VIc	1235 (aromatic ether)		4.37 (quad, 2, O-CH_2)
	1480 (s)	1085 (s)	5.30 (m, 1, O-CH_2-CH=)
	1420 (s)	1030 (s)	6.88 (m, 1, C_6H_3-CH=)
		885 (s)	6.21–6.92 (m, 3, C_6H_3—)
	1200 (s)	820 (s)	
	1120 (m)	750 (s)	
VId	1230 (aromatic ether)		4.53 (quad, 2, O-CH_2—)
	1610 (s)	1195 (s)	5.38 (m, 1, O-CH_2-CH=)
	1570 (s)	1110 (s)	6.20 (m, 1, C_6H_4-CH=)
	1480 (s)	1040 (s)	6.60–7.13 (m, 4, C_6H_4)
	1380 (s)	930 (s)	
	1360 (s)	750 (s)	
IX[a]	1220 (aromatic ether)		4.65 (quad, 2, O-CH_2)
	1580 (s)	1010 (s)	5.60 (m, 1, O-CH_2-CH=)
	1510 (s)	810 (s)	6.92 (m, 1, $C_{10}H_6$-CH=)
	1460 (s)	800 (s)	7.10–7.89 (m, 6, $C_{10}H_6$—)
	1180 (s)	742 (s)	
	1085 (s)	718 (s)	

[a] The uv spectrum of IX showed bands at 218, 261 (sh), 290 (sh), 303, 316, and 349 mμ (lit.[9] uv bands at 242, 261 (sh), 290 (sh), 301, 314, and 347 mμ).

(14) E. E. Schweizer and R. Bach, *J. Org. Chem.*, **29**, 1746 (1964).

(15) N. M. Cullinane, N. M. Morgan, and C. A. Plummer, *Rec. Trav. Chim. Pays-Bas*, **56**, 629 (1937).

TABLE III

$$\text{Ia–d} + \text{III} \xrightarrow[\text{solvent}]{\text{NaH}} \text{VI} + (C_6H_5)_3PO$$

Compd (mol)	NaH, mol	Temp, °C	Solvent	Time	Product (yield, %)	Bp, (mm) or mp, °C	Refractive index	—Calcd, %— C	H	—Found, %— C	H
Ia (0.0721)	0.0625	Reflux	Acetonitrile	5 days	VIa (57.5)	91–92 (0.85)[a]	$n^{29}D$ 1.5860				
IIb (0.016)		155–160 (2.0 mm)	Fusion		VIb (27.2)	125–126		61.01	3.99	60.78	4.03
Ic (0.064)	0.064	100	DMF	3 days	VIc (29)[b]	79.5–80 (1.0)		64.88	4.23	64.81	4.07
IId (0.06)		Reflux	Acetonitrile	24 hr	VId (71)[c]	63–67 (3.0)[d]	$n^{20}D$ 1.5886				
VIII (0.065)	0.054	Reflux	Acetonitrile	5 days	IX (13.7)	34–35[e]					

[a] Lit.[8] bp 115–118° (1.0 mm) bath temp, $n^{16}D$ 1.5917. [b] In an unsuccessful attempt to obtain VIc, the only product was 1.1 g (9%) of a dimeric acetal, mp 176–178°. Analysis and ir and nmr spectra are in agreement with assigned structure for anhydro di(chlorosalicylaldehyde) (lit.[16] mp 172°). [c] The acetonitrile is distilled off. Remains are distilled to yield product. [d] Lit.[11] bp 49.5–50.0° (1.0 mm), $n^{20}D$ 1.5879. [e] Purification by sublimation at 60° (0.05 mm) (lit.[9] mp 40–41.5°).

heated to reflux for 5 days, cooled to room temperature, poured into 1 l. of a 10% sodium hydroxide solution, and extracted with ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled affording 5.75 g (57.5%) of 8-methoxy-2H-1-benzopyran (VIa): bp 91–92° (0.85 mm); $n^{29}D$ 1.5860 (lit.[8] bp 115–118° (1.0 mm), bath temperature; $n^{16}D$ 1.5917). The ir and nmr data may be found in Table II; the reaction conditions employed and, in case the product is a new compound, the analyses may be found in Table III.

Fused Reaction. Preparation of 6-Nitro-2H-1-benzopyran (VIb).—5-Nitrosalicylaldehyde (5 g, 0.03 mol) was added slowly to a stirred mixture of 2.9 g of a sodium hydride dispersion in mineral oil (52% NaH, 1.5 g, 0.0625 ml) and 100 ml of ether. After the gas evolution abated, the reaction mixture was cooled to ice-bath temperature and filtered under a nitrogen cover. The precipitated sodium salt of nitrosalicylaldehyde was washed with cold ether and dried over night. Salt III (6.3 g, 0.017 mol) was intimately blended with 3.0 g (0.016 mol) of the sodium salt of IIb and heated *in vacuo* in a sublimer. At 155–160° (2.0 mm), a yellow solid was collected on the cold finger of the sublimer which upon recrystallization from methanol afforded 0.76 g (27.2%) of 6-nitro-2H-1-benzopyran, mp 125–126°. Analysis is found in Table III.

(16) W. P. Bradley and F. B. Dains, *Amer. Chem. J.*, **14**, 293 (1892).

The preparation of 4-methyl-2H-1-benzopyran and 4-phenyl-2H-1-benzopyran has been attempted by two workers more than ten times (in each case) using both the synthetic procedures described above.

In the case of the 4-methyl-2H-1-benzopyran, the vapor phase chromatogram showed a small peak of a compound boiling higher than DMF but lower than the starting material. The amount of material was too small to allow identification of this product. A trace amount of triphenylphosphine oxide was identified by melting point and ir spectrum. The presence of it indicates that the products are formed but only in very small yields.

In the case of 4-phenyl-2H-1-benzopyran, the vapor phase chromatogram also showed a peak which would be assumed to originate from the product, but the amount was too small to allow positive identification. A trace amount of isolated triphenylphosphine oxide hints toward a reaction in very low yield.

Registry No.—VIa, 16336-25-7; VIb, 16336-26-8; VIc, 16336-27-9; VId, 254-04-6; IX, 229-80-1.

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The Selective Reduction of the Carbobenzoxy Group in Carbobenzoxyamino Acid and Peptide *p*-Nitrophenyl Esters

J. KOVACS AND R. L. RODIN

Department of Chemistry, St. John's University, Jamaica, New York 11432

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The N-carbobenzoxy group of *p*-nitrophenyl esters of N-carbobenzoxyamino acids and N-carbobenzoxy peptides can be removed by catalytic hydrogenation in the presence of 1 equiv of hydrochloric acid without noticeable reduction of the nitro group. This method can be used for preparing oligo peptides by Goodman's "backing-off" procedure and for preparing polyamino acids and sequential polypeptides when the *t*-butyl ester groups are present.

Removal of the N-carbobenzoxy group from N-carbobenzoxyamino acid and N-carbobenzoxy peptide *p*-nitrophenyl esters is usually achieved by treatment with hydrogen bromide in glacial acetic acid,[1] since catalytic hydrogenation is expected to reduce the nitro group under the usual conditions. In the case of trifunctional amino acids, where, in addition to the N-carbobenzoxy group, an acid-sensitive group such as the *t*-butyl group[2] is also present, the hydrogen bromide method cannot be used.

In this paper, a method is described for the selective removal of the N-carbobenzoxy group by catalytic hydrogenation from N-carbobenzoxyamino acid and N-carbobenzoxy peptide *p*-nitrophenyl esters, without noticeable reduction of the nitro group. This method can be used with the "backing-off" procedure of Goodman[3] as well as for preparing C-activated peptides or amino acids where *t*-butyl containing trifunctional amino acids are present. These C-activated peptides and amino acids can, in turn, be polymerized to sequential polypeptides and polyamino acids.

This selective catalytic hydrogenation procedure was studied on N-carbobenzoxyglycine *p*-nitrophenyl ester, N-carbobenzoxy-L-phenylalanine *p*-nitrophenyl ester, N-carbobenzoxy-α-*t*-butyl-L-glutamic acid *p*-nitrophenyl ester, and N-carbobenzoxy-L-phenylalanylglycine *p*-nitrophenyl ester. The procedure was best illustrated by the preparation of α-*t*-butyl-L-aspartic acid *p*-nitrophenyl ester hydrochloride and the polym-

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