ported from the infrared spectra obtained on an Infracord 337. Nmr spectra were run on chromatographically isolated fractions to which were then added trifluoroacetic acid as external standard for F^{19} spectra and tetramethylsilane in carbon tetrachloride as external reference standard for H^1 spectra.

2-(1,2,2,2-Tetrafluoroethyl)pyridine.—To a 500-ml stainless steel pressure vessel were added 99.7 g (1.05 mol) of pyridine N-oxide and 80 g (0.53 mol) of hexafluoropropylene, and the resulting mixture was heated at 62° for 16.5 hr. Then the gases (5.1 g) were bled off at ambient temperatures to a residual pressure of one atmosphere. The off-gas contained CO_2, COF_2, CF_3CFHCF_3, and a small amount of $CF_3CF{=}CF_2$. The residue (174 g of brown liquid) from the pressure vessel was transferred to a suitable flask and was distilled by short-path distillation at a pot temperature of 25–90° (0.1 mm) to yield 92 g of slightly colored oil. This oil was added to 300 ml of water with stirring. After all the carbon dioxide had evolved, the water layer was made basic (pH 8) with 50% aqueous KOH. The bottom (oil) phase was then separated, the water phase was washed twice with 20-ml portions of methylene chloride, and the organic phases were combined and dried ($MgSO_4$). After the salt was removed by filtration and the solvent removed by flash evaporation under reduced pressure, the remaining liquid was distilled at 142° (ambient pressures) on a spinning-band column to yield 42 g (44% yield based on hexafluoropropylene) of a colorless oil: $n^{28}\text{D}$ 1.4109; mol wt (*m/e* found by mass spectroscopy) 179 (calcd 179); infrared spectrum, 1600 (m, doublet), 1270 (s), 1190 (s), 1140 (s); F^{19} nmr spectrum (ppm), 0.75 (doubled doublet, CF_3), 121.6 (doubled quartet, CFH); H^1 spectrum (ppm), 5.41 (doubled quartet, CFH), 6.49–7.27 (complex bands, H_3, H_4, H_5), 8.04 (doublet, H_6).

Anal. Calcd for $C_7H_5F_4N$: C, 46.95; H, 2.81; F, 42.43; N, 7.82. Found: C, 47.08; H, 3.06; F, 42.15; N, 7.56.

6-(1,2,2,2-Tetrafluoroethyl)-2-picoline.—To a 100-ml stainless steel pressure vessel were added 14.5 g (0.14 mol) of 2-picoline N-oxide and 10 g (0.067 mol) of hexafluoropropylene. After the mixture was heated at 68° for 67 hr and then cooled, the gases (4.3 g) were removed and were found to consist mainly of CO_2 and CF_3CFHCF_3. The remaining contents of the pressure vessel were distilled by short-path distillation at a pot temperature of 25–63° (0.01 mm) to give 9.1 g of yellow liquid. Isolation and purification of the product was made by vpc to give a colorless liquid (19% yield based on hexafluoropropylene). Physical properties of the product are as follows: bp (micro) 154°; $n^{25}\text{D}$ 1.4189; mol wt (*m/e* found by mass spectroscopy) 193 (calcd 193); infrared spectrum, 1600 (m doublet), 1275 (s), 1190 (s), 1400 (s); F^{19} nmr spectrum (ppm), 0.68 (doubled doublet, CF_3), 121.1 (doubled quartet, CHF); H^1 spectrum (ppm), 1.88 (singlet, CH_3), 6.41–7.13 (broad lines, H_3, H_4, H_5), 5.32 (doubled doublet, CFH).

Anal. Calcd for $C_8H_7F_4N$: C, 49.75; H, 3.65; F, 39.34; N, 7.25. Found: C, 50.39; H, 4.14; F, 40.00; N, 7.39.

2- and 6-(1,2,2,2-Tetrafluoroethyl)-3-picoline.—To a 100-ml stainless steel vessel were added 21.8 g (0.2 mol) of 3-picoline N-oxide and 15.0 g (0.1 mol) of hexafluoropropylene, and the resulting mixture was heated at 60° for 16.5 hr. The work-up procedure, similar to that used for the 2-picoline N-oxide reaction, gave a colorless oil (36% yield based on hexafluoropropylene). Physical properties of the product are as follows: bp (micro) 166°; $n^{26}\text{D}$ 1.4248; mol wt (*m/e* found by mass spectroscopy) 193 (calcd 193); infrared spectrum, 1610 (s), 1270 (s), 1190 (s), 1140 (s); F^{19} nmr spectrum (ppm), 0.59 (doubled doublet, CF_3), 119.6 (doubled quartet, CFH); H^1 spectrum (ppm), 2-substituted 3-picoline, 1.82 (str doublet, CH_3), 5.56 (doubled quartet, CFH), 6.96, 6.60, 7.91 (H_4, H_5, H_6, respectively) 6-substituted 3-picoline, 1.68 (wk singlet, CH_3), 5.56 (doubled quartet, CFH), 7.87, 6.91, 6.78 (H_2, H_4, H_5, respectively).

Anal. Calcd for $C_8H_7F_4N$: C, 49.75; H, 3.65; F, 39.34; N, 7.25. Found: C, 49.95; H, 4.17; F, 39.94; N, 7.25.

2-(1,2,2,2-Tetrafluoroethyl)-4-picoline.—To a 60-ml stainless steel pressure vessel were added 21.8 g (0.20 mol) of 4-picoline N-oxide and 15.0 g (0.10 mol) of hexafluoropropylene, and the resulting mixture was heated at 47–74° for 17.5 hr. The work-up procedure, similar to that used for the 2-picoline N-oxide reaction, gave a colorless oil (36% yield based on hexafluoropropylene). Physical properties of the product are as follows: bp (micro) 166°; $n^{26}\text{D}$ 1.4248; mol wt (*m/e* found by mass spectroscopy) 193 (calcd 193); infrared spectrum, 1610 (s), 1270 (s), 1190 (s), 1140 (s); F^{19} nmr spectrum (ppm), 0.53 (doubled doublet, CF_3), 121.7 (doubled quartet, CHF); H^1 spectrum (ppm), 1.71 (singlet, CH_3), 6.88, 6.50, 7.88 (H_3, H_5, H_6, respectively, 5.41 (doubled quartet, CHF).

Anal. Calcd for $C_8H_7F_4N$: C, 49.45; H, 3.65; F, 39.34; N, 7.25. Found: C, 50.46; H, 3.86; F, 39.23; N, 7.26.

Miscellaneous.—Short-path distillation of the crude reaction mixture to yield the crude product can be eliminated if the mixture is added directly to water. The procedure can be continued as in the preparation of 2-(1,2,2,2-tetrafluoroethyl)pyridine, or it can be modified to include steam distillation.

Registry No.—2-(1,2,2,2-Tetrafluoroethyl)pyridine, 16876-47-4; 6-(1,2,2,2-tetrafluoroethyl)-2-picoline, 16876-48-5; 6-(1,2,2,2-tetrafluoroethyl)-3-picoline, 16876-49-6; 2-(1,2,2,2-tetrafluoroethyl)-3-picoline, 16876-50-9; 2-(1,2,2,2-tetrafluoroethyl)-4-picoline, 16876-51-0.

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Reaction of Aziridines with Benzoic Anhydride

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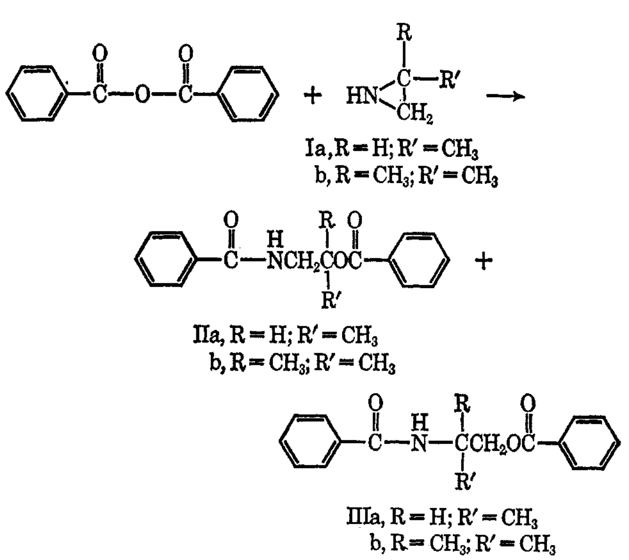
At least two examples of the reaction of anhydrides with aziridines are reported in the patent literature. Ester amides were prepared from N-alkylethylenimines and anhydrides of saturated monocarboxylic acid,[1] while poly(ester amides) were obtained from the reaction of N-alkylethylenimines and phthalic anhydride.[2] In both of these cases, only one isomer is possible through ring opening of the aziridine moiety.

We wish to report on the reactions of 2-methylethylenimine (Ia) and 2,2-dimethylethylenimine (Ib) with benzoic anhydride in acetone or tetrahydrofuran. The quantitative identification of the reaction products from these reactions was accomplished with the aid of



Ia, R = H; R′ = CH_3
b, R = CH_3; R′ = CH_3

IIa, R = H; R′ = CH_3
b, R = CH_3; R′ = CH_3

IIIa, R = H; R′ = CH_3
b, R = CH_3; R′ = CH_3

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[1] Bradische Anilin and Soda-Fabrik Aktiengesellschaft of Germany, British Patent, 784,058 (1957).

[2] Bradische Anilin and Soda-Fabrik Aktiengesellschaft of Germany, British Patent, 784,059 (1957).

TABLE I

NMR SPECTRAL DATA

Ester amide	Chemical shifts, δ, ppm[a]				
	Methyl	*J*, cps	Methylene	*J*, cps	Methinyl
N,O-Dibenzoyl(1-amino-2-propanol) (IIa)	1.45 (d)	6	3.7 (t)	5.5	5.39 (m)
N,O-Dibenzoyl(2-amino-1-propanol) (IIIa)	1.33 (d)	6	4.47 (d)		4.5 (m)
N,O-Dibenzoyl(1-amino-2-methyl-2-propanol) (IIb)	1.63 (s)		3.88 (d)	4.5	
N,O-Dibenzoyl(2-amino-2-methyl-1-propanol) (IIIb)	1.55 (s)		4.56 (s)		

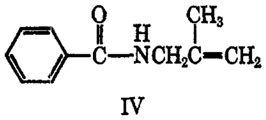
[a] Spectra were determined in CDCl$_3$ using TMS as a standard. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet.

proton nmr spectroscopy. This technique was especially suitable for differentiating the resulting ester amide isomers, since the chemical shifts were significantly different and distinguishable. For example, the assignments presented in Table I were based on authentic model compounds of the four possible ester amide isomers which could result from the reaction of benzoic anhydride with Ia or Ib.

The isomer ratios in the reaction mixtures could be conveniently determined by integrating the areas of the methylene and methinyl protons of IIa and IIIa, or simply the methylene protons in the case of IIb and IIIb, if all the isomers were indeed formed. Product identification *via* gas-liquid partition chromatography (glpc) was used to supplement the nmr spectra of the mixtures. Finally, the products of the reaction were isolated and their structures were confirmed by comparison with the corresponding authentic model compounds.

It was found that the reaction of Ia with benzoic anhydride in either THF or acetone resulted in the formation of the two isomeric ester amides IIa and IIIa. Integration of the nmr spectrum of the reaction mixture indicated that the mole ratio of IIa and IIIa was 3:1. Furthermore, since the amount of unreacted benzoic acid in the mixture is indicative of the moles of by-product in the reaction, the ratio of the benzoic acid nmr signal at δ 9.9 to the total ester amide integration was used as the criterion for estimation of yield. A yield of 80% was generally obtained utilizing this procedure.

In the case of the reaction of benzoic anhydride with Ib, the only ester amide produced was IIb, along with a considerable amount of N-(β-methylallyl)benzamide (IV) and benzoic acid. The important chemical shifts of IV appeared as a broad signal at δ 4.88 due to the terminal vinylic protons, at 1.77 due to the methyl group, and 3.98 due to the methylene protons. Since overlapping of the methylene protons of IIb and IV occurred in the nmr spectrum of the reaction mixture, it was necessary to subtract a quantity equal to the signal produced by the terminal vinyl protons of IV from the area integration produced by the overlapping methylene protons of both IIb and IV. This could be done since the signal produced by the vinylic protons of IV is exactly equal in area to the signal of its methylene protons. This procedure afforded a product ratio of 1.7:1 of IIb to IV, respectively. The total yield of IIb in the reaction mixture was 63%.



IV

Experimental Section[3]

Preparation of Authentic Compounds.—1-Amino-2-propanol, 2-amino-1-propanol, and 2-amino-2-methyl-1-propanol were allowed to react with benzoyl chloride at a 1:2 mole ratio in a CH$_2$Cl$_2$–H$_2$O solvent mixture utilizing NaOH as the acid acceptor. The resulting dibenzoyl ester amides were isolated from the dried organic phase *via* vacuum stripping followed by recrystallization from acetone: **N,O-dibenzoyl(1-amino-2-propanol) (IIa)**, mp 106° (lit.[4] 102–104°); **N,O-dibenzoyl(2-amino-1-propanol) (IIIa)**, mp 102–103° (lit.[5] 104–105°); **N,O-dibenzoyl(2-amino-2-methyl-1-propanol) (IIIb)**, mp 112–114° (lit.[6] 111–112°). **1-Amino-2-methyl-2-propanol** was prepared by a literature method:[7] bp 146–148°, n^{25}_{D} 1.4440 (lit.[7] 147.8–148°, n^{25}_{D} 1.4435).

N,O-Dibenzoyl(1-amino-2-methyl-2-propanol) (IIb) was prepared by treating 2 g of 1-amino-2-methyl-2-propanol (0.02 mol) with 6.5 g of benzoyl chloride (0.05 mol) in 40 ml of CHCl$_3$ and utilizing 5 g of pyridine as the acid acceptor. On completion of the addition of benzoyl chloride to the amino alcohol, the mixture was refluxed for 4 hr. Then 30 ml of a 6 *N* HCl solution was added to the cooled mixture. This mixture was extracted three times with 100-ml portions of diethyl ether, and the ether extract was washed with a dilute HCl solution, followed by two washings with water. The ether extract was evaporated to dryness. Recrystallization of the crude solid from acetone yielded IIb, mp 136–138°.

Anal. Calcd for C$_{18}$H$_{19}$NO$_3$: C, 72.73; H, 6.40; N, 4.71. Found: C, 72.51; H, 6.58; N, 4.87.

N-(β-Methallyl)benzamide (IV) was prepared from benzoyl chloride and β-methallylamine,[8] mp 69.5–70.5°. The reported melting point of IV is 67.5–69°.[8]

Reactions of Benzoic Anhydride with 2-Methylethylenimine (Ia) or 2,2-Dimethylenimine (Ib).—To a solution of 11.3 g (0.05 mol) of benzoic anhydride in 71.3 g of THF or acetone was added either 2.85 g (0.05 mol) of Ia or 3.60 g (0.05 mol) of Ib, maintaining the reaction temperature of 25° during the addition with an ice bath. When the addition was completed, the reaction was stirred at 25° for 4 hr, followed by heating at reflux for 20 hr. The solution was then cooled to room temperature, and an aliquot sample was removed for glpc analysis. The rest of the reaction mixture was vacuum stripped at room temperature to remove the solvent. An nmr spectrum was obtained on the solvent-free product. In the case of the benzoic anhydride–Ia reaction, both analyses confirmed that the product was composed mainly of a mixture of IIa and IIIa (3:1 mole ratio) along with benzoic acid and a small amount of an undetermined impurity. Glpc and nmr analysis of the benzoic anhydride–Ib reaction mixture indicated that it was composed of IIb and IV (at a 1.7:1 mole ratio) along with some benzoic acid. The solvent-stripped reaction syrup was next extracted with a large volume of ether.

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(3) The nmr analysis was carried out on a Varian A-60A spectrometer in CDCl$_3$ solutions at room temperature, with tetramethylsilane (TMS) as an internal standard. Gas chromatography was conducted with an F & M 810 gas chromatograph utilizing a 6 ft × 0.125 in. o.d. column of 10% SE 30 on Diatoport S (60–80 mesh). The column temperatures were programmed from 100 to 250°, at a rate of 20°/min. Melting points were determined on a "Mel-Temp" melting point apparatus, and all temperature measurements are uncorrected. Molecular weights were determined by vapor pressure osmometry in acetone (Mechrolab osmometer, Model 301A). Elemental analyses were performed by the Analytical Department of the Interchemical Central Research Laboratories.

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(7) R. A. Bafford, Ph.D. Thesis, University of Maryland, College Park, Md., p 27, 1960.

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In the case of the benzoic anhydride–Ia reaction mixture, the extraction left 10.5 g of a mixture of IIa and IIIa (74.2% yield). Fractional recrystallization of this mixture with acetone afforded 8.7 g of IIa, mp 104–106°, and 1.1 g of IIIa, mp 101–103°. The ether extract was washed several times with a 5% NaOH solution, and the aqueous layer was acidified by the addition of Dry Ice. Extraction of the aqueous solution with fresh ether, drying with anhydrous $MgSO_4$ and evaporation of the ether yielded 0.5 g of benzoic acid, mp 121–122°. The benzoic anhydride–Ib reaction mixture was treated in a similar manner, resulting in the isolation of 8.8 g of the ether-insoluble IIb (59% yield), mp 136–138°, and 1.8 g of benzoic acid. Finally, the original water-washed ether layer was dried with anhydrous $MgSO_4$ and evaporated to dryness. Recrystallization of the crude semisolid from petroleum ether resulted in the recovery of 2.3 g of IV, mp 67–69°. Mixture melting points of isolated IIa, IIb, IIIa, IV, and benzoic acid with the corresponding authentic samples were not depressed.

Registry No.—Benzoic anhydride, 93-97-0; IIa, 16888-96-3; IIb, 16888-97-4; IIIa, 16888-98-5; IIIb, 16888-99-6.

The Condensation of Enamines with Substituted *p*-Benzoquinones

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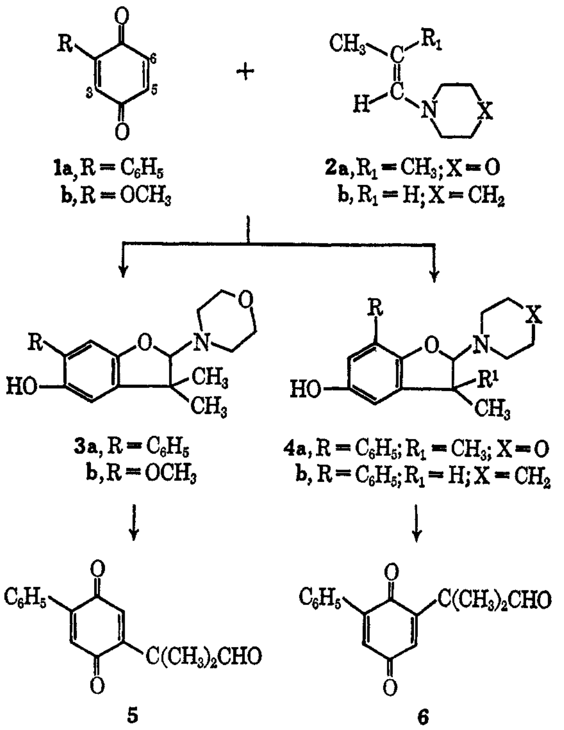
The introduction of a formylalkyl group into quinones by oxidation of 2-amino-2,3-dihydrobenzofurans **3**, which are available from the interaction of quinones **1** and enamines **2**,[1-3] was recently reported[1] (see Scheme I). The purported preparation of the 5-phenyl-2-formylalkylquinone **5**, mp 142–143°, by oxidation of the dihydrobenzofuran **3a** is illustrative of this procedure. Our experience[4] with the condensation of benzoquinones and enamines led us to believe that the quinone of mp 142–143° is, in fact, the 6-phenyl isomer **6**. Thus, inasmuch as the formation of the dihydrobenzofurans **3** and **4** probably proceeds by nucleophilic addition of the enamine to the benzoquinone and subsequent cyclization,[3] the position assumed by the quinone substituent in the product will reflect its electronic and steric character. Electron-withdrawing groups direct reaction toward C-3 in **1** or, alternatively, in the presence of strong steric effects, *e.g.*, phenyl, toward C-6, whereas electron-donating groups favor condensation at C-5.[5]

SCHEME I



Indeed, as predicted by these considerations, condensation of 2-phenyl-1,4-benzoquinone (**1a**) with isobutenylmorpholine (**2a**)[6] gave 70% 7-phenyldihydrobenzofuran **4a** (δ 6.45 and 6.75, J = 3.0 cps), accompanied by 7% 6 isomer **3a** (δ 6.67). The reaction of **1a** with 1-propenylpiperidine (**2b**)[7] to give 62% dihydrobenzofuran **4b** (δ 6.46 and 6.78, J = 3.0 cps) as the sole product further illustrates the directive influence of the phenyl substituent. In the instance of 2-methoxy-1,4-benzoquinone (**1b**), reaction with **2a** affords the expected 6-methoxydihydrobenzofuran **3b** (87%) (δ 6.45 and 6.51, unsplit). The position of the aryl substituent in the dihydrobenzofurans **3** and **4** follow from the cited proton resonances and their splitting patterns.

Oxidation of the 6-phenyldihydrobenzofuran **3a** with ferric chloride[1] afforded the 5-phenylquinone **5**, mp 127–128° (δ 6.60 and 6.78, unsplit), whereas a similar oxidation of the 7-phenyl isomer **4a** gave the 6-phenylquinone **6**, mp 141–142° (δ 6.76 and 6.84, J = 2.4 cps). These data clearly indicate that the quinone of mp 142–143°, to which structure **5** was previously assigned,[1] must possess the isomeric structure **6**. Moreover, the reaction of quinones and enamines in this and related examples proceeds in a predictable manner, the verification of which is readily furnished by nmr spectroscopy.[8]

Experimental Section[9]

Reaction of 1,4-Benzoquinones with Enamines.—The following experiment illustrates the general procedure. A solution of 1.49 g (10 mmol) of isobutenylmorpholine (2a) in 3 ml of methanol was added dropwise over 30 min to an ice-cooled, stirred mixture of 1.84 g (10 mmol) of 2-phenyl-1,4-benzoquinone (1a) in 7 ml of methanol. The solid dissolved to give a red solution that was stirred at ambient temperature for 1 hr. The solvent was removed, and the residue was dissolved in ether. This solution was passed through a magnesia–silica gel column, using ether as the eluting solvent. The yellow eluate was

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(8) These results indicate that the Bunte salt derived from 2-phenyl-1,4-benzoquinone is most likely sodium 2,5-dihydroxy-3-biphenylylthiosulfate rather than sodium 2,5-dihydroxy-4-biphenylylthiosulfate: W. Alcalay, *Helv. Chim. Acta*, **30**, 578 (1947). If true, the derived 2-methylmercapto-1,4-benzoquinone is the 6-phenyl isomer, rather than the previously assigned 5-phenyl isomer.

(9) Melting points are uncorrected. Evaporations were carried out under reduced pressure. Nmr spectra were determined in deuteriochloroform using tetramethylsilane as an internal standard on a Varian A-60 spectrometer.