The first three were identified as 5-hexen-1-ol (3%),[12] 5-hexen-1-yl acetate (12%), and 2-acetoxymethyltetrahydropyran (37%), by comparison[13] with authentic samples. The component of longest retention time (21% yield) was not identified. Its infrared spectrum indicated unsaturation but showed no band in the carbonyl region.

(b) **In Cyclohexane.**—A mixture of 2 g of 5-hexen-1-ol, 8.86 g of lead tetraacetate, and 100 ml of cyclohexane was heated to reflux overnight. It was cooled to room temperature and the products were isolated as described for the reaction in benzene.

(c) **In Pyridine.**—A mixture of 2 g of 5-hexen-1-ol, 8.86 g of lead tetraacetate, and 100 ml of dry pyridine was sitrred at room temperature overnight. The solution was diluted with 100 ml of water and extracted with three 100-ml portions of ether. The ether extracts were combined and washed with 6 *N* hydrochloric acid, water, 10% sodium bicarbonate, water and brine, and dried over magnesium sulfate. Gas chromatography (column B, 135°) revealed three components which were identified as 5-hexen-1-ol,[13] 5-hexen-1-yl acetate,[13] and 5-hexenal (λ_{max} 3080, 2930, 2810, 2710, 1730, 995, 915, 730 and 695 cm^{-1}; nmr (CCl_4) τ 0.27 (triplet, 1 H), 4.30, 4.90, 5.10 (multiplets, 3 H), and 7.8 (multiplets 6 H).

Reaction of 4-Cycloocten-1-ol with Lead Tetraacetate.—A mixture of 5.0 g of 4-cycloocten-1-ol, 20.0 g of lead tetraacetate, and 200 ml of dry benzene was heated under reflux with stirring for 12 hr. It was cooled to room temperature, 5 ml of ethylene glycol was added, and the mixture was stirred at room temperature for 30 min. The organic layer was separated and washed successively with water, 20% potassium iodide, water, and brine. The benzene solution was dried over magnesium sulfate and concentrated by distillation. The product was distilled through a spinning-band column, giving 1.97 g, bp 75–76 (0.7 mm). The distillate contained, in addition to the alcohol and the acetate, a mixture of two isomeric acetoxy ethers, later shown to be 2,5-epoxycyclooct-1-yl acetate (**4a**) and 2,6-epoxycyclooct-1-yl acetate (**4b**).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.22; H, 8.69. Found: C, 64.92; H, 8.66.

The mixture of the acetoxy ethers **4a** and **4b** was reduced with lithium aluminum hydride to a mixture of alcohols. The tosylates, prepared by treatment of the alcohols with tosyl chloride in pyridine, were treated with lithium aluminum hydride, giving a mixture of 1,4-and 1,5-epoxycyclooctane[10] in a relative ratio of 40:60 as shown by gas chromatography (column C).

Acknowledgment.—This work was supported in part by grants provided by Research Corp. and the Petroleum Research Fund of the American Chemical Society (PRF 1773-A4). We are grateful to the National Science Foundation for an institutional grant toward the purchase of a Varian A-60 nmr spectrometer, and to J. M. Lodge for her assistance in the initial stages of this problem.

[12] The yield was from gas chromatographic analysis corrected by the use of an internal standard and based on starting material.

[13] The products were isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples, and by their retention times on gas chromatography.

Reaction of Benzoylacetonitrile and α-Benzoylphenylacetonitrile with Acetic Anhydride in the Presence of Boron Trifluoride[1]

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Received May 25, 1966

It has been shown that certain β-ketonitriles can be converted in good yields to the corresponding β-ketoamides by means of boron trifluoride in aqueous acetic acid.[2]

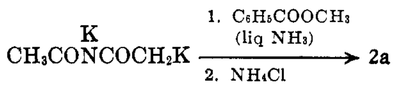
In the present study we have found that two such β-ketonitriles, benzoylacetonitrile (**1a**) and α-benzoylphenylacetonitrile (**1b**), were converted to the respective N-acetyl-β-ketoamides **2a** and **2b**, by a modification of the above procedure in which excess acetic anhydride was added to the reaction mixture. Thus, when **1a** and **1b** were allowed to react with a mixture of acetic anhydride and boron trifluoride–diacetic acid complex (BTDA) at room temperature, **2a** and **2b** were produced in yields of 90 and 82%, respectively (eq 1).

$$C_6H_5COCHRCN \xrightarrow[\text{2. aq } CH_3COONa]{\text{1. } (CH_3CO)_2O\text{, BTDA}} C_6H_5COCHRCONHCOCH_3 \quad (1)$$

1a, R = H
d, R = C_6H_5

2a, R = H
b, R = C_6H_5

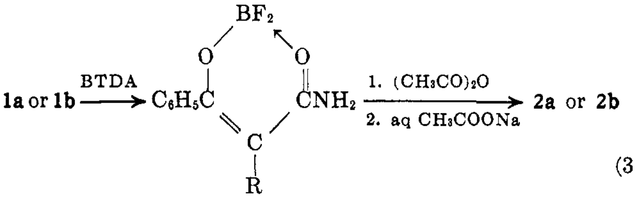
The identity of **2a** was established by comparison with an authentic sample, which was synthesized independently from the dipotassio salt of diacetylimide and methyl benzoate[3] (eq 2). Structual assignment



$$CH_3CO\overset{K}{N}COCH_2K \xrightarrow[\text{2. } NH_4Cl]{\text{1. } C_6H_5COOCH_3 \text{ (liq } NH_3)} \mathbf{2a} \quad (2)$$

2b was based on analysis and spectral studies. The infrared spectrum had N–H absorption at 3.10 μ and carbonyl absorptions at 5.80 and 5.95 μ.[4] The nmr spectrum[5] had singlets at 2.20 and 6.60 ppm for the methyl protons of the N-acetyl group and the methinyl hydrogen, respectively. In addition, there was complex aromatic absorption centered at 7.80 ppm. The integrated intensity of this latter multiplet indicated that the imide proton signal was obscured by the aromatic absorption.

Since Hauser and Eby[2] have demonstrated that their method for conversion of β-ketonitriles to β-ketoamides involves intermediate formation of boron difluoride complexes of the β-ketoamides, it is suggested that the present conversion may involve initial reaction of **1a** and **1b** with BTDA to form boron difluoride complexes **3a** and **3b**,[6] followed by N acetylation of the complexes[7] to afford **2a** and **2b** (eq 3). This sequence was supported



(3)

3a, R = H
b, R = C_6H_5

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society, Grant No 344-G.

[2] C. R. Hauser and C. J. Eby, *J. Am. Chem. Soc.*, **79**, 725 (1957).

[3] S. D. Work, D. R. Bryant, and C. R. Hauser, *ibid.*, **86**, 872 (1964).

[4] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 221.

[5] The nmr spectrum was obtained on a Varian Associates A-60 spectrometer using dimethyl-d_6 sulfoxide as the solvent and tetramethylsilane as external standard. Peak areas were consistent with the assignments given in the Discussion.

[6] Although we have chosen structures **3a** and **3b** to represent the boron difluoride complexes, other structures are possible and are discussed in ref 2 and 7.

[7] See J. F. Wolfe, C. J. Eby, and C. R. Hauser [*J. Org. Chem.*, **30**, 55 (1965)] for a report of the acetylation of a related boron difluoride complex under similar conditions.

by isolation of boron difluoride complexes **3a** and **3b** from the reactions of β-ketonitriles **1a** and **1b** with BTDA in the absence of acetic anhydride, and by subsequent conversion of these complexes to **2a** and **2b** under conditions of the original over-all reaction. In addition, benzonitrile, which would not be expected to form a cyclic boron difluoride complex, failed to undergo conversion to N-acetylbenzamide with BTDA and acetic anhydride. Instead a complex mixture of products was obtained (see Experimental Section).

The present reaction which appears to represent a potentially useful and convenient method for the preparation of certain N-acetyl-β-ketoamides, could presumably be extended in scope by using BTDA and acetic anhydride with other β-ketonitriles.

Experimental Section[8]

Reaction of Benzoylacetonitrile (1a) with Acetic Anhydride and BTDA.—A mixture of 14.52 g (0.10 mole) of benzoylacetonitrile,[9] 81.6 g (0.435 mole) of BTDA,[10] and 32.4 g (0.317 mole) of acetic anhydride was stirred 24 hr at room temperature. The reaction mixture, which contained a heavy white precipitate, was then added to a solution of 60 g of sodium acetate trihydrate in 300 ml of water. The resulting mixture was stirred at room temperature for 48 hr, neutralized with solid sodium bicarbonate to pH 6–7, and extracted with five 100-ml portions of ether–ethyl acetate (1:1). The combined extracts were dried ($MgSO_4$) and concentrated. The resulting crude product was recrystallized from 95% ethanol to give 18.42 g (90%) of pure N-acetyl-α-benzoylacetamide (**2a**) as colorless needles, mp 103–105° (lit.[3] mp 104.5–105°). A mixture melting point with an authentic sample of **2a** (mp 104–105°) prepared from dipotassiodiacetylimide and methyl benzoate,[3] was not depressed. The infrared spectra of the two samples were identical.

Reaction of α-Benzoylphenylacetonitrile (1b) with Acetic Anhydride and BTDA.—A mixture of 8.84 g (0.04 mole) of α-benzoylphenylacetonitrile,[9] 81.6 g (0.435 mole) of BTDA, and 43.2 g (0.423 mole) of acetic anhydride was stirred at room temperature for 24 hr. The homogeneous reaction mixture was processed as in the above procedure. Two recrystallizations of the resulting crude product from 95% ethanol afforded 9.22 g (82%) of pure N-acetyl-α-benzoylphenylacetamide (**2b**) as colorless needles, mp 191–192°.

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.41; H, 5.40; N, 4.75.

Reaction of 1a with BTDA to Form Boron Difluoride Complex 3a.—A 1.0-g (0.0069 mole) sample of **1a** was stirred at room temperature with 13.6 g (0.0725 mole) of BTDA. After 16 hr the homogeneous reaction mixture was added to 100 ml of ice–water to precipitate 1.2 g of boron difluoride complex **3a**, mp 182–185°, and 185–187° (lit.[2] mp 186.5–188.5°) after two recrystallizations from ether–petroleum ether (bp 30–60°); infrared absorption (KBr) at 2.9, 3.1, 6.0, and 6.2 μ.

In a similar experiment **3a** was isolated in 96% yield by removal of the excess BTDA under reduced pressure at room temperature.

Reaction of 1b with BTDA to Form Boron Difluoride Complex 3b.—A 1.0-g (0.0045 mole) sample of **1b** was stirred at room temperature with 13.6 g (0.0725 mole) of BTDA. After 16 hr the reaction mixture was processed as in the preceding experiment to give 1.23 g (75%) of crude **3b**, mp 154–160°. Three recrystallizations of the crude material from ether–petroleum ether (bp 30–60°) afforded an analytical sample: mp 168–170°; infrared absorption (KBr) at 2.9, 3.0, 6.1, and 6.2 μ.

Anal. Calcd for $C_{15}H_{12}BF_2NO_2$: C, 62.75; H, 4.21; N, 4.88. Found: C, 62.62; H, 4.34; N, 4.98.

In another experiment **3b** was obtained in 93% yield by evaporation of the excess BTDA under vacuum at room temperature.

Acetylation of Boron Difluoride Complexes 3a and 3b with Acetic Anhydride and BTDA.—A 1.0-g (0.0047 mole) sample of **3a** was stirred at room temperature with 4.08 g (0.0435 mole) of BTDA and 3.24 g (0.0317 mole) of acetic anhydride. After 12 hr the reaction mixture was hydrolyzed with aqueous sodium acetate and processed in the usual manner to produce 0.88 g (90%) of **2a**.

Similarly, reaction of 0.8 g (0.0028 mole) of **3b** with 4.1 g (0.0435 mole) of BTDA and 2.16 g (0.0211 mole) of acetic anhydride afforded, after hydrolysis, 0.64 g (82%) of **2b**.

Reaction of Benzonitrile with Acetic Anhydride and BTDA.—A mixture of 10.3 g (0.1 mole) of benzonitrile, 81.6 g (0.435 mole) of BTDA, and 32.4 g (0.317 mole) of acetic anhydride was stirred at room temperature for 24 hr. The reaction mixture was hydrolyzed with sodium acetate solution as described above and processed in the usual manner to afford a dark red oil which failed to crystallize. A thin layer chromatogram indicated the presence of benzamide and at least four other components.

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[8] Melting points were taken on a Thomas–Hoover melting point apparatus in open capillary tubes, and are corrected. Analyses were by Galbraith Laboratories, Knoxville, Tenn., and by Thomas D. Greenwood using an F & M Model 185 C, H, and N analyzer. Infrared spectra were taken on a Beckman IR-5 infrared spectrophotometer. Thin layer chromatograms were carried out with an Eastman chromagram apparatus using chromagram sheets Type K301R (silica gel) with fluorescent indicator and chloroform as the developing solvent. Spots were detected with ultraviolet light.

[9] C. R. Hauser and C. J. Eby, *J. Am. Chem. Soc.*, **79**, 723 (1957).

[10] This liquid coordination complex ($BF_3 \cdot 2CH_3COOH$), which contained 36% by weight of BF_3, was obtained from the Harshaw Chemical Co. and used without further purification.