The quantity of μ_{EDA} may be approximated to the dipole moment of EVE, 1.25 D, because the polarity change due to the EDA complex formation is presumed to be very small. The estimation of $\mu_{\pm}$ by the use of the literature value[12] of q results in 15 ± 1 D, which is surprisingly in accordance with value of the TCNE–*n*-butyl vinyl ether system.[4a] Due to the presumed zwitterionic character[1] of (TS), the relative rate of the cycloaddition may be correlated with the electron density on the β carbon on vinyl ether. On the other hand, there are some suggestions that the interaction with the α-carbon is very important in (TS) as well as the EDA complex formation.[13] The origin of high dipole moment of (TS) is left unsolved. Studies of the effect of electron densities of α- and β-carbons on volume changes are in progress.

Experimental Section

All chemicals were commercially obtained. Tetracyanoethylene (TCNE) was sublimed three times under vacuum at 50–55 °C in the presence of active carbon, mp 201 °C. Ethyl vinyl ether (EVE) was washed five times with slightly alkaline water (pH 8), dried over KOH for 30 h, and then distilled three times, bp 35.5 °C. Chloroform (Spectrograde Reagent, Nakarai Chemicals Ltd.) was used without further purification.

The cycloadduct (P) was prepared from CH_2Cl_2 solution for the purpose of identification. Although the same reaction occurs in $CHCl_3$, the preparation in CH_2Cl_2 is easier because the solubility of TCNE is about fivefold larger in CH_2Cl_2. To 100 mL of CH_2Cl_2 containing 8 mmol of TCNE 1 mol of EVE was added slowly at room temperature. The TCNE dissolved in the course of the reaction. After about 10 h, a large quantity of petroleum ether was added to the solution, and then the precipitate was recrystallized from CH_2Cl_2. The product was identified as (P): mp 141 °C; NMR (JEOL JNM-PS-100, in Me_2CO-d_6) δ 1.32 (t, 3, CH_3), 3.12, 4.00 (m, 4, OCH_2 and CH_2), 5.12 (t, 1, CH). Anal. Calcd: C, 59.99; H, 4.03; N, 27.99; O, 7.99. Found: C, 59.39; H, 3.95; N, 38.54; O, 8.00.

Kinetic Experiment. The UV spectrum and reaction rate at atmospheric pressure were determined with a double-beam spectrophotometer (Shimadzu UV 200S) and a rapid mixing apparatus (Union Giken MX-7-03) in 10-mm quartz cuvettes. The concentration after mixing was 1–5 mmol/kg for TCNE and 0.05–0.7 mol/kg for EVE.

The high-pressure experiment was carried out by using the in situ mixing technique described elsewhere.[8] The TCNE solution was in a reaction cell made of nonmagnetic stainless steel having two quartz windows (path length 8 mm) and containing a Teflon-coated magnet attached to a glass capsule containing EVE solution. These inner cell parts were assembled in the high-pressure bomb equipped with two sapphire windows, the pressure was raised, and after attainment of thermal equilibrium the glass capsule was broken with the aid of movement of the magnet caused by an electrical trigger. The solutions were mixed completely within 5 s. The transmittance at 428 nm was followed with a single-beam spectrophotometer (Hitachi-139). The reference light intensity was taken for TCNE solution before mixing; the TCNE was transparent at 428 nm.

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Registry No.—EVE, 109-92-2; TCNE, 670-54-2; P, 39963-85-4.

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Pentafluorophenyl Acetate: A New, Highly Selective Acetylating Agent[1]

Lajos Kisfaludy,* Tivadar Mohacsi, Miklos Low, and Ferenc Drexler

Chemical Works of Gedeon Richter Ltd., 1475-Budapest, Hungary

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The remarkable success of pentafluorophenyl esters in peptide chemistry[2] prompted us to examine the potential application of esters of this type in acylation reactions beyond the scope of peptide chemistry. We are now reporting pentafluorophenyl acetate[3,4] (1) as a new, highly reactive acetylating agent, useful for acetylation of N and O functions under mild conditions, with outstanding selectivity toward the former. Compound 1 is easily accessible in ≥90% yield from pentafluorophenol (2) and acetyl bromide and is stable at room temperature.

Pentafluorophenyl acetate (1), applied in 3 molar equiv, reacts smoothly with primary and secondary amines in dimethylformamide (DMF), usually at ordinary temperature, to give the corresponding *N*-acetyl derivatives in high yields. According to TLC, the reactions go to completion within 2–12 h. The following amines were acetylated: ethylamine (81), isopropylamine (88), *tert*-butylamine (77), cyclohexylamine (81), dicyclohexylamine (72), morpholine (81), aniline (84), *N*-methylaniline (83), benzylamine (82), and α-phenylethylamine (75). The numbers in parentheses indicate the percent yields of purified acetylated amines obtained from 1–2 mmol of amines in 3 mL of DMF. Acetylation of dicyclohexylamine required heating 4 h at 80 °C.

The acetylation of alcohols requires the presence of a tertiary base, such as triethylamine (TEA). Thus, acetylation of ethanol in a mixture of 1.7 mmol of EtOH, 5.1 mmol of 1, and 5.1 mmol of TEA in 1 mL of DMF went to 10, 36, and >90% completion in 20, 120 min, and ~24 h, respectively, at room temperature. At 80 °C the reaction was complete in 68, 87, and 90% yield in 60, 140, and 160 min, respectively, according to GC. Under identical conditions at 80 °C, acetylation of isopropyl alcohol was complete in 16, 60, and 92% in 1.4, 5.75, and 15.5 h, respectively, according to GC.

The following alcohols and phenols were acetylated by heating 1–3 mmol of each with 3 molar equiv of both 1 and TEA in 3 mL of DMF at 80 °C for 12–60 h: ethylene glycol (72%), 1,2-propanediol (75%), glycerol (74%), cyclohexanol (80%), benzyl alcohol (92%), benzyl lactate (78%), and estradiol (82% 3-acetate and 67% diacetate). Pentafluorophenol (2) formed in the reaction was removed during distillation or crystallization of the products. The reactions were followed by GC or TLC, and the products were ≥99% pure according to GC.

The outstanding difference in the reactivity of 1 toward amines and alcoholic hydroxyl groups in the absence of tertiary base together with sufficient activation of 1 by TEA to acetylate primary and secondary alcohols in DMF render 1 a highly advantageous acetylating agent for both selective N-acetylation and N,O-diacetylation of amino alcohols in the

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Table I. Acetylation of Amino Alcohols

amino alcohol	registry no.	*N*-acetylation % yield	registry no.	N,O-diacetylation % yield	registry no.
2-aminoethanol	141-43-5	78	142-26-7	84	16180-96-4
3-aminopropanol	156-87-6	91	10601-73-7	87	68423-09-6
DL-1-amino-2-propanol	1674-56-2	83	68423-06-3	79	68423-10-9
DL-1-phenyl-2-aminoethanol	1936-63-6	89	68423-07-4	77	68423-11-0
DL-norephedrine	54680-46-5	86	38014-69-6	75	68423-12-1
(−)-ephedrine	299-42-3	85	2272-83-5		
3	716-61-0	88	4423-58-9	84[a]	40958-11-0
				78[b]	51259-82-6
D-glucosamine	3416-28-4	88	7512-17-6		
L-threonine benzyl ester	33640-67-4	82	68423-08-5	79	68423-13-2

[a] Diacetate. [b] Triacetate.

absence and presence of TEA, respectively. Moreover, even the conditions necessary for O-acetylation appear to be mild enough to prevent undesirable side reactions, such as dehydration or rearrangement, occasionally occurring in the case of sensitive molecules with the usual acetylating agents, such as acetic anhydride.

Table I lists some amino alcohols which were both N- and N,O-acetylated. N-Acetylations were carried out at ordinary temperature with 3 molar equiv of **1**. N,O-Acetylations were accomplished with 6 molar equiv of both **1** and TEA, usually at 80 °C. D(−)-*threo*-1-(*p*-Nitrophenyl)-2-amino-1,3-propanediol (**3**) was selectively diacetylated at the amino and the primary alcoholic hydroxyl groups at ordinary temperature and triacetylated at 80 °C, respectively.

Experimental Section

The NMR spectra were determined on a Varian EM 360 spectrometer (60 MHz, Me_4Si as an internal standard), and IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. All materials were commercially available and purified, when necessary, by distillation or crystallization by known methods. DMF was freshly distilled under vacuum from phosphoric anhydride. All acetylated products were purified by crystallization or distillation and identified by TLC or GC using authentic samples, as well as by melting point, boiling point, n_D, IR, and some of them by elemental analysis and NMR.

Preparation of Pentafluorophenyl Acetate (1). Acetyl bromide (25 mL, 0.34 mol) was added to pentafluorophenol (**2**; 50 g, 0.27 mol), and the mixture was allowed to stand for 2 h. The mixture became homogeneous within 20–30 min with vigorous liberation of HBr and spontaneous cooling. The flask was attached to a distilling apparatus, and air passed through $CaCl_2$ was passed through the mixture at 60–80 torr internal pressure at room temperature for 1 h to remove HBr. The internal temperature was then raised to 80 °C to distill excess acetyl bromide, followed by distillation of the product to give 55.9 g of pentafluorophenyl acetate: 91% yield; mp 26–27 °C; bp 59–60 °C (12 torr); $d^{26} = 1.48$ g/mL; n^{26}_D 1.4150; IR ($CHCl_3$) $\nu_{C=O}$ 1792 cm^{-1}; NMR ($CDCl_3$) δ 2.43; MS was fully compatible with structure, molecular ion at m/e 226.[5] The yield was decreased to 75–80% when undried air was passed through the contents of the flask throughout the procedure.

General Procedure for the Acetylation of Amines. Compound **1** (3 molar equiv) was added to a solution of 1–2 mmol of amine in 3 mL of DMF, and the mixture was kept at room temperature until TLC no longer revealed the presence of free amine. The solution was evaporated to dryness in a rotary evaporator at 40 °C, and the residue was worked up according to one of the following procedures.

(a) The residue was dissolved in 20–50 mL of water and excess **1** was separated. After removal of water, the residue was either distilled from glass wool or triturated with 5–10 mL of hexane containing 1–2 drops of ether, followed by crystallization.

(b) The residue was repeatedly triturated with hexane–ether as above and crystallized from a suitable solvent.

(c) The residue (in the case of *N,N*-dicyclohexylacetamide) was treated with charcoal in ether, evaporated, triturated with 3 mL of water containing 1–2 drops of ethanol, and kept overnight in the cold. The crystalline product was recrystallized from water, mp 101–102 °C.

General Procedure for the Acetylation of Alcohols. A solution of 1–3 mmol of the alcohol and 3 equiv of both **1** and TEA (per OH group) in 3 mL of DMF was heated at 80 °C until GC no longer revealed the presence of unchanged or partially acetylated alcohol. Then (dimethylamino)ethylamine was added at ordinary temperature in 10% excess based on the excess of **1**, and the mixture was kept for 2 h. After evaporation at 40 °C, the residue was dissolved in 50 mL of ether and the solution was washed with 1 N HCl, $NaHCO_3$ solution, and water, dried over Na_2SO_4, and evaporated. The residue was either distilled from glass wool or crystallized from a suitable solvent.

Illustrative Example for the Acetylation of Amino Alcohols. A. N-Acetylation. A mixture of 122.2 mg (2 mmol) of ethanolamine and 1.356 g (6 mmol) of **1** in 3 mL of DMF was kept overnight and evaporated to dryness under vacuum. The residue was dissolved in 30 mL of water, excess **1** was separated, and the solution was evaporated again. The residue was distilled from glass wool to give 162.5 mg of *N*-(2-hydroxyethyl)acetamide: 78% yield, bp 140–142 °C (2 torr); n^{22}_D 1.4713.

B. N,O-Acetylation. A mixture of 122 mg (2 mmol) of ethanolamine, 2.713 g (12 mmol) of **1**, and 1.66 mL (12 mmol) of Et_3N in 3 mL of DMF was heated at 80 °C for 3 h and evaporated. The residue was dissolved in 30 mL of water, and the solution was extracted with 2 × 5 mL of ether, stirred with Dowex 50 (H^+) resin for 5 min, and evaporated, followed by distillation of the residue from glass wool to give 243.8 mg of *N*-(2-acetoxyethyl)acetamide: 84% yield; bp 140–142 °C (5 torr); n^{24}_D 1.4517.

The following compounds appear to be unavailable in the literature.

DL-2-Acetamino-1-phenylethyl Acetate: oil; n^{27}_D 1.5165; IR ($CHCl_3$) ν_{max} 3290, 1735, 1655, 1545, 1230, and 1040 cm^{-1}; NMR ($CDCl_3$) δ 1.92 (s, 3 H, $NHCOCH_3$), 2.08 (s, 3 H, CH_3CO_2), 3.62 (broad d, 2 H, β-CH_2), 5.86 (dd, 1 H, α-CH), 6.4 (broad, 1 H, NH). Anal. $C_{12}H_{15}NO_3$ (221.3) requires: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.23; H, 6.70; N, 6.40.

***N,O*-Diacetyl-DL-norephedrine:** mp 82–83 °C; IR ($CHCl_3$) ν_{max} 3260, 1745, 1640, 1550 cm^{-1}; NMR ($CDCl_3$) δ 1.06 (d, J = 7 Hz, 3 H, $CHCH_3$), 1.92 (s, 3 H, $NHCOCH_3$), 2.14 (s, 3 H, CH_3CO_2), 4.15–4.70 (m, 1 H) [after D_2O exchange: δ 4.45 (dq, J = 4.5 and 7 Hz, NH–CH)], 5.88 (d, J = 4.5 Hz, 1 H, O–CH), 6.2 (broad d, $J \sim 10$ Hz, 1 H, NH). Anal. $C_{13}H_{17}NO_3$ (235.3) requires: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.45; H, 7.30; N, 5.96.

***N*-Acetyl-L-threonine Benzyl Ester:** mp 98–99 °C; $[\alpha]^{20}_D$ −7.2° (*c* 1, EtOH); IR ($CHCl_3$) ν_{max} 3470, 3320, 1645, 1545 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (d, $J \sim 6.5$ Hz, 3 H, $CHCH_3$), 2.03 (s, 3 H, CH_3CONH), 3.4 (broad s, 1 H, OH), 4.1–4.8 (m, 2 H, CH) [after D_2O exchange: δ 4.32 (dq, J = 4 and 6.5 Hz, 1 H, O–CH), 4.62 (d, J = 4 Hz, 1 H, NH–CH)], 5.18 (s, 2 H, CH_2), 6.7 (broad d, $J \sim 9$ Hz, 1 H, NH). Anal. $C_{13}H_{17}NO_4$ (251.3) requires: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.20; H, 6.85; N, 5.69.

***N,O*-Diacetyl-L-threonine Benzyl Ester:** mp 80–81 °C; $[\alpha]^{20}_D$ −9.5° (*c* 1, EtOH); IR ($CHCl_3$) ν_{max} 3250, 3200, 3060, 1740, 1640, 1560, 1240, 1070 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (d, $J \sim 6.5$ Hz, 3 H, $CHCH_3$), 1.87 (s, 3 H, CH_3CONH), 2.09 (s, 3 H, CH_3CO_2), 4.89 (dd, J = 9 and 3.5 Hz, 1 H, NH–CH), 5.48 (dq, J = 3.5 and 6.5 Hz, 1 H, O–CH), 5.18 (s, 2 H, CH_2), 6.4 (broad d, $J \sim 9$ Hz, 1 H, NH); the signal at δ 4.89 collapsed into a doublet ($J \sim 3.5$ Hz) after D_2O exchange. Anal. $C_{15}H_{19}NO_5$ (293.3) requires: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.46; H, 6.30; N, 4.70.

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for the GC analyses, IR, NMR, and mass spectra, respectively.

Registry No.—1, 19220-93-0; 2, 771-61-9.

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Facile Preparation of Cyclic Ethylene Thioketals and Thioacetals with 2-Phenyl- and 2-Chloro-1,3,2-dithiaborolanes[1]

Douglas R. Morton* and Steven J. Hobbs

Experimental Chemistry Research, The Upjohn Company, Kalamazoo, Michigan 49001

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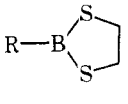
The importance of cyclic ethylene thioacetals and thioketals in organic synthesis as temporary protecting forms for aldehydes and ketones has been well documented in the literature.[2] The advantages of cyclic ethylene thioacetals and thioketals relative to their oxygenated counterparts include: (1) ease of formation from dithiols and carbonyl substrates; (2) relative resistance to acidic and basic reaction conditions;[2a,3] (3) relative resistance to cleavage by organometallic reagents (e.g., Grignard and alkyllithium reagents);[2a,4] (4) lack of double bond migration with α,β-unsaturated carbonyl substrates;[2a,5] and (5) availability of mild conditions for hydrolysis back to the carbonyl substrate.[3,5,6]

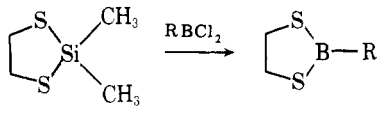
Despite these advantages, however, the formation of cyclic ethylene thioacetals and thioketals from carbonyl substrates generally requires the presence of a strong acid catalyst. As a consequence, their use as carbonyl protecting forms is not always feasible when other acid sensitive functional groups are present in the substrate molecule. Evans has provided an alternative method which circumvents this problem by the use of methylthiotrimethylsilane.[7] Mild methods for effecting thioketallization have also been developed using alkyl orthothioborates;[8-10] however, no work has been reported to date on the use of alkyl orthothioborates as thioketallizing agents for carbonyl substrates with any degree of complexity. Further, no attempts have been made to our knowledge to generate cyclic ethylene thioacetals and thioketals from carbonyl substrates and 2-substituted 1,3,2-dithiaborolanes (e.g., **1**). Accordingly, we have investigated the nature and scope of the reaction of **1a** and **1b** with a variety of carbonyl substrates and report our findings below.



1a, R = C_6H_5
b, R = Cl

Results and Discussion

The dithiaborolanes **1a** and **1b** were synthesized by the methods of Abel et al.[11] Briefly, these reagents were prepared



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by the reaction of an appropriately substituted boron dichloride with 2,2-dimethyl-1,3-dithia-2-silacyclopentane, and the latter compound was synthesized in good overall yield (ca. 90%) from dichlorodimethylsilane.[11b] Although these reagents are quite reactive, they may be conveniently stored at or below room temperature under nitrogen without appreciable decomposition.

The reactions of 2-phenyl-1,3,2-dithiaborolane (**1a**) with a variety of carbonyl substrates are summarized in Table I. In the majority of examples described, the yields of thioacetal or thioketal products are comparable to or better than those reported in the literature for reaction of the carbonyl substrate and ethanedithiol in the presence of an acid catalyst. Simple aromatic aldehydes (e.g., **2** and **8**) react rapidly with **1a** to give the corresponding thioacetal in essentially quantitative yield, and simple dialkyl ketones (e.g., **4**) react to give the thioketal in high yield. Diaryl ketones, on the other hand, are slow to react. Fluorenone (**6**) only affords a thioketal product in poor yield after greater than 12 h at reflux temperature in chloroform. In similar fashion, benzophenone fails to undergo any detectable reaction with **1a**. The reagent **1a** also displays good steric selectivity with multicarbonyl substrates as evidenced by the reactions of **12** and **17**.[21] Further, even though **1a** is rapidly decomposed by water and simple alcohols, it appears to be unaffected by a hindered alcohol (e.g., **15**).

In all of the above cited examples, the boron-containing byproduct formed is triphenylboroxine (**19**),[10a] and this substance is most easily removed by chromatography. In many instances, a quick chromatographic filtration over silica gel is all that is required to purify the reaction mixture. Examination of these reactions in a variety of different solvents at 25 °C revealed that polar solvents enhance the rate of reaction (chloroform > benzene > carbon tetrachloride) while polar solvents containing heteroatoms (e.g., tetrahydrofuran, dioxane, or acetonitrile) appear to act as Lewis bases and reduce the reactivity of **1a** presumably by a complexation phenomenon.

The reactions of 2-chloro-1,3,2-dithiaborolane (**1b**) with three carbonyl substrates are also summarized in Table I. Reagent **1b** is very much more reactive than **1a** as evidenced by the fact that both fluorenone (**6**) and benzophenone (**20**) are quantitatively converted to their thioketals at room temperature. This increased reactivity is also reflected by the observations that **1b** is violently decomposed by water and simple alcohols and that it reacts with multicarbonyl substrates with little or no selectivity (e.g., **12**).

In conclusion, the reactions of **1a** and **1b** with carbonyl substrates to form cyclic ethylene thioacetals and thioketals have been shown to be synthetically useful. Several advantages of the reaction are: (1) the thioacetals and thioketals are formed under mild and anhydrous conditions; (2) the reaction proceeds at room temperature and often at lower temperatures; (3) reagents **1a** and **1b** are readily prepared from commercially available materials and can be kept almost indefinitely in closed containers under nitrogen; (4) the reagent **1a** is selective in its thioketallization capacity for unhindered carbonyls and also displays differential reactivity between aryl and alkyl ketones; (5) the reagent **1b** is extremely reactive toward diaryl ketones and would be useful in the thioketallization of these and other ketones of low reactivity; and (6) the reagent **1a** is mild enough to use with acid sensitive compounds (e.g., furaldehyde and prostaglandins).

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