To a solution of 12.9 g (0.042 mol) of *endo*-7-(methanesulfonyloxy)-methyl-*cis*-decalin-2-one ethylene ketal (**10**) in 120 mL of ether was added 12.6 g (0.1 mol) of oxalic acid dihydrate and 40 mL of water, and the resulting mixture was stirred at ambient temperature for 7 h.

The reaction mixture was mixed with 150 mL of water and extracted with three 50-mL portions of ether. The combined ether extracts were washed with 50 mL of 5% sodium carbonate solution and then with water and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 8.5 g (78% yield) of crude *endo*-7-(methanesulfonyloxy)methyl-*cis*-decalin-2-one (**1**): IR (neat) 1710 ($\nu_{C=O}$), 1350, 1180 ($\nu_{S=O}$), 960, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9–2.6 (complex m, 15 H), 3.00 (s, 3 H, CH_3SO_2), 3.9–4.1 (m, 2 H, CH_2OSO_2); ^{13}C NMR ($CDCl_3$) δ_C 22.9 (t), 26.0 (t), 29.5 (t), 29.6 (t), 34.1 (d), 37.1 (d), 37.9 (q), 38.4 (d), 40.9 (t), 47.4 (t), 74.3 (t), 211.5 (s, C=O); mass spectrum, *m/e* (rel intensity) 164 (41), 107 (41), 106 (100), 99 (47), 93 (53), 91 (62), 79 (78), 77 (46), 67 (53), 55 (42), 53 (50), 41 (97), 39 (97).

2,4-Bishomobrendan-7-one (2). A solution of 10.2 g (0.039 mol) of the crude *endo*-7-(methanesulfonyloxy)methyl-*cis*-decalin-2-one (**1**) obtained above in 100 mL of benzene was added at ambient temperature with efficient stirring to a suspension of 4.7 g (0.20 mol) of sodium hydride in 100 mL of benzene, and the resulting mixture was heated under reflux with stirring for 6 h.

The reaction mixture was filtered, and the filtrate was concentrated. The concentration residue was absorbed on a silica gel packed column and eluted with *n*-hexane to afford 3.4 g (53% yield) of crude 2,4-bishomobrendan-7-one (**2**). Golay column GC–MS showed the sample to be of 92% purity. VPC fractionation yielded a pure sample: IR (neat) 1710 ($\nu_{C=O}$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.8 (complex m); ^{13}C NMR ($CDCl_3$) δ_C 24.2 (t), 28.3 (t), 31.6 (t), 32.5 (t), 33.1 (d), 33.4 (d), 34.7 (t), 39.1 (t), 41.1 (d), 50.2 (d), 217.2 (s, C=O); mass spectrum, *m/e* (rel intensity) 164 (93, M^+), 109 (65), 107 (34), 93 (41), 91 (35), 80 (50), 79 (92), 77 (41), 67 (100), 66 (39), 53 (42), 41 (93), 39 (94).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.3; H, 9.7.

After the 2,4-bishomobrendanone **2** had been eluted, the silica gel column was further eluted with ether. Evaporation of the solvent left 3.4 g (33% recovery) of the starting keto methanesulfonate **1**.

Wolff–Kishner Reduction of the Cyclization Product. A sample (0.1 g, 0.61 mmol) of the crude 2,4-bishomobrendan-7-one (**2**) obtained above was reduced in the usual manner with 0.2 g (4.0 mmol) of 100% hydrazine hydrate and 0.2 g of potassium hydroxide in 20 mL of diethylene glycol to give 0.035 g (38% yield) of the reduction product. The sample was shown upon Golay GC–MS to contain five constituents, of which the major one (93%) agreed with 2,4-bishomobrendane (**3**).[5] The absence of tricyclo[4.4.1.0^{3,8}]undecane (**5**) in the above sample was confirmed by comparison of the GC–MS behaviors of the sample with those of an authentic specimen of **5**.[6]

Registry No.—**1**, 68423-44-9; **2**, 68423-45-0; **3**, 51027-87-3; **6**, 20917-92-4; **7**, 68423-46-1; **8**, 68423-47-2; **9**, 68423-48-3; **10**, 68423-49-4; ethylene glycol, 107-21-1; methyltriphenylphosphonium bromide, 1779-49-3; methanesulfonyl chloride, 124-63-0.

References and Notes

(1) (a) H. W. Whitlock, Jr., *J. Am. Chem. Soc.*, **84**, 3412 (1962); H. W. Whitlock, Jr., and M. W. Siefken, *ibid.*, **90**, 4929 (1968); (b) J. Gauthier and P. Deslongchamps, *Can. J. Chem.*, **45**, 297 (1967); also cf. A. Belanger, J. Poupart, and P. Deslongchamps, *Tetrahedron Lett.*, 2127 (1968); (c) K. A. Adachi, K. Naemura, and M. Nakazaki, *ibid.*, 5467 (1968); (d) J. E. McMurray, *J. Am. Chem. Soc.*, **90**, 6821 (1968); (e) E. Piers, R. W. Britton, and W. de Waal, *Chem. Commun.*, 1069 (1969); E. Piers, W. de Waal, and R. W. Britton, *J. Am. Chem. Soc.*, **93**, 5113 (1971); (f) K. J. Schmeizl and R. N. Mirrington, *Tetrahedron Lett.*, 3219 (1970); *J. Org. Chem.*, **37**, 2877 (1972); (g) S. A. Monti and S.-S. Yuan, *ibid.*, **36**, 3350 (1971); S. A. Monti and J. H. Harless, *J. Am. Chem. Soc.*, **99**, 2690 (1977); S. D. Larsen and S. A. Monti, *ibid.*, **99**, 8015 (1977); (h) J.-L. Gras, *Tetrahedron Lett.*, 4117 (1977); (i) C. H. Heathcock and B. E. Ratcliffe, *J. Org. Chem.*, **37**, 1298 (1972).

(2) Z. Majerski, Z. Hamersak, and D. Skare, *Tetrahedron Lett.*, 3943 (1977).

(3) E. Osawa, K. Aigami, N. Takaishi, Y. Inamoto, Y. Fujikura, Z. Majerski, P. v. R. Schleyer, E. M. Engler, and M. Farcasiu, *J. Am. Chem. Soc.*, **99**, 5361 (1977).

(4) A. G. Anderson, Jr., and D. O. Barlow, *J. Am. Chem. Soc.*, **77**, 5165 (1955).

(5) Y. Fujikura, M. Ohsugi, Y. Inamoto, N. Takaishi, and K. Aigami, *J. Org. Chem.*, **43**, 2608 (1978), and the references cited therein.

(6) N. Takaishi, Y. Fujikura, Y. Inamoto, and K. Aigami, *J. Org. Chem.*, **42**, 1737 (1977).

(7) C. A. Cupas, W. E. Heyd, and M.-S. Kong, *J. Am. Chem. Soc.*, **93**, 4623 (1971).

(8) If we take **1s** as the ground state for **4t**, separately from that (**1g**) for **2t**, the same conclusion holds true (Curtin–Hammett principle). Cf. E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 238.

(9) A similar conformational situation with respect to the relative orientation of the two competitive carbanions (C-5 and C-7) and the sulfonate was encountered with 6-keto-*exo*-1-*cis*-decalyl tosylate [C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Am. Chem. Soc.*, **89**, 4133 (1967)], and here again the selectivity was exhibited toward the cyclization via the C-5 anion. The cause was attributed in this case to an electronic effect arising from a better orbital overlap with C-5 than with C-7 between the vacant p orbital formed on the leaving of the tosylate and the anionic p orbital. However, no such preference in the electronic factor is found with our **4t** and **11t** because of conformational mobility of the mesyloxy group.

(10) S. Natelson and S. Gottfried, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, 1955, p 382.

High-Pressure Kinetics of Electron Donor–Acceptor Complex Formation and Cycloaddition with Tetracyanoethylene and Ethyl Vinyl Ether

Muneo Sasaki,* Hideaki Tsuzuki, and Masami Okamoto

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, 606 Japan

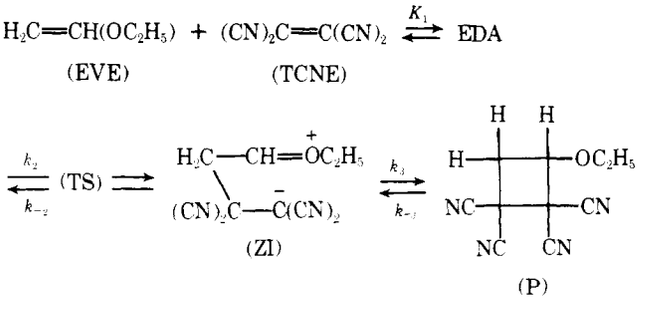
Received September 8, 1978

The cycloaddition of tetracyanoethylene (TCNE) to electron-rich olefins such as enol ether is supposed to take place through a zwitterionic intermediate or transition state, as supported by a strong dependency on solvent polarity,[1] incomplete stereospecificity,[2] and acetal formation in alcoholic solvents.[3] Strong evidence for the high polarity of the transition state was also obtained from high-pressure kinetics which gives the volume of activation. The overall values of the volume of activation for the cycloaddition of TCNE with enol ether are largely negative,[4] and even the cycloreversion has a negative volume of activation,[5,6] despite the bond-breaking process. These mechanistic studies so far, however, have not evaluated the role of the colored electron donor–acceptor complex (EDA complex) which appears immediately after the mixing of TCNE and enol ether, and which fades with the formation of the cycloadduct.

In the case of the Diels–Alder reaction between TCNE and 9,10-dimethylanthracene, the EDA complex was proved to be a true intermediate by the fact that the overall enthalpy of activation was negative.[7] The present work determines the volume change of each reaction step, both the EDA complex formation and the cycloaddition, in the reaction between TCNE and ethyl vinyl ether (EVE) in chloroform, based on the reaction scheme that the EDA complex is part of the pathway to the cycloaddition.

The disappearance of the EDA complex is too fast to be followed by conventional method under high pressure. The technical difficulty has restricted the high-pressure study of thermal reactions in which such short-lived species occur. The

Scheme I



0022-3263/79/1944-0652$01.00/0

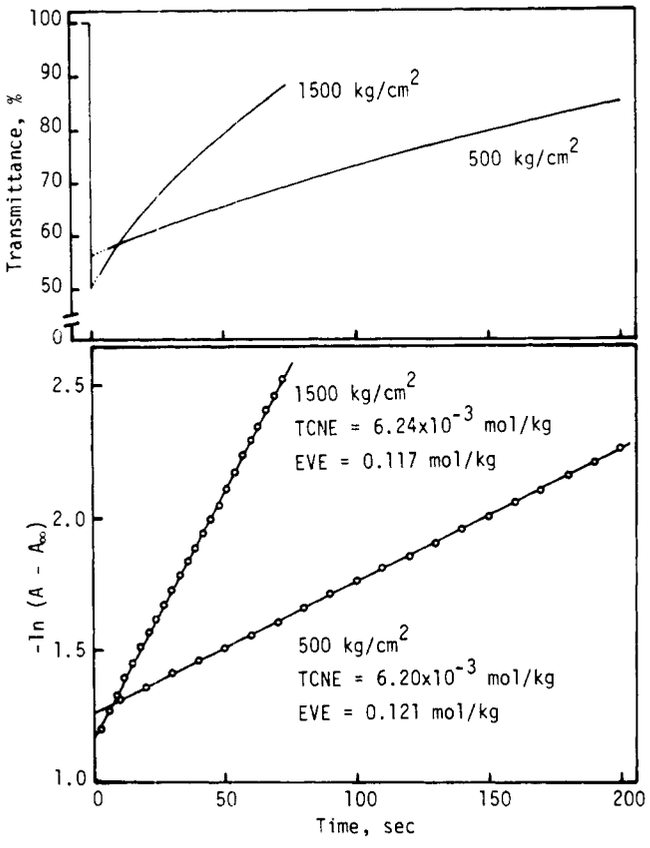


Figure 1. Photometric decay curve and its first-order plot of EDA complex between TCNE and EVE in chloroform at 25 °C.

problem was solved by using the in situ mixing technique developed by the present authors.[8]

The time dependence of absorbance at 428 nm (λ_{max} of the EDA complex) obeys the first-order rate equation very well when EVE is in large excess over TCNE, as shown in Figure 1; it was extrapolated to $t \rightarrow 0$, and with the absorbance A_0 at $t = 0$, the equilibrium constant of the EDA complex formation K_1 was determined by the Benesi–Hildebrand equation.

$$\frac{a}{A_0} = \frac{1}{\epsilon l} + \frac{1}{K_1 \epsilon l}\frac{1}{d} \tag{1}$$

In this equation, a is the initial TCNE concentration, d the EVE concentration, ϵ the molal absorption coefficient of the EDA complex, and l the optical path length. From the slope of the plot a/A_0 vs. $1/d$ and the known quantities of ϵ and l,[9] the values of K_1 at 25 °C were determined at pressures up to 1500 kg/cm² (1 kg/cm² = 0.9806 × 10^5 Pa).

The cycloreversion is practically negligible in the course of the disappearance of the EDA complex under the present experimental conditions, and the zwitterionic intermediate (ZI) was not accumulated. So, k_{-3}/k_3 and/or k_{-2} in Scheme I are considered to be very small, and k_2 is held to be the rate-determining step. The kinetic analysis gives the observed first-order rate constant k_{obsd} as represented by

$$k_{obsd} = \frac{k_2 K_1 d}{(1 + K_1 d)} \tag{2}$$

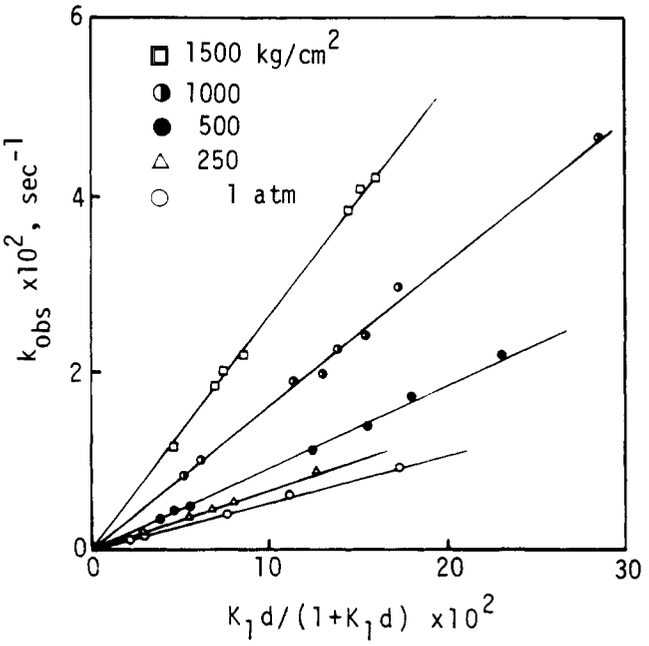


Figure 2. Dependence of k_{obsd} on EVE concentration. The slope of each line gives the value of k_2 at that pressure (eq 2).

As seen in Figure 2, the plot of k_{obsd} vs. $K_1 d/(1 + K_1 d)$ gives straight lines passing the origin. The equilibrium constant and the rate constant k_2 are shown in Table I together with the volume change ΔV_1 and the volume of activation $\Delta V_2^{\ddagger}$ at 1 atm, which can be calculated from the relation $\{\partial \ln K_1(\text{or } k_2)/\partial P\}_T = -\Delta V_1(\text{or } \Delta V_2^{\ddagger})/RT$.

The sum of ΔV_1 and $\Delta V_2^{\ddagger}$ agrees very well with the overall volume of activation $\Delta V_{exp}^{\ddagger}$ (= −38.0 cm³/mol) which was previously determined by observing the disappearance of TCNE in dichloromethane.[4b] The EDA complex is not highly polar, and the volume change accompanying its formation is known to be in the range of −3 to −10 cm³/mol;[10] the contraction is mainly due to the structural contribution as the component molecules come close together. The radius of the complex r_{EDA} based on the ideal and spherical model is estimated to be 4.2 Å from ΔV_1 and from the molar volume of TCNE and EVE,[11] under the assumption that the solvation term in ΔV_1 is negligible.

For the activation process of the cyclobutane ring formation, the EDA complex is expected to further contract by nearly 4 cm³/mol, since the overall volume of activation (i.e., the difference of molar volume between the adducts and the transition state) has been found to be about −14 cm³/mol.[4a] The radius of the transition state (TS) is 4.17 Å by a similar calculation. The solvation part in $\Delta V_2^{\ddagger}$, $\Delta V_2^{\ddagger}$ (solv) = $\Delta V_2^{\ddagger}$ − (−4) = −24 cm³/mol, is reasonably assumed to come from the change in solvation between the EDA complex and (TS), as expressed by Kirkwood's relation.

$$\Delta V_2^{\ddagger}(\text{solv}) = -N\left(\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} - \frac{\mu_{EDA}^2}{r_{EDA}^3}\right) q$$

$$q = \frac{3}{(2D + 1)^2}\left(\frac{\partial D}{\partial P}\right)_T \tag{3}$$

Table I. Equilibrium Constant, Rate Constant, and Volume Change at 25 °C in Chloroform

pressure, kg cm^{-2}	1	250	500	1000	1500
K_1, kg mol^{-1}	0.37 ± 0.01	0.42 ± 0.02	0.49 ± 0.02	0.56 ± 0.02	0.63 ± 0.03
k_2, s^{-1}	0.053 ± 0.002	0.069 ± 0.002	0.093 ± 0.003	0.161 ± 0.004	0.271 ± 0.005
ΔV_1, cm^3 mol^{-1}	−10.3 ± 1.4				
$\Delta V_2^{\ddagger}$, cm^3 mol^{-1}	−28.0 ± 2.0				

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.

Acknowledgment. This work was partly financed by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 147007).

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

References and Notes

(1) G. Steiner and R. Huisgen, *J. Am. Chem. Soc.*, **95**, 5056 (1973); *Tetrahedron Lett.*, 3769 (1973).
(2) R. Huisgen and G. Steiner, *J. Am. Chem. Soc.*, **95**, 5054, 5055 (1973).
(3) R. Huisgen, R. Schug, and G. Steiner, *Angew. Chem., Int. Ed. Engl.*, **13**, 80 (1974).
(4) (a) K. Fleischman and H. Kelm, *Tetrahedron Lett.*, 3773 (1973); (b) G. Swieton, J. V. Jouanne, and H. Kelm, *Proc. Int. Conf. High Pressure, Kyoto, 4th*, 652 (1974).
(5) W. J. le Noble and R. Mukhtar, *J. Am. Chem. Soc.*, **97**, 5938 (1975).
(6) J. Osugi, M. Sasaki, H. Tsuzuki, Y. Uosaki, and M. Nakahara, *Proc. Int. Conf. High Pressure, Boulder, Colorado*, to be published.
(7) V. D. Kiselev and J. G. Miller, *J. Am. Chem. Soc.*, **97**, 4036 (1975).
(8) M. Sasaki, M. Okamoto, H. Tsuzuki, and J. Osugi, *Chem. Lett.*, 1289 (1976).
(9) In this work, the value of ϵl which was determined very carefully at 1 atm was used for the determination of K_1 at high pressure without any correction for the small changes of λ_{max} and ϵ.[10]
(10) A. H. Ewald, *Trans. Faraday Soc.*, **64**, 733 (1968); A. H. Ewald and J. A. Scudder, *J. Phys. Chem.*, **76**, 249 (1972); T. Nakayama, M. Sasaki, and J. Osugi, *Rev. Phys. Chem. Jpn.*, **46**, 57 (1976).
(11) The partial molar volume has to be actually considered, but when the solvation term is negligible, the use of molar volume is permissible.
(12) H. Hartmann, A. Neumann, and A. P. Schmidt, *Ber. Bunsenges. Phys. Chem.*, **72**, 877 (1968).
(13) T. Arimoto and J. Osugi, *Rev. Phys. Chem. Jpn.*, **44**, 25 (1974).

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

Received June 27, 1978

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

0022-3263/79/1944-0654$01.00/0