Experimental Section

The melting points were taken on a Thomas–Hoover capillary melting point apparatus and were corrected. Analyses for the rate study were obtained on an F & M Model 720 vapor fractometer using a 6-ft 10% Squalane on Haloport column (U column). All other vapor chromatographic analyses were determined on a 6-ft Carbowax 1500 on Teflon column using a Perkin-Elmer vapor fractometer. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer.

Materials.—Phenyl-2-butenyl ether was prepared according to the method of Goering and Jacobson.[17] Tri-2-butenyl orthoformate was prepared by the exchange reaction of triethyl orthoformate and but-2-en-1-ol, bp 138° (11 mm), n^{20}D 1.4543. Dimethyl sulfoxide and 1,2-dimethoxyethane were distilled over Linde Molecular Sieve 13X before use in the rate study. Potassium *t*-butoxide was purchased from City Chemical Corp.

Rate Study. A. Preparation of Reaction Mixture.—A solution containing 0.6862 (0.00463 mole) of phenyl-2-butenyl ether and 0.324 g of pentane (internal standard) in 7 ml of the desired solvent (DMSO or DME) was prepared and purged with nitrogen. The vial was cooled in Dry Ice and 0.5120 g (0.00457 mole) of potassium *t*-butoxide was added to the solution and the solution purged with nitrogen again before sealing with a serum cap. Each solution was 0.66 *M* in reactant and base. The vial was then placed in a constant-temperature bath, stirred by means of a magnetic stirrer, and then sampled and analyzed.

B. Analyses of Reaction Mixtures.—Aliquots (0.2 ml) were withdrawn at the requisite time and injected in a serum cap sealed vial containing 3 ml of water and 1 ml of isooctane. This sample was cooled in Dry Ice and the hydrocarbon layer was sampled for butadiene by gas chromatography with a pre-cooled syringe. The lower boiling components were analyzed with a U column on the F & M Model 720 vapor fractometer at 50° and the higher boiling components analyzed by programming to 170° at 30°/min. The yield of butadiene was calculated from the gc area of pentane (internal standard) and the gc area of butadiene.

Reaction of 2-Butenyl Phenyl Ether with Potassium *t*-Butoxide.—A suspension of 11.2 g (0.1 mole) of potassium *t*-butoxide in 14.8 g (0.1 mole) of 2-butenyl phenyl ether was heated during 1 hr from 25 to 126° and the gas evolved was passed through a bromine solution in carbon tetrachloride (36 g in 35 ml). After the 1-hr heating period, the gas evolution ceased and the reaction mixture was diluted with 50 ml of water. An organic layer formed which was separated, dried ($MgSO_4$), and filtered. This liquid (6.4 g, 0.043 mole) was shown by infrared analysis to be unreacted starting ether. An additional 1.0 g (0.007 mole) of starting material was obtained by ether extraction of the aqueous reaction mixture. Acidification of the quenched reaction mixture with 3 *N* HCl and subsequent ether extraction provided 3.3 g (0.035 mole) of phenol identified as its tribromo derivative (mp 92–94°).

Evaporation of the bromine–carbon tetrachloride solution provided 16 g (0.043 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutane, mp 115–118° and 37–40° (isomers, lit.[18] mp 116–117° and 38°). The gaseous product was collected as a liquid at low temperature in one experiment and its infrared spectrum in carbon tetrachloride was identical with the spectrum of 1,3-butadiene in the same solvent. In addition this gaseous product formed a solid upon heating with maleic anhydride in benzene, mp 97–99.5° (1,3-butadiene–maleic anhydride adduct, lit.[19] mp 101–103°).

Reaction of 2-Butenyl Orthoformate with Potassium *t*-Butoxide.—A suspension of 11.2 g (0.1 mole) of potassium-*t*-butoxide in 22.6 g (0.1 mole) of 2-butenyl orthoformate was heated during 2 hr from 25 to 95° and the gas evolved was bubbled through a bromine solution in carbon tetrachloride (20 g in 35 ml). Evaporation of the bromine–carbon tetrachloride solution gave 14 g (0.037 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutanes. Infrared analysis of the gaseous product from this reaction proved its identity as 1,3-butadiene. The reaction mixture was distilled at atmospheric pressure to give several liquid fractions. These fractions upon glpc analysis showed the following components present: 2-buten-1-ol (5.0 g, 0.069 mole), 1,3-butadiene (0.87 g, 0.016 mole), *t*-butyl alcohol (3.65 g, 0.049 mole), unknown liquid (0.86 g). The residue which remained in the flask was suspended in 35 ml of a 10% solution of anydrous hydrogen chloride in diethyl ether and stirred at 25° for 1 hr. The ether layer was separated from the solid and evaporated to 4.36 g of a viscous liquid, from which 0.47 g (0.01 mole) of formic acid was isolated. The remaining 3.89 g remained unidentified. Infrared analysis showed the unknown liquid to be a carbonyl compound.

Cleavage Reaction Using Potassium *t*-Butoxide in DMSO. A. 2-Butenyl Phenyl Ether.—A solution of 11.9 g (0.017 mole) of potassium *t*-butoxide and 15.9 g (0.107 mole) of 2-butenyl phenyl ether in 75 ml of DMSO was stirred at 25° for 2 hr. This system was connected to a trap containing a bromine solution in carbon tetrachloride (20 g in 35 ml). Very little gassing occurred at this temperature but heating the solution at 70° for 1 hr produced vigorous gas evolution. The solution was stirred an additional 16 hr at 25° and was then quenched with an equal volume of water. Evaporation of the bromine–carbon tetrachloride solution gave 15 g (0.040 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutanes. Extraction of the aqueous solution with ether provided 7.2 g (0.048 mole) of starting ether. Acidification of the aqueous phase with 3 *N* HCl and subsequent ether extraction gave 3.6 g (0.038 mole) phenol (phenylurethan derivative, mp 123–124°, lit.[20] mp 126°).

B. 2-Butenyl Orthoformate.—A solution of 11.2 g (0.10 mole) of potassium-*t*-butoxide and 22.6 g (0.10 mole) of ortho ester in 75 ml of DMSO was stirred at 25° for 10 min. This system was connected to a bromine trap as described above. There was very little gas evolution at 25° but when the reaction mixture was heated at 70° considerable gassing was observed. After 2 hr at this temperature the reaction was stopped. Dilution of the reaction mixture provided no organic layer. Evaporation of the bromine solution gave 6.6 g (0.017 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutanes. Both 2-buten-1-ol and *t*-butyl alcohol were qualitatively identified as additional products of this reaction by distillation of the reaction mixture before quenching it with water. Quantitative determination of the latter compounds and formic acid was interfered with by the presence of DMSO.

(17) H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

(18) R. A. Jacobson, *ibid.*, **54**, 1545 (1932).

(19) M. C. Klotetzel, *Org. Reactions*, **IV**, 41 (1949).

(20) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p 91.

Tautomerism in N-Acetyl Sulfonamides. A Clarification

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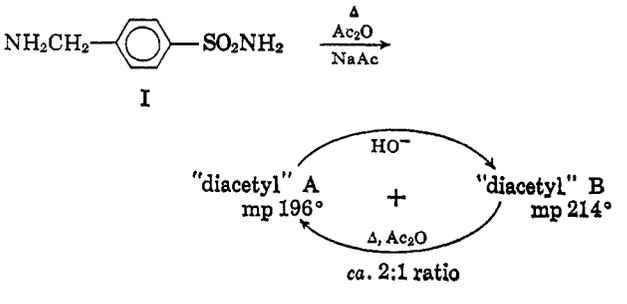
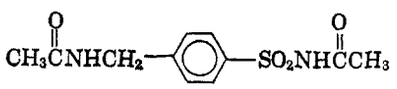
Ishidate and Momose[1] have reported the isolation of two diacetyl-4-(aminomethyl)benzenesulfonamides and assumed the products to be the amide–imide tautomers, $AcNHCH_2C_6H_4SO_2NHAc$ and $AcNHCH_2C_6H_4SO(OH)=NAc$. This conclusion was based on the interconversion of the two products A and B as shown in Scheme I.

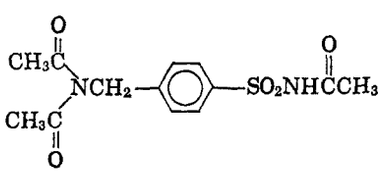
SCHEME I



We have re-examined the reaction and have found that the two "tautomers" are actually the N^1,N^4-diacetyl (mp 214°) II and N^1,N^4,N^4-triacetyl (mp 196°) III derivatives. Reaction of N^4-acetyl-4-(aminomethyl)benzenesulfonamide with 1 mole of acetic anhydride gave the N^1,N^4-diacetyl compound in 99% yield. Increasing the anhydride/sulfonamide molar ratio to three resulted in the isolation of the triacetyl and diacetyl compounds in an 11:3 ratio (over-all 70% yield). When 4-(aminomethyl)benzenesulfonamide was treated with 8 moles of anhydride, only the triacetyl derivative was obtained (68% yield).



II



III

The position of the third acetyl group was ascertained by inspection of the infrared and pmr spectra. Transformation of the methylene doublet to a singlet with a concomitant downfield shift of δ 0.67 unambiguously places the third acetyl group on the benzylamine nitrogen. This assignment is confirmed by the absence of the 6.1-μ carbonyl band (shown by the N^4-acetyl and N^1,N^4-diacetyl derivatives) and the presence of two new carbonyl bands at 5.80 and 5.94 μ in the infrared spectrum of the triacetyl compound[2] (Table I).

TABLE I

SPECTRA OF ACETYLATED 4-(AMINOMETHYL)BENZENESULFONAMIDES

Derivative of 4-(aminomethyl)-benzenesulfonamide	Mp, °C	Pmr, δ[a]	Infrared C=O μ[b]
N^4-Acetyl	175–176.5[c]	1.93 (3, s), 4.37 (2, d)	6.1
N^1,N^4-Diacetyl	214–216	1.93 (3, s), 1.95 (3, s), 4.37 (2, d)	5.84, 6.1
N^1,N^4,N^4-Triacetyl	195–196	2.37 (6, s), 1.95 (3, s), 5.03 (2, s)	5.8, 5.84, 5.94

[a] With respect to internal standard of tetramethylsilane in deuterated dimethyl sulfoxide; spectra obtained on a Varian A-60 spectrometer. Number of protons is in parentheses: s, singlet; d, doublet. [b] KBr disks. [c] J. Klarer [U. S. Patent 2,288,531 (June 30, 1942); *Chem. Abstr.* **37**, 888 (1943)] reported mp 177°.

(1) M. Ishidate and T. Momose, *J. Pharm. Soc. Japan*, **67**, 214 (1947); *Chem. Abstr.*, **45**, 8994*a* (1951).

(2) Cyclic diacylimides show two carbonyl bands for apparently equivalent moieties (H. M. Randall, R. G. Fowler, N. Fuson, and J. Dangl, "Infrared Determination of Organic Structures," Van Nostrand Co., Inc., New York, N. Y., 1949, pp 14, 20). R. A. Abramovitch [*J. Chem. Soc.*, 1413 (1957)] has demonstrated that symmetrically substituted N,N-diacetylanilines reported [J. F. Grove, P. W. Jeffs, and D. W. Rustidge, *J. Chem. Soc.*, 1956 (1956)] to possess only one carbonyl band do in fact on refinement of experimental technique (slit schedules narrowed to 0.5 mm) possess two bands in the carbonyl region. T. Uno and K. Machida [*Bull. Chem. Soc. Japan*, **34**, 545 (1961)] have reported that diacetamide exists in two forms, the "A" *cis–trans* form (relative to the nitrogen proton) in which the compound is usually found showing two carbonyl bands in mulls. Unpublished X-ray data (T. Watanabé and K. Osaki) is cited as establishing the geometric isomerism. C. M. Lee and W. D. Kumler [*J. Am. Chem. Soc.*, **84**, 571 (1962)] have from dipole moment data reached the same conclusion. The less stable "B" form, considered by Uno and Machida to be the *trans–trans* isomer, displays only one major carbonyl band (slight shoulders excluded, slit schedule not specified).

(3) K. B. Sandell, *Monatsh. Chem.*, **92**, 1066 (1961).

(4) N. Bacon, A. J. Boulton, R. T. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Chem. Soc.*, 5230 (1965).

(5) We thank W. Fulmor and associates for the spectra and L. Brancone and associates for the microanalytical data. Melting points were determined in a Mel-Temp apparatus and are corrected. R_f values are for descending partition paper chromatography in *n*-BuOH–concentrated NH_4OH–H_2O 9:1:8.

(6) See footnote *c* of Table I.

The triacetylsulfonamide was found to be readily hydrolyzed in dilute base at room temperature to the N^1,N^4-diacetyl compound. Therefore, the interconversion of A and B is merely a hydrolysis–reacetylation process.

It is of interest to note that, not surprisingly, the claim of Sandell[3] that primary benzenesulfonamides exist partially or predominantly in the imido form has been demonstrated recently by Katritzky and coworkers[4] to be incorrect.

Experimental Section[5]

Preparation of N^1,N^4-Diacetyl-4-(aminomethyl)benzenesulfonamide.—A mixture of 6.0 g of 4-(N-acetylaminomethyl)benzenesulfonamide[6] (R_f 0.66) and 2.65 g of acetic anhydride in 15 ml of pyridine was refluxed for 2 hr. The pyridine was removed by evaporation in a stream of air and the residue was dried in a vacuum oven at 70–80°. The white solid, 7.05 g (99%), melted at 207–211°. Crystallization from ethanol gave a sample melting at 211–213° (R_f 0.21).

Anal. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.9; H, 5.2; N, 10.4; S, 11.9. Found: C, 48.9; H, 5.2; N, 10.2; S, 11.7.

Mixture of N^1,N^4-Diacetyl and N^1,N^4,N^4-Triacetyl Derivatives.—Acetic anhydride (6.5 g) and 4.6 g of 4-(N-acetylaminomethyl)-benzenesulfonamide were refluxed for 2 hr. The addition of 40 ml of water to the cooled solution produced an oil which soon crystallized to give 3.5 g of white solid, mp 185–189° (55%). Recrystallization of 0.6 g from 40 ml of ethanol yielded 0.37 g, mp 195–196°, of the triacetyl derivative.

Anal. Calcd for $C_{13}H_{16}N_2O_5S$: C, 50.0; H, 5.2; N, 9.0; S, 10.3. Found: C, 50.5; H, 5.2; N, 8.8; S, 10.3.

On standing, the filtrate of the 3.5 g of crop yielded 0.8 g (15%) of material melting over a range of 170–185° and possessing an infrared spectrum superimposable upon that of N^1,N^4-diacetyl-4-(aminomethyl)benzenesulfonamide.

Preparation of N^1,N^4,N^4-Triacetyl Derivative from 4-(Aminomethyl)benzenesulfonamide and Hydrolysis to N^1,N^4-Diacetyl Derivative.—A solution of 4.65 g of 4-(aminomethyl)benzenesulfonamide, 2.05 g of sodium acetate, and 20.4 g of acetic anhydride was refluxed for 2 hr. The addition of 125 ml of water produced 5.2 g of the triacetyl compound, mp 196–198°, yield 65%.

This material (0.5 g) was dissolved in 10 ml of 0.4 *N* NaOH solution and allowed to stand at room temperature for 1.5 hr. Adjustment of the pH to 3.5 with 1 *N* HCl solution resulted in the precipitation of 0.33 g of N^1,N^4-diacetyl-4-(aminomethyl)-benzenesulfonamide, mp 214–216°.

Tetrahydro-2-pyranyl Derivatives of Purines

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Robins and co-workers[1] have reported that certain 6-substituted purines react with 2,3-dihydro-4H-pyran

(1) R. K. Robins, E. F. Godefroi, E. C. Taylor, L. R. Lewis, and A. Jackson, *J. Am. Chem. Soc.*, **83**, 2574 (1961). L. R. Lewis, F. H. Schneider, and R. K. Robins, *J. Org. Chem.*, **26**, 3837 (1961). W. A. Bowles, F. H. Schneider, L. R. Lewis, and R. K. Robins, *J. Med. Chem.*, **6**, 471 (1963).