1489, 1450, 1362, 1316, 1288, 1068, 979, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.76 (1 H, s), 4.84 (1 H, dd, J = 7, 5 Hz), 3.63 (3 H, s), 1.85 (2 H, m), 0.97 (3 H, t, J = 6.5 Hz).

Acknowledgment. We thank Mr. Francis Connor for assistance with the field work and Dr. Klaus Ruetzler of the Smithsonian Institution for identifying the sponge. H. B. Wilkinson and Continental Corporation Fellowships awarded to J.H.C. by the Bermuda Biological Station supported the field work.

Registry No. 1, 79121-29-2.

Notes

Molecular Rearrangements. 19. Thermolysis and Photolysis of *N*-Arylbenzenesulfonamides

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The cleavage of sulfonamides had been frequently used since the famous Hinsberg reaction was discovered[1] for identification and separation of amine mixtures. Three modes of bond cleavages were known, involving the S–N, C–S, or C–N bond[2] according to the type of reagent used.

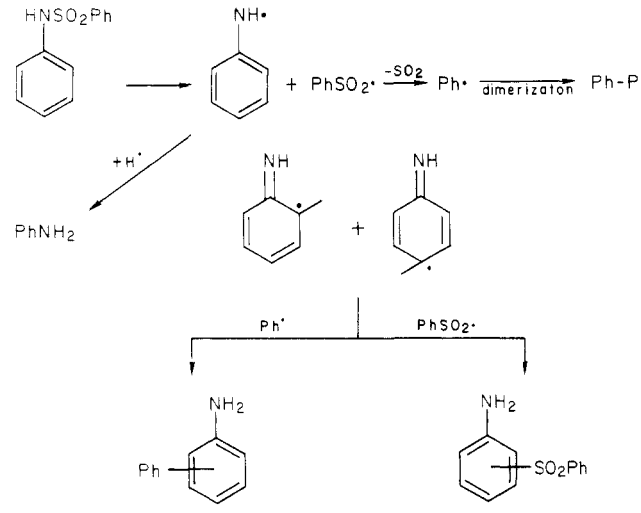
The *N*-phenylsulfonyl group of *N*,*N*-bis(*p*-toluenesulfonyl)aniline has been observed to migrate[3] under the influence of anhydrous aluminium chloride to the aniline nucleus, and this also occurs when solutions of sulfonamides in nitrobenzene or aniline are refluxed[3] or when alkylithium is used as a promoter.[4]

Recently, photolysis of *N*-alkylarenesulfonamides was found to produce the free alkylamine in good yield in addition to other products.[5,6] On the other hand, irradiation of *N*-arylarenesulfonamides induced the Fries-type rearrangement, yielding the diaryl sulfones and the free arylamines together with unidentified byproducts.[6a] Far less is known about the behavior or sulfonamides on thermolysis.

The present work describes the behavior of *N*-arylbenzenesulfonamides on thermolysis and photolysis. Heating *N*-phenylbenzenesulfonamide in a nitrogen atmosphere at ca. 300 °C for 15 h gave sulfur dioxide, aniline, biphenyl, carbazole and a mixture of isomeric *o*- and *p*-aminobiphenyl together with trace amounts of *o*- and *p*-aminobiphenyl sulfones.

The process appears to involve the homolytic fission of an S–N bond to form anilino and phenylsulfonyl radical pairs. The ease of bond rupture parallels the decrease in bond dissociation energy values, being 184, 167, and 116 kcal mol^{-1} (at 25 °C) for the C–N, C–S, and N–S bonds, respectively.[7]

Scheme I



As shown by Scheme I, the anilino radicals abstract hydrogen to form aniline or are subjected to attack by phenylsulfonyl radicals in ortho and para positions forming *o*- and *p*-aminophenyl sulfones. Moreover, the phenylsulfonyl radicals can favorably extrude sulfur dioxide, forming phenyl radicals that couple with the anilino radical in the ortho or para position to form the isomeric aminobiphenyls, whereas dimerization of phenyl radicals leads to the formation of biphenyl.

The appearance of only trace amounts of aminophenyl phenyl sulfones so identified in the products can be interpreted in terms of their thermal instability under such pyrolytic conditions. To confirm this, we heated the isomeric aminophenyl phenyl sulfones and found that sulfur dioxide was extruded in addition to the formation of biphenyl and a mixture of *o*- and *p*-aminobiphenyls and aniline.

It may be suggested that biphenyl can arise from deamination of aminobiphenyls.[8] However, this possibility was ruled out by the observed stability of the isomeric aminobiphenyls under the pyrolytic conditions used. This was further confirmed by the absence of ammonia or ammonium salts among the products.

Possible routes for carbazole formation are cyclization of either *o*-aminobiphenyl (route a of Scheme II) or 2,2′-diaminobiphenyl regarded as the ortho dimer of the anilino radicals (route b of Scheme II).

However, the absence of either ammonia or 2,2′-diaminobiphenyl among the products strongly favors the

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(2) S. Searles and S. Nukina, *Chem. Rev.*, **59**, 1077 (1959), and references cited therein; P. J. Pierre and P. Charles, *J. Chem. Res.*, 1, 20 (1979); *Chem. Abstr.*, **91**, 534 (1979).
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(4) D. Hellwinkel and M. Supp, *Chem. Ber.*, **109**, 3749 (1976).
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(6) (a) J. A. Pincock and A. Jurgens, *Tetrahedron Lett.*, 1029 (1979); (b) H. Nazaki, T. Okada, R. Noyori, and M. Kawanisi, *Tetrahedron*, **22**, 2177 (1966).
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(8) M. Z. A. Badr, M. M. Aly, and A. E. Abdel Rahman, *Indian J. Chem., Sect. B*, **15B**, 381 (1977).

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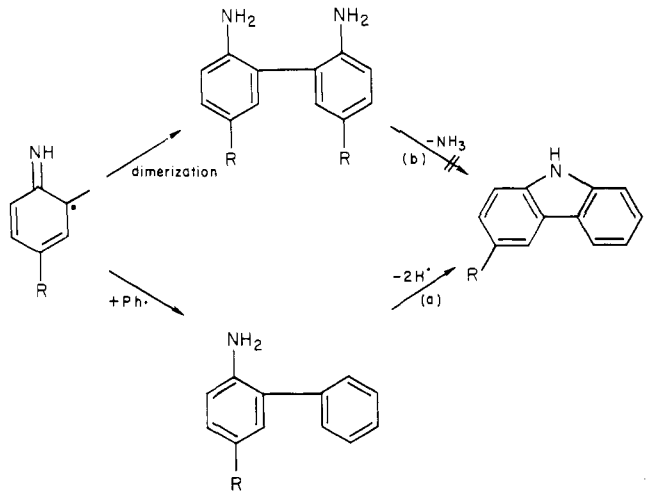
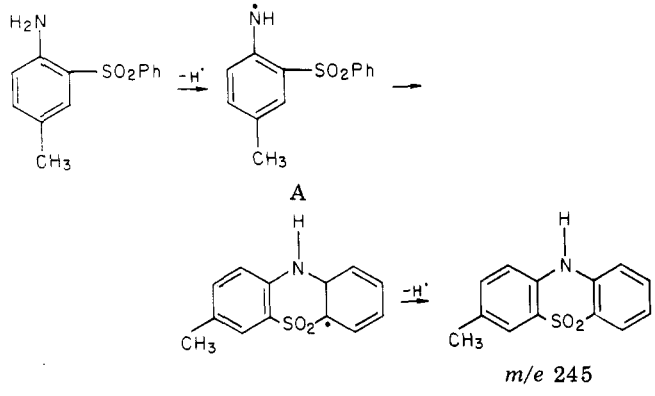
Scheme II[a]



[a] *m/e* 167, R = H; *m/e* 181, R = CH_3.

Scheme III



m/e 245

suggested formation of carbazole through cyclization of *o*-aminobiphenyl (route a of scheme II). The absence of 3,6-dimethylcarbazole among the pyrolysis products of *N*-*p*-tolylbenzenesulfonamide supports this suggestion.

Pyrolysis of *N*-phenylbenzenesulfonamide in presence of isoquinoline as a radical scavenger leads to phenylation of isoquinoline at position 1, and the yields of *o*- and *p*-aminobiphenyl are greatly suppressed. This points to the intermolecular nature of the sulfonamide rearrangement on thermolysis. Similar results are obtained on thermolysis of *N*-*p*-tolylbenzenesulfonamide, yielding *p*-toluidine, biphenyl, 2-amino-5-methylbiphenyl, 3-methylcarbazole, sulfur dioxide together with trace amounts of 3-methylphenothiazine 5,5-dioxide and 9-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide, which were separated and tentatively identified. Furthermore, when the thermolysis of *N*-*p*-tolylbenzenesulfonamide was effected in presence of aniline, carbazole together with *o*- and *p*-aminobiphenyl are obtained in addition to the previously mentioned products.

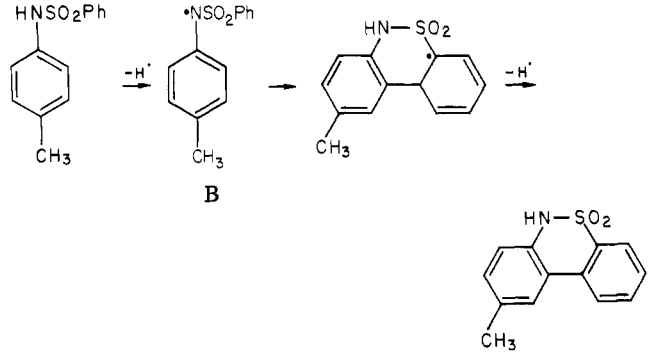
The formation of such products may be explained on grounds similar to those suggested for *N*-phenylbenzenesulfonamide pyrolysis.

The phenothiazine dioxide can rationally be assumed to take place through cyclization of intermediate radical A of Scheme III.

On the other hand, the dibenzothiazine dioxide was suggested to be formed through prior hydrogen abstraction from the parent sulfonamide molecule followed by cyclization of intermediate radical B as in Scheme IV.

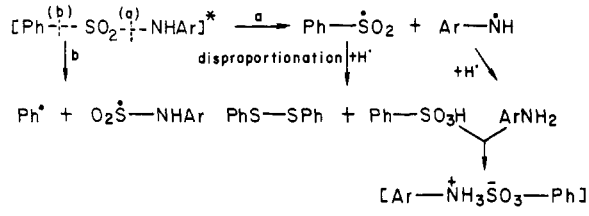
The products obtained from the direct irradiation of *N*-phenylbenzensulfonamide and/or *N*-*p*-tolylbenzenesulfonamide in 2-propanol are quite different from the thermolysis products of these compounds. No sulfur dioxide was detected during photolyses, and a dark brown solid gradually developed, which was identified as the corresponding arylamine salt of benzenesulfonic acid together with the arylamine and diphenyl disulfide. The nature of the products implies that the S–N bond homolysis of the excited sulfonamide molecule cleaves homolytically to give the arylamino and phenylsulfonyl radical pair (route a, Scheme V). The latter radicals undergo disproportionation into benzenesulfonate and phenyl sulfide radicals that ultimately lead to the formation of the identified products (cf. Scheme V).

Scheme IV



m/e 245

Scheme V



Cage coupling of phenylsulfonyl and arylamino radicals to form the isomeric aminophenyl phenyl sulfones was not observed even if the solvent viscosity was varied from 2-propanol to cyclohexane (i.e., a decrease in viscosity by about 54.2%),[9] showing that the noncage process is the one to be favored where the radicals generated from the photoexcited sulfonamide are significantly separated. This was confirmed by the absence of "cage combination" in the product formation such as that frequently found in concerted processes. The only observed effect of increasing solvent viscosity is that the photodecomposition is slowed down, probably due to the decrease in the rate of diffusion of the radicals so formed out of the solvent cage. Moreover, the aminophenyl phenyl sulfones supposed to be formed, if coupling occurs, are as unstable to photolysis as the diaryl sulfone systems and are observed to easily extrude sulfur dioxide.[10]

The other possible mode of fragmentation of the excited sulfonamide molecule (route b, Scheme V) involving C–S bond homolysis is not detected. This is expected since it would lead to a radical pair less stable than the resonance-stabilized pair obtained from route a of Scheme V.[11] Moreover, such a mode of cleavage is ruled out by the absence of biphenyl (by GLC and TLC) in the photoly-

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(10) R. S. Givens and B. Matuszewski, *Tetrahedron Lett.*, 861 (1978).
(11) E. S. Huyser, "Free-Radical Chain Reactions", Wiley, New York, 1970, p 163.

Table I. Products, Solvent, and Sulfonamide in Grams (% Yield) for *N*-Arylbenzenesulfonamide Thermolysis

	expt no.[p]			
	1	2	3	4
solvent (amt, g)		isoquinoline (10)		aniline (10)
sulfonamide consumed	20	24	21	25
used	24	24	25	25
sulfur dioxide	exists	exists	exists	exists
arylamine	6.2 (31)[a]	6.5 (27)[a]	7.6 (36.2)[b]	5.7 (22.8)[c]
aminodiaryl	1.3 (6.5)[d]	0.85 (3.5)[d]	1.3 (6.2)[e]	2.8 (9.6)[f]
aminophenyl phenyl sulfones	0.68 (3.4)[h]	*n*	1.2 (5.71)[i]	*n*
biphenyl[j]	3.43 (17.15)	2.65 (11)	2.5 (11.9)	2.3 (9.2)
carbazoles	2.8 (14)[k]	1.2 (5)[k]	2.2 (10.5)[l]	3.4 (13.6)[l]
other products		5.85 (13.5)[m]	*o*	
residue	4 (20)	6.5 (27)	5.3 (25.24)	8.5 (34)

[a] Aniline, n^{20}_D 1.5857; acetyl derivative, mp and mmp 113–114 °C. [b] *p*-Toluidine, mp 45–46 °C; acetyl derivative, mp and mmp 154 °C. [c] *p*-Toluidine mixed with aniline (the solvent used) from which it was separated by fractional crystallization of their acetyl derivatives. [d] Bp 132–140 °C (3 mmHg). Found by TLC to contain mixture of *o*- and *p*-aminobiphenyls in the ratio 1:3 and separated in the form of their acetyl derivatives: ortho isomer acetyl derivative, mp and mmp 120–121 °C; para isomer acetyl derivative, mp and mmp 169–170 °C. [e] Viscous oil [bp 132–140 °C (3 mmHg)] identified as 2-amino-5-methylbiphenyl by its IR spectrum as compared with an authentic sample (ν (NH_2) 3450 and 3375 cm^{-1}) and by its mass spectrum (*m/e* 183). [f] Found by TLC to contain *o*- and *p*-aminobiphenyl together with 2-amino-5-methylbiphenyl: R_f values of 0.56, 0.45, and 0.30, respectively. [h] Bp 146–160 °C (3 mmHg). Separated by column chromatography over silica gel (80–120 mesh) and eluted with 1:2 (v/v) ether/petroleum ether (bp 40–60 °C) into ortho and para isomers in the ratio 1:3: ortho isomer, mp and mmp 174–175 °C; para isomer, mp and mmp 120–121 °C [i] Tentatively identified as the expected product 2-amino-5-methylbiphenyl sulfone through direct deamination of the crude product by the method of Witt and Uermenyi,[23] yielding phenyl *m*-tolyl sulfone, mp and mmp 125 °C. Calcd for $C_{13}H_{12}O_2S$: C, 67.22; H, 5.21. Found: C, 67.18; H, 5.28. [j] Mp and mmp 70 °C; 4,4'-dinitro derivative, mp and mmp 234 °C. [k] Carbazole, mp and mmp 245 °C; picrate mp and mmp 185–186 °C. [l] 3-Methylcarbazole, mp and mmp 207 °C; picrate mp and mmp 179 °C. [m] 1-Phenylisoquinoline, bp 120–125 °C (3 mmHg), mp and mmp 94 °C; picrate, mp and mmp 165 °C. Calculated on the basis of consumed isoquinoline (3 g). [n] Trace amounts detected by TLC. [o] 3-Methylphenothiazine 5,5-dioxide: mp and mmp 283–284 °C: NMR (250 MHz, $CDCl_3$, Me_4Si reference) δ 2.27 (CH_3), 6.64 (NH), 6.69 and 7.47 (m, Ar 3 H and 4H). Calcd for $C_{13}H_{11}NSO_2$: C, 63.35; H, 4.5; N, 5.6. Found: C, 63.51; H, 4.52; N, 5.62. 9-Methyl-6*H*-dibenzo[*c,e*][1,2]thiazine 5,5-dioxide: mp 228–231 °C. Calcd for $C_{13}H_{11}NSO_2$: C, 63.65; H, 4.5; N, 5.7. Found: C, 63.54; H, 4.59; N, 5.75. The NMR (250 MHz, $CDCl_3$, Me_4Si reference) is coincident with that of above isomer with a slight shift for proton at δ 6.73 ($HNSO_2$). [p] Experiments 1 and 2 used *N*-phenylbenzenesulfonamide; experiments 3 and 4 used *N*-*p*-tolylbenzenesulfonamide.

Table II. Products Isolated (in Grams) from Photolysis of Sulfonamides

product	*N*-phenylbenzene-sulfonamide	*N*-*p*-tolylbenzene-sulfonamide
arylammonium benzenesulfonate	0.64[a]	0.71[b]
arylamine	0.15[c]	0.13[d]
diphenyl disulfide	0.20	0.14

[a] Anilinyl benzenesulfonate, mp and mmp 225–226 °C. [b] *p*-Toluidinyl benzenesulfonate, mp and mmp 205 °C. [c] Aniline. [d] *p*-Toluidine.

sates. A rearrangement similar to the solution photolysis of the sulfonamides was also observed in the solid-state photolysis, and the same products were identified in both cases.

Experimental Section

Melting points were obtained with a hot-stage apparatus calibrated with known samples, and boiling points are uncorrected. The IR spectroscopic analyses were carried out on a Pye-Unicam IR spectrophotometer, Model SP 8000. GLC was carried out on a Pye-Unicam IR spectrophotometer, Model SP 8000. GLC was carried out on a Pye-Unicam gas chromatograph, Series 104, equipped with a flame-ionization detector, Model 24, and using a 4 ft × 5 mm column packed with 20% SE-30 on Chromosorb W (35–80 mesh). TLC was carried out on glass plates covered with silica gel (100–150 mesh) and eluted with 1:4 (v/v) ether/petroleum ether (bp 40–60 °C) or benzene/cyclohexane (3:1 v/v). Molecular weight determination of some reaction products was carried out on a mass spectrophotometer, Model AEIMS 902. Ultraviolet irradiations were carried out by using a Mallinkrodt 150-W mercury discharge lamp. The solvents used were of analytical grade and used without further purification.

Thermolysis of *N*-Arylbenzenesulfonamides. The sulfonamide was heated under reflux or in a sealed tube in a nitrogen atmosphere at 300 °C for about 15 h either alone or in the presence of aromatic solvents such as isoquinoline or aniline. The sulfur dioxide evolved was detected by the benzidine blue test.[12]

The products were separated into amine and neutral products by means of hydrochloric acid.[13] The separated products were subjected to further separation into their constituents by fractional vacuum distillation and column chromatography and were identified by TLC, GLC, or comparison of their infrared spectra with those of authentic samples. The results are given in Table I.

Thermolysis of Aminophenyl Phenyl Sulfones. *o*- and/or *p*-aminophenyl phenyl sulfones (10 g) were heated in a sealed tube under a nitrogen atmosphere for 10 h. The tube was chilled in ice and opened, releasing any sulfur dioxide that had been evolved. The products were separated as usual and identified as biphenyl (0.51 g), aniline (1.62 g), *o*-aminobiphenyl (1.2 g), and *p*-aminobiphenyl (1.53 g).

Photolysis of *N*-Arylbenzenesulfonamides. The sulfonamide (1 g) dissolved in 2-propanol (50 mL) was irradiated under nitrogen atmosphere for 15 h at room temperature (ca. 25 °C). During this time a dark crystalline solid developed. It was separated by filtration and identified as the corresponding arylammonium benzenesulfonate salt by mixture melting point and TLC determination as compared with authentic samples. Furthermore, they were identified by their interaction with Na_2CO_3 solution liberating the corresponding free arylamine and sodium benzenesulfonate that gives positive test characteristic for sulfonic

(12) F. Feigl, "Spot Tests in Inorganic Analysis", 5th ed., Elsevier, Amsterdam 1966, p 234.
(13) M. Z. A. Badr and M. M. Aly, *Can. J. Chem.*, **52**, 293 (1974).

group.[14] The filtrate was chromatographed on silica gel. Eluting with hexane gave the arylamine followed by 20% ether–hexane to obtain diphenyl disulfide. The results are shown in Table II.

Photolysis of Solid *N*-Phenylbenzenesulfonamide. *N*-Phenylbenzenesulfonamide (0.5 g) in finely powdered state was irradiated for 20 h. During which it acquired a pale brown color. TLC analysis of the photolysate revealed the presence of anilinium benzenesulfonate (R_f 0.86), aniline (R_f 0.65), and diphenyl disulfide (R_f 0.37) together with a large proportion of brown resinous material of unknown structure.

Crossover Photolysis. A solution of *N*-*p*-tolylbenzenesulfonamide (0.5 g) and *N*-phenyl-*p*-toluenesulfonamide (0.5 g) in 2-propanol (100 mL) was irradiated for 15 h. The solid obtained, namely, the arylammonium sulfonate salt, was analyzed by TLC and mixture melting point and found to contain the crossbred *p*-toluidinium *p*-toluenesulfonate salt (mp and mmp 197–199 °C) together with the expected arylamine salts: *p*-toluidinium benzenesulfonate (mp and mmp 205 °C) and anilinium *p*-toluenesulfonate, mp and mmp 228–230 °C.

Preparation of Reference Compounds. *N*-Phenylbenzenesulfonamide:[15] crystallized from ethanol, mp 111–112 °C. *N*-*p*-Tolylbenzenesulfonamide:[15] crystallized from ethanol, mp 120–121 °C. Carbazole:[16] crystallized from benzene, mp 245–246 °C; picrate, mp 185–186 °C. 3-Methylcarbazole:[17] crystallized from ethanol, mp 209 °C; picrate mp 179 °C. 3,6-Dimethylcarbazole:[17] crystallized from ethanol, mp 219–221 °C; picrate, mp 194–195 °C. *o*-Aminophenyl phenyl sulfone:[18] crystallized from ethanol, mp 176 °C. *p*-Aminophenyl phenyl sulfone:[18] crystallized from ethanol, mp 122 °C. *o*-Aminobiphenyl:[19] crystallized from petroleum ether (bp 40–60 °C), mp 49–50 °C; acetyl derivative, mp 121 °C. *p*-Aminobiphenyl:[19] crystallized from petroleum ether (bp 40–60 °C), mp 51–52 °C; acetyl derivative, mp 171 °C. 2-Amino-5-methylbiphenyl:[20] viscous oil; bp 135–140 °C (3 mmHg); chloroacetyl derivative, mp 89 °C. 1-Phenylisoquinoline:[21] crystallized from benzene/petroleum ether (bp 60–80 °C) mmp 94–95 °C; picrate, mp 165 °C. Phenyl *m*-tolyl sulfone:[22] crystallized from ethanol, mp 125–126 °C. 3-Methylphenothiazine 5,5-dioxide:[24] sublimed, mp 283–284 °C.

Registry No. *N*-Phenylbenzenesulfonamide, 1678-25-7; *N*-(*p*-tolyl)benzenesulfonamide, 6311-65-5.

(14) F. Fiegl, "Spot Tests in Organic Analysis", 7th ed., Elsevier, Amsterdam, 1966, p 234.
(15) A. I. Vogel, "Practical Organic Chemistry", Longmans, 1971, p 656.
(16) F. R. Storrie and S. H. Tucker, *J. Chem. Soc.* 2255 (1931).
(17) S. H. Oakeshott and S. G. Plant, *J. Chem. Soc.*, 1210 (1926).
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(21) E. Spath, F. Berger, and W. Kuntara, *Ber.*, **63**, 134 (1930).
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(23) O. N. Witt and D. Uermenyi, *Ber. Dtsch. Chem. Ges.*, **46**, 296 (1913).
(24) J. I. G. Cadogan, J. N. Done, G. Lunn, and P. K. K. Lim, *J. Chem. Soc.*, Perkin *Trans. 1*, 1749 (1976).

Reduction of 1-*O*-Acyl-α-D-glucopyranoses to α-Glucosides and to 1,5-Anhydroglucitol

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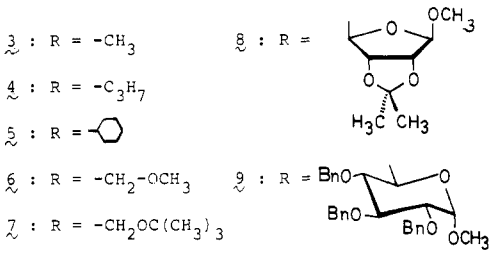
The convenient synthesis of 1-*O*-acyl-2,3,4,6-tetra-*O*-benzyl-α-D-glycopyranoses was viewed as a starting point for preparation of α-glycosides of primary alcohols by way of diborane reduction of the ester function (Scheme I, path A.[2] However, under the reaction conditions used for the reduction of esters[2] acetals are also cleaved to ethers[3] (path B). Therefore, 1-*O*-acylglycoses, structural analogues of half-acylals (1), may be attacked by reducing agents at two positions (A and B). A competitive reaction observed during the reduction of esters to ethers leads to hydrolytic cleavage of the ester bond.[2e,4]

The utility of the diborane reduction method for either the glycoside (path A) or the anhydroalditol (path B) synthesis was investigated by starting from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**2**).[5] Compound **2** was acylated with different acid chlorides[6,7] in the presence of pyridine at 0 °C. 1-*O*-Acyl-α-D-glucopyranoses **3α–9α**,[8] with minor amounts of β derivatives (**3β–9β**), were obtained in high yields (Table I).

Model reductions with **3** (α/β mixture) under different reaction conditions (varying solvent, reducting agent, Lewis acid, and molar ratio[1]) showed that the best results were obtained with **3**, sodium borohydride, and boron trifluoride etherate (molar ratio 1:4:37) with diglyme as the solvent (see the Experimental Section and Table II). Only α-glucosides were obtained as verified by an independent synthesis of **3A**.[9] The reaction conditions given for the reduction of esters to ethers[2b] led to incomplete reduction of **3**.

Table II indicates that the common acyl derivatives **3α–5α** were reduced to the α-glycosides **3A–5A** in good yields. Only minor cleavage of the ester bond was observed chromatographically, resulting in the formation of small amounts of **2** (less than 10% as byproduct[4] (Scheme II). However, introduction of α-alkoxy substituents in the acyl group (**6α, 7α**) led to preferred acetal cleavage in producing



10 and diminished ester reduction to **6A** and **7A**. This phenomenon is attributed to a different intramolecuar

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(3) B. Fleming and H. I. Bolker, *Can. J. Chem.*, **52**, 888 (1974), and references cited therein.
(4) Hydrolytic cleavage is perhaps due to the presence of traces of water or to intermediate formation of a glycosyl fluoride whichis hydrolyzed during workup.
(5) Compound **2** was obtained according to a procedure by P. J. Glaudemans and H. J. Fletcher in "Methods in Carbohydrate Chemistry", Vol. 6, R. L. Whistler and J. N. Bemiller, Eds., Academic Press, New York, 1972, p 374.
(6) Methyl 2,3-*O*-isopropylidene-β-D-ribofuranuronosyl chloride was obtained according to a procedure by R. R. Schmidt, K. H. Jung, and P. Hermentin, *Chem. Ber.*, 111, 3311 (1978).
(7) Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranuronosyl chloride was obtained according to a procedure by P. Kovac, *Carbohydr. Res.*, **31**, 326 (1973); R. R. Schmidt and E. Rücker, *Tetrahedron Lett.*, **21**, 1421 (1980); E. Rücker, Thesis, Universität Konstanz, 1980.
(8) Compound **3** was obtained according to a procedure byR. U. Lemieux, K. B. Hendriks, R. v. Stick, and K. James, *J. Am. Chem. Soc.*, **97**, 4056 (1975).
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