boiling point range; so arbitrary fractions were taken. Analysis by nmr of these fractions indicated that dimethyl pinacolylphosphonate had been concentrated in one of them. This was confirmed by glpc analysis which showed it to be present.

Reaction of Phenacyl *p*-Toluenesulfonate with Trimethyl Phosphite.—Phenacyl *p*-toluenesulfonate (2.7 g, 0.01 mole) was allowed to react with 1.24 g (0.01 mole) of trimethyl phosphite in 35 ml of ether. The mixture was allowed to stand for 4 days and was then heated under reflux for 2 days. The nmr spectrum of the residue after removal of the ether showed that dimethyl 1-phenylvinyl phosphate was a major product. All of the absorptions of the pure compound were present in the nmr of the residue. The nmr spectrum suggested that no dimethyl phenacylphosphonate was present. Its absence was confirmed by glpc analysis.

Reaction of Acetonyl *p*-Toluenesulfonate with Trimethyl Phosphite.—Acetonyl *p*-toluenesulfonate (0.57 g, 0.003 mole) was allowed to react with trimethyl phosphite (0.31 g, 0.003 mole). After 8 days at room temperature little reaction had occurred. Excess trimethyl phosphite was added. After 5 days the nmr spectrum showed that dimethyl 1-methylvinyl phosphate was present as a major reaction product and that no dimethyl acetylmethylphosphonate was present. This later conclusion was confirmed by glpc analysis.

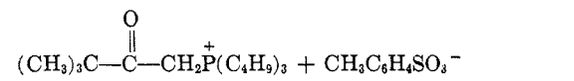
Reaction of Phenacyl *p*-Toluenesulfonates with Triethyl Phosphite.—A solution of 2.7 g (0.01 mole) of phenacyl *p*-toluenesulfonate and 1.66 g (0.01 mole) of triethyl phosphite in 35 ml of dry ether was heated under reflux for 18 hr. The ether was removed and the residue was analyzed by glpc. The vinyl phosphate was identified by its retention time which was the same as that of an authentic sample. No phosphonate was found. Addition of 1% of phosphonate gave rise to a peak which shows that phosphonate would have been detected if present in that amount.

In another experiment under essentially the same conditions, the product was investigated by nmr which indicated that vinyl phosphate was the major product of the reaction.

Reaction of Phenacyl *p*-Toluenesulfonate with Triphenylphosphine.—A solution of 2.9 g (0.01 mole) of phenacyl *p*-toluenesulfonate and 2.56 g (0.01 mole) of triphenylphosphine in 35 ml of benzene was heated under reflux for 3 days. During this time a precipitate formed. The cooled reaction mixture was filtered and the dried solid was recrystallized from ether–chloroform. The product, 4.2 g, softened at 115–120° but resolidified and melted at 146–148°. It is believed that a hydrate was obtained and the melting point behavior is due to this. The infrared spectrum indicated hydroxylic protons were present. The rest of the spectrum was in agreement with that expected. In particular there was carbonyl absorption at 1700 cm^{-1}. The nmr spectrum showed a doublet at 5.9 ppm (J = 13 cps), which is due to the methylene adjacent to the carbonyl group, a singlet at 2.27 ppm, methyl attached to the aromatic ring, and a singlet at 2.9 ppm which is assigned to the water. The aromatic region was obscured by the absorption of the chloroform which was used as solvent.

In another experiment the same quantities of reactants were allowed to react in 35 ml of benzene to which 3 ml of methanol had been added. The same material was obtained.

Reaction of Pinacolyl *p*-Toluenesulfonate with Tributylphosphine.—A solution of 0.67 g (0.003 mole) of pinacolyl tosylate and 0.51 g (0.003 mole) of tributylphosphine in 10 ml of benzene was heated under reflux for 5 hr. The benzene was removed under reduced pressure. The residue had a carbonyl band at 5.8 μ. The nmr spectrum had an A_2B_2 pattern at 7.36 ppm (aromatic hydrogens), a doublet at 4.16 ppm (J = 12 cps) (methylene adjacent to a carbonyl and positive phosphorus), singlet at 2.28 ppm (aromatic methyl), and a singlet at 1.31 ppm (t-butyl hydrogens). There were also peaks due to n-butyl hydrogens. The areas under these peaks were in accord with the assigned structure following.



$$(CH_3)_3C{-}C(=O){-}CH_2\overset{+}{P}(C_4H_9)_3 + CH_3C_6H_4SO_3^-$$

The Reaction of Dihydropyran with Substituted Benzenesulfonyl Azides[1a]

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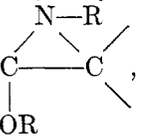
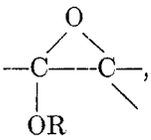
The addition of arylsulfonyl azides to dihydropyran was studied. The products obtained from this reaction were shown to be N-(arylsulfonyl)-δ-pentanimido lactones by nmr and infrared spectra and by hydrolysis studies. Hydrolysis of these compounds gave the corresponding substituted benzenesulfonamide and δ-valerolactone, isolated as its hydrazide. Eight new imido lactones were prepared.

The desire to prepare 1,2-epiimino sugars from glycals prompted an investigation of the reaction of arylsulfonyl azides with the model system, dihydropyran. The desired nitrogen analogs,  , of an epoxy ether,  , have been reported by Hatch and Cram[2] to be an intermediate in the rearrangement of ketoxime O-sulfonates to amino ketones (the Neber reaction). Lloyd and Roberts[3] found that 3,4,6-tri-O-acetyl-2-deoxy-1,2-(2,4-dinitrophenylepi-imino)-α-D-glucopyranoside was formed in small yields when 3,4,6-tri-O-acetyl-2-deoxy-2-(2,4-dinitrophenylamino)-α-D-glucopyranosyl bromide was treated with pyridine in ethanol.

Alder and Stein[4] were among the first investigators to report the formation of a substituted aziridine *via* thermal decomposition of the triazoline intermediate which is formed from the addition of phenyl azide to dicyclopentadiene. Caronna and Palazzo[5] found that a nitro group on the benzene ring of the phenyl azide makes the triazoline intermediate so unstable that it decomposes at once to the aziridine. Franz and Osuch[6] recently reported that azides of type RN_3 (R = $C_6H_5SO_2$–, p-$CH_3C_6H_4SO_2$–, CH_3SO_2–, $(C_6H_5)_2P(\rightarrow O)O$–, $(C_2H_5)_2NSO_2$–, and $N_3SO_2C_6H_4OC_6H_4SO_2$–) react with norbornene, dicyclopentadiene, and 3,6-endomethylenetetrahydrophthalic anhydride to yield aziridines and imines without pyrolysis of an intermediate triazoline. They found, in agreement with

(1) (a) This work was supported by Research Grant CA-06140 from the National Cancer Institute, Public Health Service. Part of this investigation was reported at the 150th Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, and in *Chem. Ind.*, 1264 (1965). (b) Taken in part from the thesis of D. L. Rector submitted as partial fulfillment of the requirements for the Master of Arts Degree. (c) To whom inquiries should be addressed.

(2) M. S. Hatch and D. J. Cram, *J. Am. Chem. Soc.*, **75**, 38 (1953).

(3) P. F. Lloyd and G. P. Roberts, *J. Chem. Soc.*, 2962 (1963).

(4) K. Alder and G. Stein, *Ann.*, **501**, 1 (1933).

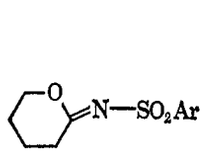
(5) G. Caronna and S. Palazzo, *Gazz. Chim. Ital.*, **82**, 292 (1952).

(6) J. E. Franz and C. Osuch, *Tetrahedron Letters*, **No. 13**, 837 (1963).

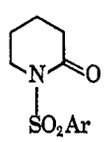
an earlier report by Fusco and co-workers,[7] that enamines reacted with *p*-toluene- or benzenesulfonyl azides to give rearranged products. For example, 1-(1-cyclohexen-1-yl)pyrrolidine and benzenesulfonyl azide gave a substituted cyclopentanecarboxamidine. Franz and Osuch also reported that vinyl ethers such as butyl vinyl ether, dihydropyran, and 2,3-dihydro-2-methoxypyran react with benzene and *p*-toluenesulfonyl azides to give rearranged products which were not completely characterized.

Vinyl ethers and enamines contain double bonds which are more "electron-rich" than the usual olefinic linkage. It has been noted by Huisgen[8] that azides undergo cycloaddition reactions more rapidly with enamines than with vinyl ethers.

In the present investigation, the adducts from 2,3-dihydro-4H-pyran and various arylsulfonyl azides were prepared using a variety of reaction solvents. The addition of arylsulfonyl azides to excess dihydropyran, or to a stoichiometric amount of dihydropyran in a solvent, resulted in nitrogen evolution within 3–20 min after mixing, depending on the type of substituted benzenesulfonyl azide used. Electron-withdrawing substituents did not result in the formation of compounds having different structures as was noted by Caronna and Palazzo[5] in the case of the phenyl azides. This conclusion was based on the similarities of the infrared spectra[9] of the products obtained from these reactions. These compounds did not exhibit a peak at 1190 cm^{-1} characteristic of ring-fused aziridines.[10] The nmr spectra of these compounds exhibited multiplets which could be characteristic of either structures 1 or 2 below. Structure 2 which



1



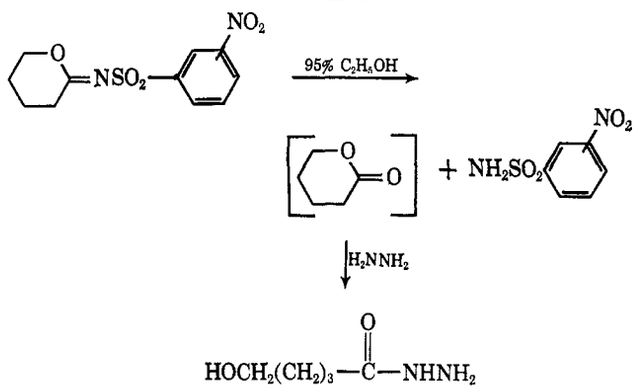
2

might result from the Chapman rearrangement[11] of structure 1 was eliminated as a possibility because the compounds did not show an infrared peak[12] at 1637 cm^{-1} but did show a peak in the range of 1565–1600 cm^{-1} for the $-C{=}NSO_2$ function.[13]

Compound I obtained from the reaction of *m*-nitrobenzenesulfonyl azide with dihydropyran gives an nmr spectrum[14] which shows a multiplet, relative to tetramethylsilane in deuterated chloroform, centered at 117 cps for the two equivalent methylene groups, a multiplet centered at 164 cps for a methylene attached to the imidate lactone function, and a multiplet centered at 268 cps for the methylene attached to the oxygen lactone ring. The multiplets centered at 564, 510, and 532 cps are consistent with the *m*-nitrophenylsulfonyl substituent.[15]

Chemical evidence for the assignment of structure 1 to these adducts was obtained by hydrolysis of these compounds in 95% ethyl alcohol. Compounds I, IV, and VI gave the corresponding sulfonamide and δ-valerolactone which was isolated as its hydrazide. (See Scheme I.)

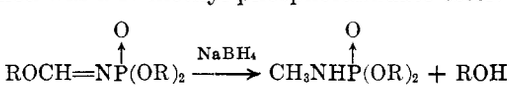
SCHEME I



We obtained δ-valerolactone and *p*-toluenesulfonamide from hydrolysis of compound XII which was obtained from the reaction of *p*-toluenesulfonyl azide and dihydropyran. Similar results were reported by Huisgen and co-workers.[16]

Attempts to prove the structure of compound XII by converting it to N-(tetrahydropyran-2-yl)-*p*-toluenesulfonamide (XXIII) using hydrogen and platinum oxide or sodium borohydride in aqueous ethanol failed. Compound XXIII was prepared according to the method of Speziale and co-workers[17] by treating *p*-toluenesulfonamide with dihydropyran in ether using hydrogen chloride as a catalyst. We obtained better yields of compound XXIII by using *p*-toluenesulfonic acid as a catalyst.

The failure to obtain compound XXIII by reduction of XII was because of hydrogenolysis of the carbon–oxygen bond in XII to give N-(5-hydroxypentyl)-*p*-toluenesulfonamide (XXIV). The structure which is assigned compound XXIV is based on its infrared spectra. Berlin and co-workers[18] reported that sodium borohydride reduction of imidate esters, which were formed by adding phosphoryl azides to vinyl ethers, resulted in carbon–oxygen cleavage. The product obtained was a N-methyl phosphoramidate ester.



It is generally agreed that photochemical and thermal reaction of azides with olefins proceed *via* the decomposition of the azides to a nitrene which then adds to the olefin.[19]

(7) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Ber.*, **96**, 802 (1963).

(8) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," S. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 843.

(9) The infrared spectra were taken on a Beckman infrared IR-8 spectrometer.

(10) J. B. Patrick, R. P. Williams, W. E. Meyer, W. Fulmore, D. B. Cosulich, R. W. Broschard, and J. S. Webb, *J. Am. Chem. Soc.*, **86**, 1889 (1964).

(11) J. W. Schulenberg and S. Archer, *Org. Reaction*, **14**, 1 (1965).

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 214.

(13) H. L. Yale and J. T. Sherhan, *J. Org. Chem.*, **26**, 4315 (1961).

(14) We wish to express our gratitude to Dr. George Slomp and Mr. Forrest MacKellar of The Upjohn Co. for assistance in the determination and interpretation of the nmr spectra which were taken on a Varian A-60 spectrometer.

(15) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, p 62.

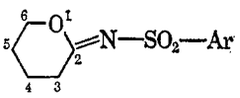
(16) R. Huisgen, L. Mobus, and G. Szeimies, *Ber.*, **98**, 1138 (1965).

(17) A. J. Speziale, K. W. Ratts, and G. J. Marco, *J. Org. Chem.*, **26**, 4311 (1961).

(18) K. D. Berlin and M. Khayat, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 58S.

(19) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964); W. Lwowski and J. S. McConaghy, Jr., *J. Am. Chem. Soc.*, **87**, 5490 (1965).

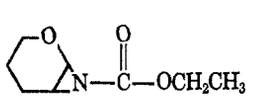
TABLE I

CHARACTERIZATION DATA[a] ON 

Compd	Aryl substituent	Reaction solvent[b]	Reaction temp, °C[c]	Reaction time, hr	Yield, %	Mp,[d] °C	Formula	Carbon, %[e] Calcd	Carbon, %[e] Found	Hydrogen, %[e] Calcd	Hydrogen, %[e] Found	Nitrogen, % Calcd	Nitrogen, % Found
I	*m*-Nitro	A	25[c]	30	75	100–101	$C_{11}H_{12}N_2O_5S$	46.48	46.66	4.23	4.23	9.86	9.73
		B	25[c]	30	84								
		C	25[c]	30	82								
		D	25[c]	36	82								
		E	25[c]	30	82								
IV	*o*-Nitro	A	55–25[c]	10	85	105–105.5	$C_{11}H_{12}N_2O_5S$	46.48	46.53	4.23	4.38	9.86	10.03
		B	50	20	86								
		E	25[c]	15	79								
VI	*p*-Nitro	A	55–25[c]	10	95	131–132	$C_{11}H_{12}N_2O_5S$	46.48	46.69	4.23	4.45	9.86	10.05
		B	55	20	90								
		C	53–25[c]	15	76								
		D	50	20	80								
		E	25[c]	35	68								
VIII	*p*-Bromo	A	60–25[a]	60	31	108–110	$C_{11}H_{12}BrNO_3S$	41.51	41.49	3.77	3.73	4.40	4.39
		B	55	48	39								
		C	40	20	53								
		E	75	4	18								
IX	2,5-Dibromo	A	25[c]	26.5	83	125–127	$C_{11}H_{11}BrNO_3S$	33.25	33.30	2.75	2.75	3.53	3.38
		B	25[c]	26.5	66								
		D	25[c]	26.5	50								
		E	25[c]	29	87								
X	3,4-Dichloro	A	55–25[c]	60	55	104–105	$C_{11}H_{11}Cl_2NO_3S$	42.86	43.02	3.57	3.76	4.55	4.52
		C	53–25[c]	8	86								
		E	25[c]	30	94								
XI	2,5-Dichloro	A	25[c]	35	48	96.5–97.5	$C_{11}H_{11}Cl_2NO_3S$	42.86	42.96	3.57	3.66	4.55	4.51
		C	25[c]	35	49								
		E	25[c]	30	36								
XII	*p*-Methyl	C	25[a]	264	86	74–75[f]	$C_{12}H_{15}NO_3S$	56.92	57.12	5.93	6.09	5.53	5.39
XIII	*p*-Methoxy	A	47	96	47	93–94.5	$C_{12}H_{15}NO_4S$	53.53	53.30	5.58	5.58	5.20	5.33

[a] See Tables II and III for infrared and nmr spectral data. [b] A = dihydropyran, B = tetrahydrofuran, C = benzene, D = *p*-dioxane, E = xylene. [c] At 25° or ambient temperature. [d] Melting points were taken in a stirred silicone oil bath and are corrected. [e] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [f] Lit.[16] mp 73.5–74.5.

Brown and Edwards[20] postulated that the photolysis of ethyl azidoformate and dihydropyran yields a very reactive aziridine intermediate of this structure.



However, the reaction of dihydropyran with arylsulfonyl azides at or near 25° probably does not proceed by generation of "nitrene" intermediates, since no side products resulting from insertion reactions are obtained. When Heacock and Edmison[21] decomposed benzenesulfonyl azides in aromatic solvents heated under reflux they obtained benzenesulfonamides and benzenesulfonanilides.

Recently, Oehlschlager and Zalkow[22] have reported some kinetic evidence which seems to support the existence of an unstable triazoline intermediate in the reaction of sulfonyl azides with norbornylene. This intermediate may decompose to zwitterionic structure (D), an imine (G), or an aziridine (A or E).

They reported the entropy of activation for the reaction of norbornylene benzenesulfonyl azide to be ΔS^* −28 cal/deg which is in good agreement with that reported[23] for the reaction of norbornylene with phenyl azides to give triazolines.

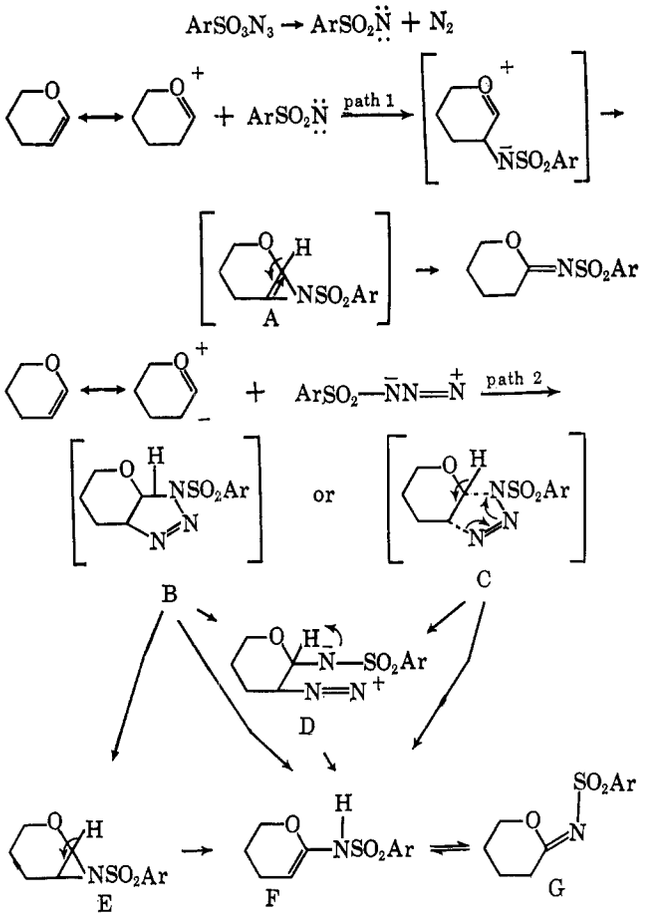
We feel that reaction of dihydropyran with an arylsulfonyl azide proceeds through the unstable triazoline intermediate (B or C) shown in path 2 and not through the nitrene intermediate shown in path 1 to give N-(arylsulfonyl)-δ-pentanimido lactone (G) shown in Scheme II.

The possibility of a triazoline intermediate is supported by Baldwin and co-workers[24] who reported, however, that an aziridine such as structure E, Scheme II is not an intermediate in the thermal decomposition of the triazoline. This conclusion is based on the product obtained from the thermal decomposition of the phenyl azide cyclopentene adduct in the presence of phenylisothiocyanate as shown in Scheme III.

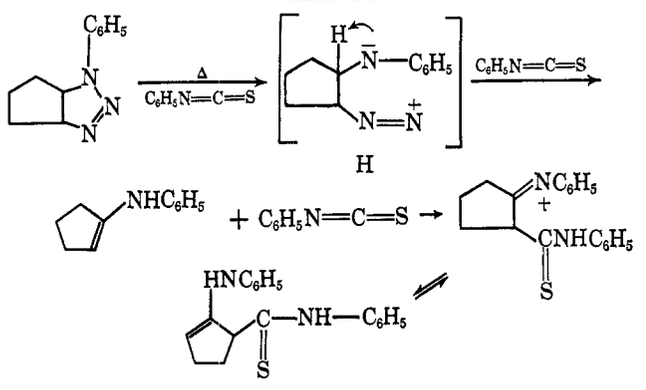
The addition of an arylsulfonyl azide to dihydropyan to form a triazoline can only be achieved by bending the linear azide system. A LCAO calculation by Roberts[25] has shown that such bending requires an energy of about 5 kcal/mole. This amount of energy is readily obtainable in the 1,3-dipolar addition of sulfonyl azides to dihydropyran. Huisgen and coworkers[8] have suggested that the energy lost in break-

(20) I. Brown and O. E. Edwards, *J. Can. Chem.*, **43**, 1264 (1965).
(21) J. F. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, **82**, 3460 (1960).
(22) A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, **30**, 4205 (1965).
(23) P. Scheiner, J. H. Shomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).
(24) J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *ibid.*, **87**, 4114 (1965).
(25) J. D. Roberts, *Ber.*, **94**, 273 (1961).

SCHEME II



SCHEME III



ing one bond of the azide is partially compensated for by a gain in energy through rehybridization.

It has been found that sulfonyl azides are more reactive than the phosphoryl azides,[26] acyl azides, alkyl azides, or aryl azides[16] toward vinyl ethers.

In the present investigation, a solvent effect and a substituent effect was noticed for the reaction of substituted benzenesulfonyl azides with dihydropyran. According to Pasto and co-workers[27] the pK_a value of phenylsulfonylacetic acid increased when electron-withdrawing substituents were placed on the benzene ring and they suggested that electronic effects are transmitted across the sulfonyl group.

(26) K. D. Berlin and L. A. Wilson, *Chem. Commun.*, 280 (1965).

(27) D. J. Pasto, D. McMillan, and T. Murphy, *J. Org. Chem.*, **30**, 902 (1963).

The observation in this investigation that electron-withdrawing substituents on the benzene ring of the phenylsulfonyl azides increased the rate of addition of these compounds to dihydropyran while electron-donating substituents decreased the rate of addition would seem to support their observations.

The addition of arylsulfonyl azides to dihydropyran proceeded more rapidly in *p*-dioxane and tetrahydrofuran than in benzene or xylene. However, the nature of the solvent did not influence the yield of products as shown in Table I.

Six new substituted benzenesulfonyl azides were prepared by treating various arylsulfonyl chlorides with sodium azides in aqueous acetone using a modification of the procedure of Leffler and Tsuno.[28] Further studies are in progress to determine the effect of various substituents and solvents on the course of this reaction.

Experimental Section

Solvents used were purified by distillation. Xylene and benzene were stored over metallic sodium. The tetrahydrofuran and dioxane solvents were stored over calcium hydride. The dihydropyran used was a sample generously supplied by the Quaker Oats Company.

General procedure for the preparation of N-(arylsulfonyl)-δ-pentanimido lactones, compounds I, IV, VI, VIII, IX, X, XI, XII, and XIII.

TABLE II

SUMMARY OF INFRARED SPECTRA[a] AND THE STRUCTURAL INTERPRETATION[b] FOR ADDUCTS OF DIHYDROPYRAN AND ARYLSULFONYL AZIDES

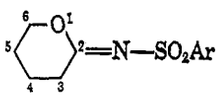
Compd	SO_2—N=C[c]	C—O—C[d]	Ar—SO_2—N[e]	—NO_2[f] (if any)	C—H[g] out-of-plane bending
I	1580	1056	1350 1169 1155	1525	812
IV	1580	1051	1345 1173 1152	1525	740
VI	1600	1048	1340 1170 1141	1520	827
VIII	1575	1051	1345 1167 1141	...	810
IX	1600	1055	1348 1170 1153	...	806
X	1565	1050	1342 1160 1152	...	802
XI	1600	1058	1350 1170 1155	...	812
XII	1570	1053	1345 1175 1150	...	822
XIII	1580	1050	1345 1176 1147	...	818

[a] Absorption maxima are expressed in cm^{-1}. [b] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, pp xii and 683. [c] Very strong. [d] Moderate. [e] Strong. [f] Moderate to strong.

(28) J. E. Leffler and Y. Tsuno, *ibid.*, **28**, 902 (1963).

TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRA[a] OF



Compd	Aryl substituent	Position on tetrahydropyran nucleus: 3	4 and 5	6	Aryl group
I	*m*-Nitro	164 t[b]	117 q[c]	271 t	465 t 510 t 532 t
IV	*o*-Nitro	163 t	113 q	263 t	468 d[d] 493 complex multiplet
VI	*p*-Nitro	165 t	112 q	269 t	487–513 complex multiplet
VIII	*p*-Bromo	160 t	112 q	264 t	452–486 complex multiplet
IX	2,5-Dibromo	164 t	113 q	265 t	456 d
X	3,4-Dichloro	162 t	115 q	268 t	452, 476, 485 complex multiplets

[a] These spectra were determined on a Varian A-60 spectrometer and were run as 0.20 *M* solutions in perdeuterated chloroform or dimethyl sulfoxide with tetramethylsilane as an internal standard. The nmr values cited in cps are located at the center of each multiplet in the spectra. The qualitative assignments of multiplicity to each splitting pattern are tentative. [b] t = triplet. [c] q = quintet. [d] d = doublet.

I, II, and III for reaction conditions and physical data for these compounds.

Hydrolysis of Compounds I, IV, and VI.—A solution of 0.011 mole of I in 20 ml of 95% ethyl alcohol heated under reflux for 5 hr gave 2.12 g, 94% of *m*-nitrobenzenesulfonamide, mp 166–168° (lit.[29] mp 167–168°). The filtrate was treated with a slight excess of 95% hydrazine, and the resulting solution was heated under reflux for 7 hr. White platelets separated upon reduction of the volume of the solution in vacuo.

The product was collected by vacuum filtration and washed with cold ethanol. Recrystallization of the product from ethanol gave 0.78 g, 53%, of 5-hydroxypentanohydrazide (III): mp 104–106° (lit.[30,31] mp 105 and 107°); ν_{max} (Nujol) 3325 (OH), 3160, 3140, 3050 (NH), and 1640 (C=O), hydrazide) cm^{-1}.

Hydrolysis of compound IV gave 95% yield of *o*-nitrobenzenesulfonamide (V), mp 191–192°, lit.[29] mp 193°, and 47% yield of compound III, mp 105–105.5°. Hydrolysis of compound VI gave 87% yield of *p*-nitrobenzenesulfonamide, mp 177–179°, lit.[29] mp 179–180°, and a 56% yield of compound III, mp 106–107°.

Preparation of Arylsulfonyl Azides, Compounds XIV, XV, XVI, XVII, XVIII, XIX, XX, XXI, and XXII.—A slight modification of the method Leffler and Tsuno[28] was used. To a solution of 0.154 mole of sodium azide in a 70% acetone–water mixture at 0° was added 0.135 mole of an arylsulfonyl azide in 50 ml of acetone at 0°. The reaction mixtures were stirred from 1 to 2 hr at 0°, allowed to come to room temperature and then poured over 500 ml of crushed ice with vigorous stirring. The solids were collected by vacuum filtration, washed with cold water, and recrystallized from hot absolute ethanol. See Table IV for the physical properties of these compounds.

TABLE IV

PHYSICAL PROPERTIES OF ARYLSULFONYL AZIDES[a]

Ar—SO_2—N_3

Compd	Aryl substituent	Yield, %	Mp, °C[b]	Formula	Carbon %[c] Calcd	Carbon %[c] Found	Hydrogen %[c] Calcd	Hydrogen %[c] Found	Nitrogen %[c] Calcd	Nitrogen %[c] Found
XIV	*o*-Nitro	78	71–72.5[d]							
XV	*p*-Nitro	88	101–102	$C_6H_4N_4O_4S$	32.02	31.73	1.75	1.90	24.56	24.84
XVI	*m*-Nitro	99	78–80	$C_6H_4N_4O_4S$	32.02	31.74	1.75	1.87	24.56	24.72
XVII	*p*-Bromo	97	53–53.5	$C_6H_4BrN_3O_2S$	27.48	27.70	1.53	1.52	16.03	16.22
XVIII	3,4-Dichloro	89	60–61	$C_6H_3Cl_2N_3O_2S$	28.57	28.81	1.19	1.24	16.67	16.90
XIX	2,5-Dichloro	97	50–52.5	$C_6H_3Cl_2N_3O_2S$	28.57	28.64	1.19	1.30	16.67	16.82
XX	2,5-Dibromo	92	65–67	$C_6H_3Br_2N_3O_2S$	21.11	21.32	0.88	1.10	12.32	12.58
XXI	*p*-CH_3	86	19–20[e]							
XXII	*p*-CH_3—O	93	135 (dec)[f]							

[a] These compounds gave the following infrared spectra: 2130–2170 (azide), 1170 (—SO_2—), 810–830 (aromatic substitution) cm^{-1}. [b] Melting points were taken in capillary tubes in a stirred silicon oil bath and are corrected. [c] Analyses were performed by Galbriath Laboratories, Inc., Knoxville, Tenn. [d] Lit.[28] mp 71–73°. [e] Lit.[28] mp 19–20°. [f] Lit.[32] 135°.

To 0.010 mole of arylsulfonyl azide in 20 ml of tetrahydrofuran, dioxane, benzene, or xylene was added 0.012 mole of dihydropyran in 20 ml of one of the proceeding solvents at ambient temperature. Nitrogen evolution begins about one min after the two solutions were mixed. In some cases dihydropyran was used as the reactant and solvent. See Tables

(29) I. M. Heilbron's "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1965, p 2433.
(30) S. L. Friess, *J. Am. Chem. Soc.*, **71**, 2571 (1949).
(31) W. Reppe, *Ann.*, **596**, 80 (1955).
(32) F. H. Adams, U. S. Patent 2,830,029, April 8, 1958. *Chem. Abstr.*, **52**, 13303 (1958).