[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

On the Question of Anchimeric Assistance by Phenyl Participation. The β-Isotope Effect on Acetolysis of 2,2-Dideuterio-5,5-diphenylcyclopentyl *p*-Toluenesulfonate

BY RICHARD A. SNEEN, ROBERT W. JENKINS, JR.,[1] AND FLOYD L. RIDDLE, JR.[1]

RECEIVED JULY 12, 1961

2,2-Dideuterio-5,5-diphenylcyclopentanol and 2,2-diphenylcyclopentanol have been prepared and converted into their *p*-toluenesulfonate esters. The undeuterated ester underwent acetolysis at 50° with a rate constant of $6.54 \pm 0.17 \times 10^{-5}$ sec.$^{-1}$, greater by a factor of 1.76 than that of cyclopentyl *p*-toluenesulfonate. Further the dideuterio-diphenyl ester reacted at a rate 0.85 ± 0.04 times that of its dihydro analog, corresponding to a difference in free energies of activation of 54 ± 16 cal./deuterium atom. This value is to be compared with the corresponding values of 110–127 cal./deuterium atom reported by Streitwieser and co-workers[2] for *cis*- and *trans*-2-deuteriocyclopentyl *p*-toluenesulfonate. It is argued that the decreased sensitivity of reaction rate to β-deuterium substitution observed with the diphenylcyclopentyl esters indicates considerable dispersal of positive charge in these transition states, perhaps most reasonably by a mechanism involving phenyl participation.

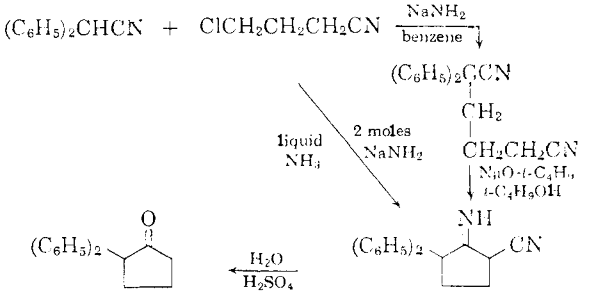
In numerous recent studies[2-4] it has been found that the effect of replacing β-hydrogen by deuterium atoms has been to reduce substantially the rates of solvolysis of certain organic esters and halides. Although the mechanism by which this effect operates has not been clearly defined, certain features of the phenomenon have emerged and some generalizations can be drawn.

In the first place the effect appears to be cumulative; each successive replacement of a β-hydrogen atom of a given degree by deuterium results in a nearly constant raising of the free energy of activation. Furthermore, the magnitude of the rate deceleration effected by β-deuterium substitution appears to be defined by rather narrow limits for a variety of compounds under various solvolytic conditions and appears to vary in an important way only with the degree of alkyl substitution at the β-carbon atom.[5] In view of the observed constancy of the effect of β-deuterium substitution, it occurred to us that mechanistic deviations from the usual SN1-type solvolysis reactions might be reflected in deviations in the magnitude of the β-isotope effect. In particular it seemed of interest to measure the effect in a system thought to solvolyze with phenyl participation. Since we had available a supply of 2,2-diphenylcyclopentanone and since the magnitude of the β-isotope effect on acetolysis of cyclopentyl tosylate had been measured by Streitwieser and co-workers,[2] we set about preparing 2,2-dideuterio-5,5-diphenylcyclopentyl *p*-toluenesulfonate with a view toward measuring its β-isotope effect on acetolysis.

In this paper we report an improved synthesis of 2,2-diphenylcyclopentanone, its conversion into the tosylates of 2,2-dideuterio-5,5-diphenylcyclopentanol and 2,2-diphenylcyclopentanol, and the measured rates of acetolysis of these esters.

Results

Our synthesis of 2,2-diphenylcyclopentanone followed that reported by Easton and Nelson.[6] The intermediate 5-cyano-2,2-diphenylcyclopentanoneimine had been prepared by these authors by the sodium *t*-butoxide-catalyzed condensation of 2,2-diphenyladiponitrile in solvent *t*-butyl alcohol; this compound, in turn, had been prepared by the sodium amide-catalyzed reaction between diphenylacetonitrile and γ-chlorobutyronitrile in benzene. We have found that the cyclic imine can be more conveniently prepared directly (70%) from the latter reactants when they are treated with 2 moles of sodium amide in liquid ammonia.



Hydrolysis and decarboxylation of the iminonitrile furnished 2,2-diphenylcyclopentanone.

The labile hydrogen atoms of 2,2-diphenylcyclopentanone were replaced by two successive room temperature exchanges with deuterium oxide in solvent dioxane, catalyzed by triethylamine. The extent of deuteration was determined after reduction and tosylate formation by analysis of the water produced on combustion of the tosylate ester. The ester was found to contain 1.89 atoms of deuterium per molecule.[7]

The results of the kinetic investigation are reported in Table I. Rates of reaction in acetic acid at 50.0° were determined by titration with lithium acetate of liberated *p*-toluenesulfonic acid to the modified methyl orange end-point. The limited solubility of the diphenyl esters in acetic acid reduced somewhat the precision of these data. However, it will be seen that the precision within any single run is in most cases better than 3% and separate runs gave rate constants well within the limits of their combined uncertainties. In order to minimize incidental errors, the deuterated and undeuterated esters were run simultaneously and under conditions as similar as possible.

---

[1] Abstracted from theses submitted by R. W. J. and F. L. R. in partial fulfillment of the requirements for the degree of Master of Science.

[2] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

[3] V. J. Shiner, Jr., *ibid.*, **83**, 240 (1961), and references cited therein.

[4] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 671 (1956).

[5] See, however, V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **82**, 2655 (1960), and ref. 3.

[6] N. R. Easton and S. J. Nelson, *J. Am. Chem. Soc.*, **75**, 640 (1953).

[7] Analysis performed by Mr. J. Nemeth, Microanalytical Laboratory, Department of Chemistry, University of Illinois.

TABLE I

RATES OF ACETOLYSIS OF SOME CYCLOPENTYL *p*-TOLUENESULFONATES AT 50.0°

Cyclopentyl tosylate	[ROTs] × 10^3		*k*, sec.$^{-1}$ × 10^5
Parent[a]	12.5		3.72 ± 0.10
	13.1		3.71 ± .12
2,2-Diphenyl	5.97		6.53 ± 0.07
	5.78		6.47 ± .16
	5.50		6.72 ± .20
	5.62		6.53 ± .16
	5.52		6.44 ± .15
		Av.	6.54 ± 0.17[b]
2,2-Dideuterio-5,5-diphenyl	5.78		5.53 ± 0.15
	5.47		5.45 ± .09
	5.54		5.57 ± .09
	5.66		5.58 ± .18
		Av.	5.53 ± 0.14[b]

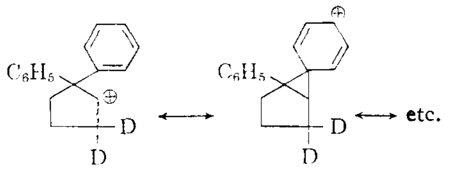
[a] S. Winstein and co-workers report *k* = 3.84 × 10^{-5} sec.$^{-1}$, *J. Am. Chem. Soc.*, **74**, 1127 (1952); H. C. Brown and G. Ham report *k* = 3.82 × 10^{-5} sec.$^{-1}$, *J. Am. Chem. Soc.*, **78**, 2735 (1956). [b] Average deviation.

Discussion

The generally accepted view that phenyl bridging is an important stabilizing factor in the solvolysis reactions of β-phenyl-substituted alkyl halides and sulfonates has recently been challenged, particularly by H. C. Brown.[8] Representative of the facts[9] which led to the suggestion of phenyl participation are the relative rates of acetolysis of ethyl tosylate and its β-substituted derivatives, mono-, di- and triphenylethyl tosylate—1.0:0.4:4.5:660; in only the second member of this series, the monophenyl compound, is the −I inductive effect of phenyl deemed sufficient to outweigh the effects of phenyl participation. On the other hand, Professor Brown[8] has suggested, partly on the basis of a linear free energy relationship between the rates of solvolysis of this series and of the rates of sodium borohydride reduction of the corresponding methyl ketones, that the rate enhancements observed with the latter two members of this series may very well be steric in origin: the bulky phenyl groups are thus presumed to enhance by steric acceleration the development of the completely classical carbonium ion.

It accordingly was of interest to obtain additional independent evidence as a basis for assessing the relative importance of these two explanations, steric and electronic, for the observed facts.

Our experimental method was based on the assumption that, to the extent that charge distribution is dispersed in the transition state of a solvolysis reaction, the sensitivity of the reaction rate to β-deuterium substitution should be diminished. According to this argument a lowering of the β-isotope effect on acetolysis of a system such as 2,2-dideuterio-5,5-diphenylcyclopentyl tosylate should be associated with charge dispersal and, accordingly, with phenyl participation due to resonance of the type



Experiments reported by Streitwieser and coworkers[2] in which the β-deuterium isotope effect on acetolysis of *cis*- and of *trans*-2-deuteriocyclopentyl tosylate and of the related 2,2,5,5-tetradeuterio ester were measured provided a convenient calibration scale for our intended studies with the 2,2-dideuterio-5,5-diphenylcyclopentyl tosylate since these authors had shown that the isotope effect in their systems appeared to be quite additive and, further, to be essentially independent of stereochemistry. Their results are summarized and compared with ours in Table II.

TABLE II

RELATIVE DEUTERIUM ISOTOPE EFFECTS ON ACETOLYSIS AT 50.0°

Cyclopentyl *p*-toluenesulfonate	k_H/k_D	$\Delta\Delta F^{\ddagger}$, cal./deuterium
Unsubstituted[a]	..	..
cis-2-Deuterio[a]	1.22	127
trans-2-Deuterio[a]	1.16	110
2,2,5,5-Tetradeuterio[a]	2.06	116
2,2-Diphenyl[b]	..	..
2,2-Dideuterio-5,5-diphenyl[b]	1.18 ± 0.02	54 ± 16

[a] Ref. 2. [b] This work.

The results of the present study would seem to be consistent with the view that β-phenyl participates to a significant extent in the solvolysis of 2,2-diphenylcyclopentyl tosylate and of its dideuterio analog. Not only is the rate of solvolysis of the diphenyl compound greater than that of the parent cyclopentyl tosylate by a factor of 1.76 (comparable in magnitude to the 4.5-fold enhancement of acetolysis rate effected by β,β-diphenyl substitution into ethyl tosylate[9]), but the magnitude of the isotope effect, expressed in units of cal./D, proved to be only about half as great as those reported by Streitwieser for the calibration compounds.[2]

In the view of the writers these conclusions are strengthened by the fact that the arguments developed above preceded the experimental findings. However, it must be admitted that although these arguments, dependent on the assumption that charge dispersal should be accompanied by a lowered isotope effect, are reasonable, they are also somewhat naive. Particularly is this true when one recognizes the uncertainties as to the mechanism by which the β-isotope effect operates. In summary it is our view that the presently reported results reinforce the suggestion that participation by phenyl is a stabilizing factor in the transition states of these solvolysis reactions[10]; but a more positive

---

(8) Expressed orally at the 139th Meeting of the A.C.S., St. Louis, Mo., March 21–30, 1961.

(9) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952); see also ref. 4, p. 723, for a summary of data and references.

(10) A similar conclusion has been arrived at by Saunders and his co-workers on the basis of quite similar experiments. These investigators measured the α- and β-deuterium isotope effects on acetolysis and formolysis of the systems 2-phenylethyl, 2-*p*-anisylethyl and 2,2-diphenylethyl *p*-toluenesulfonates. They conclude that an appreciable α-isotope effect (*ca.* 10%/D) and a negligible β-isotope effect are associated with aryl participation; W. H. Saunders, Jr., S. Ašperger and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958); W. H. Saunders, Jr., and R. Glaser, *ibid.*, **82**, 3586 (1960).

statement based on these results must await a clearer understanding of the energetics of the β-isotope effect.[11]

Experimental

5-Cyano-2,2-diphenylcyclopentanoneimine.—To 100 ml. of liquid ammonia (anhydrous) in a 1-l., three-necked flask, fitted with a Dry Ice condenser, stirrer and a dropping funnel, was added 4.0 g. (0.10 mole) of sodium amide, and the resulting mixture was stirred for 10 minutes. To the reaction mixture was then added dropwise a solution of 18.4 g. (0.95 mole) of diphenylacetonitrile[13] (m.p. 70–76°) in 250 ml. of anhydrous ether and the resulting greenish solution of sodiophenylacetonitrile was stirred for 15 minutes. To it was then added dropwise with stirring a solution of 15.2 g. (0.096 mole) of γ-bromobutyronitrile in 200 ml. of anhydrous ether, the addition taking place over a period of 30 minutes. Stirring was continued for 30 minutes and then an additional 4.0 g. (0.10 mole) of sodium amide was added. Stirring was continued overnight. Ammonia was removed by distillation and the resulting ethereal solution was washed with three portions of 10% hydrochloric acid. The aqueous extracts were combined and washed with three portions of fresh ether and the combined organic phases were then dried over magnesium sulfate. After removal of solvent the product 5-cyano-2,2-diphenylcyclopentanoneimine was crystallized in 70% yield from methanol; m.p. 149–150° (lit.[5] m.p. 149–150°).

2,2-Diphenylcyclopentanone.—To a stirred solution of 48 ml. of water in 160 ml. of concentrated sulfuric acid, heated to steam-bath temperatures, was added over a period of 1.5 hours 10.0 g. of 5-cyano-2,2-diphenylcyclopentanoneimine. Heating and stirring were continued for 0.5 hour after solution was complete. The reddish-brown solution was transferred to a 1-l., three-necked flask equipped with a reflux condenser and a Hershberg stirrer made of platinum. The solution was heated to 40° and 250 ml. of water was added in one portion. The temperature was increased to 75° and the solution was stirred vigorously for 48 hours while being maintained at this temperature. The warm reaction mixture was extracted first with benzene and then twice with ether, and the organic layers were combined. Removal of solvent left a thick brown oil which crystallized from methanol. Recrystallization from ethanol-water furnished in 65% yield 2,2-diphenylcyclopentanone as a white crystalline material, m.p. 86–87° (lit.[6] 87.5–89.5°).

2,2-Dideuterio-5,5-diphenylcyclopentanone.—Anhydrous 2,2-diphenylcyclopentanone (4.938 g., 0.0209 mole) was dissolved in a mixture of 10 ml. of purified dioxane, 2 ml. of dried triethylamine and 4.992 g. (0.249 mole) of 99.95% deuterium oxide and allowed to react at room temperature for 72 hours. Solvents were removed by vacuum distillation (0.1 mm.) and the residue was again dissolved in a mixture of 10 ml. of dioxane, 2 ml. of triethylamine and 4.492 g. of deuterium oxide and allowed to stand at room temperature for 48 hours. Vacuum distillation of solvents left a residue which was not isolated but which was dissolved in a minimum of anhydrous ether and used immediately in the preparation of 2,2-dideuterio-5,5-diphenylcyclopentanol.

2,2-Diphenylcyclopentanol.—To 100 ml. of anhydrous ether in a 300-ml. three-necked flask was added 0.53 g. (0.014 mole) of lithium aluminum hydride. The flask was equipped with a dropping funnel, a mechanical stirrer and a reflux condenser and was protected from atmospheric moisture by a drying tube. Through the dropping funnel was added 3.54 g. (0.015 mole) of 2,2-diphenylcyclopentanone at a rate sufficient to produce gentle reflux. Stirring was continued for 30 minutes after which water was added slowly through the dropping funnel to decompose excess hydride. The mixture was diluted, first with 200 ml. of ice-water and then with 500 ml. of 20% sodium hydroxide solution. The organic layer was separated and the aqueous layer was extracted twice with 100-ml. portions of ether. The ethereal layers were combined and dried over magnesium sulfate. Removal of solvent left an oily residue which was used directly in the preparation of the more tractable sulfonate derivative.

TABLE III

ACETOLYSIS OF 5.54 × 10^{-3} M 2,2-DIDEUTERIO-5,5-DIPHENYLCYCLOPENTYL p-TOLUENESULFONATE AT 50.0°

[NaOAc] = 2.01 × 10^{-2} M; blank = 0.002 ml.; theoretical infinity titer = 1.345 + 0.002 = 1.347; % of theory (1.401 − 0.002)/1.345 × 100 = 103.6%

Time, sec.	NaOAc, ml.	k, sec.$^{-1}$ × 10^5
....	0.202	..
3510	.425	5.84
5410	.520	5.53
8970	.668	5.48
10730	.730	5.41
12580	.800	5.49
14250	.875	5.77
30570	1.180	5.56
32220	1.199	5.54
34180	1.220	5.54
36060	1.238	5.55
37750	1.250	5.53
123280 (∞)	1.400	..
123750 (∞)	1.401	..
		Av. 5.57 ± 0.09

On one occasion the oily residue was crystallized from pentane to furnish white crystals, m.p. 33–35°.

2,2-Dideuterio-5,5-diphenylcyclopentanol.—The ethereal solution of deuterio ketone described above was added dropwise to a stirred ethereal solution of lithium aluminum hydride (0.0213 mole). Reaction conditions and work-up procedures were as described above for the preparation of the undeuterated alcohol. The resulting oil was used directly in the preparation of the corresponding tosylate ester.

2,2-Diphenylcyclopentyl *p*-Toluenesulfonate.—To 0.15 mole of the crude 2,2-diphenylcyclopentanol described above, dissolved in 10 ml. of dry pyridine and cooled to 0°, was added 16.4 g. (0.15 mole) of p-toluenesulfonyl chloride. The reaction mixture was allowed to stand overnight at 0°. It was then poured, with vigorous stirring, into 200 ml. of cold 3.0 N hydrochloric acid. The product was taken up in carbon tetrachloride and dried over potassium carbonate. Removal of solvent left a brownish oil which was dissolved in a minimum amount of ether and cooled to −78°. Pentane was added to incipient cloudiness and the product was allowed to crystallize overnight at −78°, m.p. 108–110°. The product was obtained in yields of 15–20%. Other preparations of the ester had widely-varying melting points, sometimes with decomposition, and the melting point appeared to be a poor criterion of purity.

2,2-Dideuterio-5,5-diphenylcyclopentyl *p*-Toluenesulfonate.—Crude 2,2-dideuterio-5,5-diphenylcyclopentanol, described above, and 4.04 g. (0.0212 mole) of p-toluenesulfonyl chloride were dissolved in 50 ml. of dry pyridine and the resulting solution was allowed to stand at 0° for 48 hours. The reaction mixture was then poured into cold 2.0 N hydrochloric acid and organic matter was extracted into ether. The ethereal solution was dried and, after removal of solvent, the resulting oil was induced to crystallize from an ether–pentane mixture at −78°. A white crystalline material was obtained, m.p. 118°.

Anal. Calcd. for $C_{24}H_{22}D_2SO_3$: C, 73.08; H, 6.44. Found: C, 72.95, 73.00; H, 6.49, 6.41; deuterium analysis[7] indicated the presence of 1.888 atoms of deuterium per molecule.

Solvents, Reagents and Other Materials.—Cyclopentyl p-toluenesulfonate, prepared according to a literature procedure,[2] had m.p. 27.5–28.5° (lit.[2] 28–29°). Commercial dioxane was dried by refluxing over sodium metal for 8 hours. After distillation the dioxane was stored over clean sodium. Commercial pyridine was refluxed over potassium hydroxide

---

[11] A necessary although not sufficient condition for the participation of phenyl in the rate-determining step of the solvolysis of 2,2-diphenylcyclopentyl tosylate requires the formation of rearranged products, the most probable of which seemed to us 1,2-diphenylcyclopentene. Accordingly, an authentic sample of this material was prepared by the method of Criegee[12] for comparison of its ultraviolet spectrum with that of our solvolysis products after extraction from the latter of contaminating p-toluenesulfonic acid. Although the spectra were qualitatively and semi-quantitatively similar, they were not identical. It would seem that, if 1,2-diphenylcyclopentene is a product of this reaction, it is not the only product.

[12] R. Criegee, A. Kerchow and H. Zinke, *Ber.*, **88**, 1878 (1955).

[13] "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 347.

pellets for 5 hours and was then distilled. Storage was over barium oxide. Commercial triethylamine (Eastman Kodak Co.) was allowed to reflux for 2 hours over *p*-toluenesulfonyl chloride and was then distilled.

Rate Measurements.—All solvolysis rates were measured in dry acetic acid at 50.0 ± 0.1° using the sealed ampoule technique. At appropriate time intervals an ampoule was cooled to room temperature and broken; a 5-ml. aliquot was removed and quenched in 10 ml. of dioxane. Titration was against *ca.* 0.02 *M* sodium acetate in acetic acid. Modified methyl orange served as the indicator. A typical kinetic run is reproduced as Table III.

Glacial acetic acid (J. T. Baker analyzed reagent), whose water content was determined by titration against Karl Fischer reagent, was heated under reflux for 24 hours with 105% of the theoretical amount of acetic anhydride. Distillation furnished acetic acid whose water content had been reduced to less than 60 mg. per liter and which was considered dry.

Acknowledgment.—This work was supported in part by a grant from the Army Research Office (Durham) and this assistance is gratefully acknowledged. R. A. S. also wishes to acknowledge many fruitful and stimulating discussions of this and related subjects with Professor H. C. Brown of this department.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY, BOSTON 15, MASS.]

Reactions of Active Nitrogen with Organic Substrates. I. The Monomeric Products of the Reaction with 1,3-Butadiene

BY AKIRA TSUKAMOTO AND NORMAN N. LICHTIN[1]

RECEIVED NOVEMBER 3, 1961

The reaction of active nitrogen with 1,3-butadiene yields important amounts of pyrrole and *cis*- and *trans*-crotononitriles which can be rationalized as resulting from addition of a nitrogen atom and loss of a hydrogen atom. Other products arise from degradative processes and include *cis*- and *trans*-1-cyano-1,3-butadiene, 3-cyano-1-butene, two nitriles tentatively identified as *cis*- and *trans*-1-cyanopentene-3, ethylene, acetylene, propylene and hydrogen cyanide, the most abundant product. A substantial quantity of polymeric material of composition approximating $(C_4H_6N)_x$ is also formed. The small dependence of the relative yields of monomeric (*i.e.*, C_4N, C_5N and C_6N) products on partial pressures of reactants suggests that they are all formed *via* the same nitrogenous intermediate. Mechanistic speculations consistent with the data are offered.

The reactions of active nitrogen with organic compounds have been studied extensively by Winkler and his co-workers.[2] With many aliphatic hydrocarbons, hydrogen cyanide is the major nitrogenous product and in some cases is the only one reported. Herron, Franklin and Bradt[3] observed the formation of nitriles, in relatively small yields, from the reaction of active nitrogen with acetylenes and propylene. The reaction with aromatic hydrocarbons has been reported to give[4] other nitrogenous products in addition to hydrogen cyanide. However, the products in the latter two cases seemed degradative in nature, *i.e.*, formed through the disruption of the organic reactants. Despite extensive study of the reaction of active nitrogen with organic compounds, little evidence of non-degradative products has been reported. It seemed, however, that, if reactions leading to such products could be found, they should provide valuable information as to the mode of interaction between active nitrogen and organic reactants. Thus, the present study has been directed toward exploring the possibility that active nitrogen reacts under suitable circumstances to yield relatively simple products without fragmentation of the carbon skeleton of the substrate and toward elucidating chemical mechanisms for such processes.

Initial experiments were concerned with an observation which Howard and Hilbert[5] recorded, without providing experimental details, that with isoprene as a substrate, "a nitrogenous low boiling liquid in good yield and generating ammonia on hydrolysis was produced." Repetition of this experiment yielded a product similar to that described by Howard and Hilbert, but gas chromatographic analysis revealed that it is a very complex mixture. Infrared analysis of the major fraction, separated gas chromatographically, indicated the formation of a nitrile and a pyrrole derivative, both non-degradative products.[1] This result encouraged exploration of the reaction of active nitrogen with substances related structurally to isoprene, *i.e.*, conjugated dienes; 1,3-butadiene was chosen as initial substrate because it was anticipated that products would be simplest and easiest to identify.

Results

The gas phase reaction of active nitrogen with 1,3-butadiene was carried out at room temperature in a conventional Pyrex flow system, the walls of which were not poisoned. The unpoisoned system was used to avoid reactions with or induced by the poisoning agents. Active nitrogen was produced by applying a microwave discharge to a highly purified nitrogen flow at pressures of 1 to 3 mm. In a few experiments a condensed discharge was employed. The results were essentially the same regardless of the means of producing active nitrogen (*cf.* Table I). The microwave discharge was employed for most of the work because it gives a cleaner and more stable system than does the condensed discharge.

The active nitrogen thus formed was allowed to react at ambient temperature with a stream of 1,3-

---

[1] For a preliminary communication see A. Tsukamoto and N. N. Lichtin, *J. Am. Chem. Soc.*, **82**, 3798 (1960).

[2] For summary see H. G. V. Evans, G. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

[3] J. T. Herron, J. L. Franklin and P. Bradt, *ibid.*, **37**, 597 (1959).

[4] P. M. Aronovich and B. M. Mikhailov, *Bull. Acad. Sci. USSR., Div. Chem. Sci.*, 544 (1956); P. M. Aronovich, N. Y. Belsky and B. M. Mikhailov, *ibid.*, 711 (1956).

[5] L. B. Howard and C. G. Hilbert, *J. Am. Chem. Soc.*, **60**, 1918 (1938).