

aqueous wash solution, and the resulting aqueous solution was heated for 30 sec. After cooling, the formaldehyde-dimedone derivative precipitated (0.532 g.) and gave m.p. 191–192° alone and on admixture with an authentic sample.

The organic layer was dried over magnesium sulfate and concentrated with a rotary evaporator. The residue was distilled to give 0.65 g. of diketone VIII, b.p. 90–100° (bath temperature) at 0.1 mm.; ν_{\max}^{film} 1750, 1740, 1720, and 1240 cm^{-1} ; n.m.r., δ 1.02 (doublet, $J = 6$ c.p.s., three protons) and 2.12 (six protons). VIII gave a negative test with methanolic ferric chloride and gave iodoform (m.p. 120°) with sodium hypiodite.

An ether solution of VIII (0.35 g.) was added to an ether solution of lithium aluminum hydride (0.5 g.) and the solution was stirred at room temperature for 2 hr. After the usual work-up, the ether layer was concentrated to yield 0.2 g. of triol IX (ν_{\max}^{film} 3400 cm^{-1}), which was directly oxidized. A solution prepared by adding 0.14 g. of IX and 0.51 g. of potassium permanganate to 20 ml. of water and 5 ml. of dioxane was stirred overnight at room temperature. After the manganese dioxide was removed by filtration, the solution was acidified with dilute hydrochloric acid and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and, upon the addition of petroleum ether (b.p. 30–60°), β -methyladipic acid (X) precipitated. After recrystallization from ether-petroleum ether, X gave m.p. 85–88° alone and on admixture with an authentic sample of β -methyladipic acid obtained by the oxidation of pulegone.¹³

Both X and the authentic sample of β -methyladipic acid were converted into their dimethyl esters with ethereal diazomethane and the g.l.c. ($1/8$ in. \times 6 ft. column of 10% silicone rubber on

(13) W. Semmler, *Ber.*, **25**, 3513 (1892).

Chromosorb W with hydrogen and nitrogen flow rates of 20 cc./min.) at 135° gave identical retention times (3.6 min.) alone and on admixture. The infrared spectra of the two ester samples were superimposable.

Pyrolysis of IV.—A solution of 0.2 g. of IV in 10 ml. of benzene was pyrolyzed as described above in the pyrolysis of V to give pyrolysate fraction A. A small sample of pyrolysate A was stored under nitrogen; the remainder was pyrolyzed under the same conditions to give pyrolysate B. G.l.c. analysis showed that pyrolysates A and B were identical. G.l.c. analysis using a $1/4$ in. \times 10 ft. column of 10% SE-30 on Chromosorb W at 145° and a helium flow rate of 50 cc./min. with a thermal detector showed the pyrolysate to contain 44% of menthofuran (III), retention time 8.0 min., identified by comparison with an authentic sample; and 56% of another component, presumably XII, retention time 9.5 min. Under these conditions the starting material IV showed a retention time of 30.5 min.

Distillation of the pyrolysate gave a 63 yield of product which was a mixture of menthofuran, III, and XII. The infrared spectrum of the mixture clearly showed the presence of menthofuran by its characteristic bands at 1570, 1108, 764, and 732 cm^{-1} ; in addition, the bands at 3080, 1660, 1640, and 888 cm^{-1} could be assigned to XII. The n.m.r. spectrum of the mixture likewise showed the presence of menthofuran by its characteristic signals at δ 1.07 (doublet, $J = 5.5$ c.p.s.) and 6.84, and the signals at 1.05 (doublet, $J = 4$ c.p.s.) and 5.07 (doublet, $J = 13$ c.p.s.), and a multiplet in region 6.7–7.0 could be assigned to XII.

Acknowledgment.—We wish to thank Mrs. A. O. Servando for some of the preliminary experimental work.

The Thermolysis of 5-Aryltetrazaoles

J. HODGE MARKGRAF, STUART H. BROWN¹, MICHAEL W. KAPLINSKY¹, AND RICHARD G. PETERSON¹

Department of Chemistry, Williams College, Williamstown, Massachusetts

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Rates of the thermal decomposition of 5-phenyltetrazole in several solvents and of 5-aryltetrazaoles in benzonitrile were measured by a precise technique over the range of 180–185°. Solvent effects caused significant differences in rate which were consistent with a competing ionization of 5-phenyltetrazole. Substituent effects led to only a small variation of rate. Although activation enthalpies and entropies varied widely, they acted in a compensatory manner. There were no satisfactory correlations by substituent constants. Product analyses, studies with sodium 5-phenyltetrazolide, and conductance measurements were carried out. The over-all behavior is consistent with the generation of a benzonitrile imine intermediate.

The thermal decomposition of 5-aryltetrazaoles has been known for some time.² During the past decade the thermolyses of both isomeric diaryltetrazaoles and 5-aryltetrazaoles have received renewed attention. The decomposition of 1,5-diaryltetrazaoles proceeded with rearrangement to diarylcarbodiimides and 2-arylarimidazoles.³ In the decomposition of 2,5-diphenyltetrazole the simple expulsion of nitrogen generated benzonitrile N-phenylimine, which in a variety of examples was intercepted by 1,3-dipolar addition.⁴ By contrast, the thermolysis of 5-phenyltetrazole has been investigated less extensively. Huisgen, Sauer, and Seidel⁵ studied its decomposition in several solvents and identified a variety of products, most of which were consistent with benzonitrile imine as the assumed intermediate. No

previous rate studies in this series, however, have been reported. In the present paper we report a kinetic study of the thermolysis of 5-aryltetrazaoles in which substituent and solvent effects are determined.

Experimental⁶

Materials.—All of the 5-aryltetrazaoles except 5-*p*-anisyltetrazole were prepared by the method of Huisgen, Sauer, Seidel, and Markgraf.⁷ 5-*p*-Anisyltetrazole was prepared by the method of Herbst and Wilson.⁸ All the compounds, which are summarized in Table I, were recrystallized from aqueous ethanol to constant melting point.

All solvents, which were commercially available, were distilled through a short column at reduced pressure under a nitrogen atmosphere; a middle fraction was collected and stored in the dark under nitrogen: benzonitrile, b.p. 76.0–76.3° (14 mm.); phenyl ether, b.p. 129.2–129.5° (13 mm.); N,N-dimethylaniline, b.p. 78.7–79.0° (12 mm.); nitrobenzene, b.p. 90.0–90.2° (12

(1) Based in part on the Honors theses of S. H. B. (1963), M. W. K. (1960), and R. G. P. (1961).

(2) (a) A. Pinner, *Ann.*, **297**, 221 (1897); (b) A. Pinner, *ibid.*, **298**, 1 (1897); (c) W. Lossen and F. Statius, *ibid.*, **298**, 91 (1897); (d) W. Lossen and J. Colman, *ibid.*, **298**, 107 (1897).

(3) (a) P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, **80**, 4647 (1958); (b) J. Vaughan and P. A. S. Smith, *J. Org. Chem.*, **23**, 1909 (1958).

(4) See R. Huisgen, *Angew. Chem.*, **75**, 741 (1963), for a comprehensive review and for references to his extensive work in this field.

(5) (a) R. Huisgen, J. Sauer, and M. Seidel, *Ann.*, **654**, 146 (1962); (b) for a preliminary report, see R. Huisgen, *Angew. Chem.*, **72**, 359 (1960).

(6) Melting points and boiling points are uncorrected. Mass spectra were determined with a C. E. C. Model 21-401 instrument at an ionization potential of 70 v.; we are indebted to Mr. R. L. Ames of Yale University for the analyses. Elemental analyses were made by Galbraith Laboratories Inc., Knoxville 21, Tenn.; nitrogen analyses were by the Dumas method.

(7) R. Huisgen, J. Sauer, M. Seidel, and J. H. Markgraf, *Chem. Ber.*, **93**, 2106 (1960).

(8) R. M. Herbst and K. R. Wilson, *J. Org. Chem.*, **22**, 1142 (1957).

TABLE I
 5-ARYLTETRAZOLES

<i>para</i> substituent	Yield, %	M.p., °C., dec.
H	85.7	214.5–215.5
NO ₂	50.2	213.5–214.7
Cl	80.3	254.4–255.2
OCH ₃	45.7	232–233
CH ₃	75.6	246.0–247.5
CF ₃ ^a	20.6	218.0–219.0

^a Anal. Calcd. for C₈H₅F₃N₄: C, 44.87; H, 2.35; F, 26.62; N, 26.16. Found: C, 44.80; H, 2.46; F, 26.43; N, 26.33.

mm.); diphenylmethane, b.p. 133.5–134.0° (13 mm.); β -phenethyl alcohol, b.p. 107.2–108.0° (13 mm.).

Apparatus.—The apparatus for measuring nitrogen evolution was similar to that described elsewhere.⁹ The constant-temperature oil bath (Precision Scientific Co., No. 66546) contained Dow Corning 550 fluid. With efficient stirring and an insulated cover it was possible to regulate the bath temperature to within $\pm 0.1^\circ$ over the range 180–185°. The thermometer was marked in tenths of a degree; its accuracy was certified by the Bureau of Standards.

Rate Measurement.—Rates of decomposition were determined by measuring nitrogen evolution as a function of time. A solution of the tetrazole (about 0.25 g.) in 10 ml. of solvent was prepared in the reaction cell, and the system was swept with nitrogen for at least 0.5 hr. The procedure was identical with that used previously.⁹ Values of Δn , the increase in the number of moles of gas between two measurements, were calculated as a function of time. Since A , the number of moles of the tetrazole initially in the cell, was known, the standard first-order kinetic treatment was applied. A plot of $\log [A/(A - \Delta n)]$ vs. time was made, and the rate constants were determined graphically. Satisfactory first-order plots were obtained in all solvents, and the intercept was the origin in all cases. The only exception to such linearity was observed with β -phenethyl alcohol, in which the decomposition of 5-phenyltetrazole exhibited minor deviations which resulted in the intercept not coinciding with the origin. These runs, therefore, are not included in Table II. The enthalpies of activation were determined graphically from $\log k/T$ vs. $1/T$, and the entropies of activation at 180° were calculated from the Eyring equation.

Products.—A solution of 5-phenyltetrazole (2.00 g., 0.0136 mole) in benzonitrile (80.0 g., 0.768 mole) was heated for 10 hr. in an oil bath at 210°. The solvent was removed at reduced pressure in a rotary evaporator. The red residue was dissolved in warm benzene and extracted three times with 10-ml. portions of 10% sodium hydroxide. The combined aqueous alkaline extract was acidified to pH 7 and the white precipitate, which formed immediately, was collected, washed, and dried. The crude triazole (0.263 g., 0.00119 mole, 8.8%) was recrystallized from dilute aqueous ethanol to yield 3,5-diphenyl-1,2,4-triazole, m.p. 190.5–191.0° (lit.¹⁰ m.p. 191°).

The benzene solution was washed, dried, and evaporated to dryness. The crude red tetrazine (1.470 g., 0.00628 mole, 92.4%) was recrystallized repeatedly from absolute ethanol, m.p. 179–185°. Purification was effected by chromatographing a solution of the tetrazine in *n*-hexane on a short column of alumina to give blue-red crystals of 3,6-diphenyl-1,2,4,5-tetrazine, m.p. 193.5–194.5° (lit. m.p. 192°,^{2a} 195°¹¹).

In all the decompositions studied, the final reaction mixture was always a yellow solution which, upon exposure to oxygen, immediately turned the bright blue-red color characteristic of the tetrazine.¹⁰

Control Runs.—The possible decomposition of the products was studied. A solution of 3,5-diphenyl-1,2,4-triazole (0.0460 g., 0.000208 mole) in 10 ml. of benzonitrile was maintained for 6 hr. in a vapor-thermostated oil bath at $186.1 \pm 0.9^\circ$; the net volume of gas evolved was 0.0 ml. Similarly, a solution of 3,6-diphenyl-1,2,4,5-tetrazine (0.185 g., 0.000792 mole) in 10 ml. of benzonitrile was maintained for 4.5 hr. at $186.5 \pm 0.5^\circ$; the net volume of gas evolved was 0.7 ml.

(9) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(10) J. Allegretti, J. Hancock, and R. S. Knutson, *J. Org. Chem.*, **27**, 14 63 (1962).

(11) K. A. Hofmann and O. Ehrhart, *Ber.*, **45**, 2731 (1912).

The total volume of gas evolved was measured for a run in which a solution of 5-phenyltetrazole (0.1767 g., 0.001209 mole) in 10 ml. of phenyl ether was maintained 13.6 hr. (8.5 half-lives) at $180.60 \pm 0.10^\circ$. The calculated volume at ambient conditions was 30.38 ml.; the observed volume was 32.20 ml. (106%).

In a similar run a solution of 5-phenyltetrazole (0.160 g., 0.00110 mole) in 10 ml. of benzonitrile was maintained for 96.5 hr. at 190°. The gases in the system comprised of the gas buret, connecting tube, and reaction flask were collected in a sample tube which had been previously swept with nitrogen and evacuated. The mass spectrometric analysis of the gas indicated the absence of hydrogen, ammonia, and hydrazoic acid.

The decomposition of sodium 5-phenyltetrazolide was studied. To a solution of sodium methoxide derived from sodium (0.151 g., 0.00655 mole) in 7 ml. of methanol was added a methanolic solution of 5-phenyltetrazole (0.9573 g., 0.00655 mole). The clear, colorless reaction solution was evaporated to dryness under a stream of nitrogen; residual traces of solvent were removed at reduced pressure. A sample of the crystalline solid dissolved immediately in water to yield a neutral solution. A standard kinetic run was carried out on a solution of sodium 5-phenyltetrazolide (0.2030 g., 0.001207 mole) in 10 ml. of β -phenethyl alcohol; the choice of this solvent was dictated by the insolubility of the salt in the other solvents studied. No evolution of gas was observed.

A kinetic run with a solution of 5-phenyltetrazole (0.2661 g., 0.001833 mole) in 10 ml. of phenyl ether was carried out in the usual manner, except that the system was saturated with oxygen for 0.5 hr. prior to placement in the constant-temperature bath. No induction period was observed, and the rate constant was unchanged.

Resistance Measurements.—Solutions were prepared by the same procedure employed for ordinary kinetic runs. The cell was a dipping electrode cell fitted with platinized electrodes; the cell constant was ca. 0.2. The resistances, which were measured after thermal equilibrium was attained, were determined with a conductivity bridge, Industrial Instruments, Inc., Model RC-M15. The measurements were made at a bridge frequency of 1000 c.p.s. in freshly distilled solvents employing 0.171 *M* solutions of 5-phenyltetrazole.

Results

Rates of decomposition of 5-aryltetrazoles are recorded in Tables II and III. Each value is the average of two separate experiments. The effect of changes in solvent was investigated with 5-phenyltetrazole.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE LOSS OF NITROGEN FROM 5-PHENYLTETRAZOLE AT 180.6°

Solvent	$A,^a M$	$k \times 10^6 \text{ sec.}^{-1}$
Benzonitrile	0.18	2.39 ± 0.004
Nitrobenzene	0.18	4.61 ± 0.08
<i>N,N</i> -Dimethylaniline	0.18	5.64 ± 0.04
Phenyl ether	0.18	12.13 ± 0.01
	0.12 ^b	12.96
	0.06 ^b	13.82
Diphenylmethane	0.18	$13.50 \pm .02$

^a Initial concentration of 5-phenyltetrazole. ^b Single run.

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE LOSS OF NITROGEN FROM 5-ARYLTETRAZOLES IN BENZONITRILE^a

Substituent	$k \times 10^6 \text{ sec.}^{-1}$	
	180.6°	185.6°
Unsubstituted	2.39 ± 0.004	4.04 ± 0.05
<i>p</i> -Nitro	2.43 ± 0.03	4.12 ± 0.02
<i>p</i> -Trifluoromethyl	2.36 ± 0.07	3.70 ± 0.06
<i>p</i> -Methoxy	2.31 ± 0.004	3.99 ± 0.004
<i>p</i> -Methyl	2.27 ± 0.01	3.74 ± 0.02
<i>p</i> -Chloro	2.24 ± 0.004	3.69 ± 0.07

^a Initial concentration of tetrazole was 0.16–0.19 *M*, except *p*-CF₃, which was 0.11–0.18 *M*.

The solvents are listed in Table II in order of increasing rate. The rates were in all cases strictly first order and, with the exception of benzonitrile, were followed to a minimum of 60% completion. The rate was observed to be linear to over 90% reaction for a run in phenyl ether. In benzonitrile positive deviations from linearity commenced midway in the reaction, and the rate constants were determined to *ca.* 40% completion.

The effect of *para* substituents was investigated with 5-aryltetrazoles in benzonitrile. The choice of solvent was based on the previous use of benzonitriles as solvents in the thermolyses of 5-phenyltetrazole^{5a} and 2,5-diphenyltetrazole.¹² The rates of decomposition of the 5-aryltetrazoles are presented in Table III. All decompositions exhibited first-order behavior. The two temperatures at which the measurements were made were limited to a narrow range because the rates were highly sensitive to temperature changes. Nevertheless, the high energy of activation of these reactions permitted the calculation of reasonably accurate ΔH^* values. The enthalpies of activation were between 40–45 kcal./mole for all decompositions except that of the *p*-trifluoromethyl substituent, for which ΔH^* was 36 kcal./mole.

5-Phenyltetrazole is a weak acid which in nonaqueous media has an acidity comparable with that of benzoic acid.^{8,13} The influence of solvent on this ionization at the temperature of decomposition was assessed by measuring the resistances of a series of solutions. The results are summarized in Table IV.

TABLE IV
APPROXIMATE RESISTANCES OF 0.17 *M* SOLUTIONS OF
5-PHENYLTETRAZOLE AT 180.6°

Solvent	Resistance, ohms ^a
Benzonitrile	4.4×10^4
Nitrobenzene	1.7×10^5
<i>N,N</i> -Dimethylaniline	6.5×10^5
Phenyl ether	$>10^6$

^a The resistances of the pure solvents at 180.6° were in all cases $>10^6$ ohms.

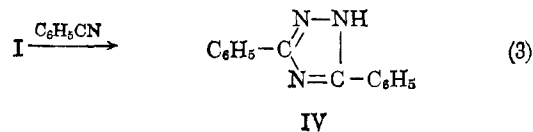
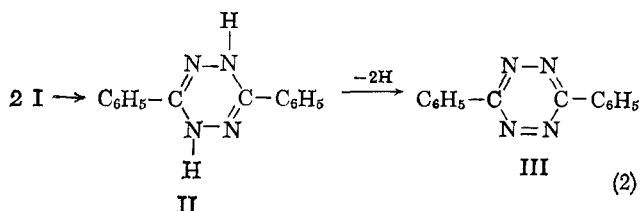
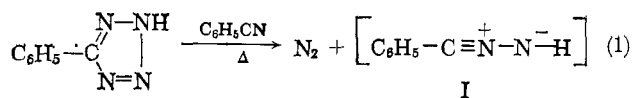
In this connection it is noteworthy that sodium 5-phenyltetrazolide led to no gas evolution at 180.6°.

Discussion

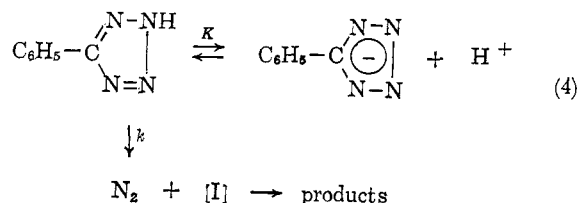
No previous kinetic study of the thermolysis of 5-aryltetrazoles has been reported. The only rate constants for any tetrazole derivatives are those of Huisgen, *et al.*,¹² who measured the rates of nitrogen evolution from 2,5-diphenyltetrazole in a series of four solvents at 175°. In the present case with 5-phenyltetrazole as substrate, the effect of solvent on the rates was moderate, the extremes differing by a factor of less than six. The interesting aspect, however, was the fact that as the solvent passed from benzonitrile to diphenylmethane the first-order rate constant increased. Such variation of k with solvent polarity is usually interpreted as indicating a decrease in charge separation in the transition state relative to starting material. It is reasonable to assume that the loss of one molecule of nitrogen from 5-phenyltetrazole is accompanied by

(12) R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, *Ann.*, **653**, 105 (1962).

(13) T. P. Maher and G. R. Yohe, *J. Org. Chem.*, **23**, 1082 (1958).



the generation of benzonitrile imine.^{5a} This assumption is consistent with the isolation of products III and IV, as well as the color change (indicative of the oxidation of II to III) observed during the work-up of the reaction mixture. Benzonitrile imine (I) is analogous to the intermediates intercepted in the thermolyses of 2,5-diphenyltetrazole,^{12,14} the isomeric 2(5)-methyl-5(2)-phenyltetrazoles,^{12,15} and 2-trimethylsilyl-5-phenyltetrazole.¹⁶ An alternate explanation to that based on differences in charge distribution between initial and transition states is one which accounts for changes in concentration of that species involved in the unimolecular decomposition. Thus, the rate of expulsion of nitrogen from 5-phenyltetrazole, a process which produces a dipolar intermediate, may decrease with increasing polarity of the solvent due to a competing ionization of the substrate. The experimental rate



constant for the mechanism given (eq. 4) would follow the rate law where k is the rate constant of the rate-

$$k_{\text{exptl}} = k / \left[1 + \left(\frac{Z^-}{ZH} \right)^{1/2} \right] \quad (5)$$

determining step and ZH and Z^- are the concentrations of the tetrazole and its conjugate base, respectively. An increase in K (*i.e.*, an increase in Z^-/ZH) will obviously decrease k_{exptl} , if K is more sensitive to solvent effects than is k . That the latter condition obtains is indicated both by the conductance data and by the insensitivity of the observed rate constant in a similar series of solvents for the thermolysis of 2,5-diphenyltetrazole, a related substrate possessing no ionizable proton.¹² This postulate is further supported by the absence of gas evolution from the conjugate base of 5-phenyltetrazole.¹⁷

(14) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).

(15) R. Huisgen, J. Sauer, and M. Seidel, *Chem. Ber.*, **94**, 2503 (1961).

(16) L. Birkofer, A. Ritter, and P. Richter, *ibid.*, **96**, 2750 (1963).

(17) From the mechanism given (eq. 4), the rate should be independent of concentration, whereas in the one case studied (*cf.* Table II) there was a 14% decrease in rate over a threefold increase in concentration. Such a relationship is not inconsistent with a secondary salt effect. In any case, the inverse variation of rate with concentration is quite small relative to solvent effects.

In view of the above discussion, a detailed commentary on the effect of *para* substituents does not seem warranted. The substituent may affect the protolytic equilibrium as well as the activation parameters for the thermolytic process. The difficulty in interpreting any substituent effect is seen, for example, in the case of the *p*-methoxy group. This compound is a weaker acid than 5-phenyltetrazole⁸ and therefore a higher concentration of the monomeric 5-*p*-anisyltetrazole might be anticipated. At the same time the *p*-methoxy group would be expected to stabilize the incipient *p*-anisonitrile imine. Both effects would lead to a predicted increase in the observed first-order rate constant, whereas the observed value is less.

There is no simple correlation with any of the substituent constants.¹⁸ Changes in the nature of the substituent have little effect on the rate. Although the

(18) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

rate differences are quite small, they reflect rather large variations in activation enthalpies which are apparently offset by compensating activation entropies. This interpretation, however, is open to question.¹⁹

A comparison of the rates in benzonitrile as solvent for 2,5-diphenyltetrazole¹² and 5-phenyltetrazole shows that the former compound undergoes a more facile decomposition. The activation parameters for the latter correspond to a rate constant at 175° of about 1.3×10^{-5} sec.⁻¹, giving $k_{2,5-(C_6H_5)_2}/k_{5-C_6H_5} = 38$.

Acknowledgment.—Exploratory work related to these studies was commenced by one of us in the laboratory of Professor R. Huisgen (Munich). His permission to continue this investigation and his interest in our work are gratefully acknowledged. We are indebted to Dr. S. D. Ross and Dr. R. C. Petersen for many valuable discussions and helpful suggestions.

(19) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 376-379.

Sterically Hindered Group IVA Organometallics. Preparation and Properties of Certain Neopentyltins¹

HANS ZIMMER, I. HECHENBLEIKNER, OTTO A. HOMBERG, AND MITCHELL DANZIK²

Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio, and the Research Laboratories, Carlisle Chemical Works, Inc., Reading 15, Ohio

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A series of 17 organotin compounds containing the neopentyl group has been prepared in an effort to determine the effect of steric hindrance on the preparation and reactivity of these compounds. The introduction of a fourth neopentyl group around the tin atom required more drastic conditions than necessary for a *n*-alkyl group, and in one instance the attempted preparation led solely to the isolation of the reduction product, hexaneopentyliditin. Once formed, the neopentyl carbon to tin bond strongly resisted cleavage; the bond was broken only slowly at elevated temperatures by bromine and failed to undergo a Kocheshkov reaction below the degradation temperature of the mixture.

The present work was undertaken as part of a study aimed at investigating the formation and reactivity of organotin compounds containing aliphatic groups exerting a steric influence in the final product. Van der Kerk and Luijten³ report that the reaction of isopropylmagnesium bromide and stannic chloride result in the formation of tetraisopropyltin in only 25% yield, accompanied by the formation of a considerable quantity of hexaisopropyliditin. Under similar conditions they observe that tetra-*n*-propyltin is isolated in a 70% yield.⁴ Similarly, the formation of tetracyclohexyltin is reported⁵ to be accompanied by the formation of a considerable quantity of distannane, while the *n*-hexyl compound may be prepared in good yield.⁴

Krause and Weinberg⁶ investigated the reaction of *t*-alkylmagnesium bromides and stannic chloride and found that the addition of the chloride to the Grignard reagent resulted in the formation of a di-*t*-alkyltin, which on treatment with bromine resulted in the formation of the corresponding di-*t*-alkyltin dibromide in al-

most quantitative yield. When the order of addition was reversed, a di-*t*-alkyltin dichloride could be isolated directly. Treatment of the dihalide with a large excess of the Grignard reagent resulted in the formation of a tri-*t*-alkyltin halide, but the authors were unable to obtain a tetra-*t*-alkyltin containing either the *t*-butyl or *t*-amyl group. Working with *t*-butyllithium and stannic chloride, Prince⁷ reported a similar series of results.

Steric effects have also been observed in the attempted formation of tetraaryltins. Tri-1-naphthyltin chloride,⁸ tri-2-biphenyltin chloride,⁸ and tri-2-biphenyltin bromide⁹ result from the reaction of the appropriate Grignard reagent and stannic halide. However, in each instance the tetraaryltin could be prepared by substituting the corresponding organolithium compound for the Grignard reagent. Tris(2-alkoxy-1-naphthyl)tin bromides and trimesityltin bromide were the only products isolated on treatment of stannic bromide with the appropriate Grignard reagent.¹⁰ In the latter case, the authors were unable to prepare the tetraaryltins even with the organolithium, -sodium, or -potassium reagents.

(1) Taken in part from the doctoral degree dissertations of M. D. (1963) and O. A. H. (presumably 1965), University of Cincinnati.

(2) Research Corporation Fellow, 1959-1960.

(3) G. J. M., Van der Kerk, and J. G. A. Luijten, *J. Appl. Chem.* (London), **6**, 49 (1956).

(4) G. J. M., Van der Kerk, and J. G. A. Luijten, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Middlesex, England, 1955.

(5) E. Krause and R. Pohland, *Ber.*, **57**, 532 (1924).

(6) E. Krause and K. Weinberg, *ibid.*, **63**, 381 (1930).

(7) R. H. Prince, *J. Chem. Soc.*, 1783 (1959).

(8) E. Krause and K. Weinberg, *Ber.*, **62**, 2235 (1929).

(9) G. Bähr and R. Gelius, *ibid.*, **91**, 812 (1958).

(10) I. I. Lapkin and V. A. Sedel'nikova, *Zh. Obshch. Khim.*, **30**, 2771 (1960); *Chem. Abstr.*, **55**, 14,346b (1960).