TABLE I

ULTRAVIOLET ABSORPTION SPECTRA

Pyrazine	Solvent[a]	λ_{max}, mμ	log ϵ
2-Chloro-3,6-dimethyl-	A	214, 281, 295 (sh)	4.90, 3.89, 3.74
2-Hydroxy-3,5-dimethyl-	A	228, 327	4.06, 3.92
2-Hydroxy-3,6-dimethyl-[b]	B	223, 321	3.97, 3.95
3-Chloro-2,5-dimethyl-, 1-oxide	B	221, 267, 308, 312	4.21, 4.04, 3.74, 3.72
3-Hydroxy-2-methyl-, 1-oxide	B	219, 266, 315	4.23, 3.79, 3.72
3-Hydroxy-2,5-dimethyl-, 1-oxide[c]	B	225, 272, 328	4.18, 3.79, 3.74
2-Ethoxy-	A	211.5, 279, 295 (sh)	3.93, 3.61
3-Ethoxy-, 1-oxide	B	217.5, 261, 305	4.31, 4.05, 3.68
2-Ethoxy-, 1,4-dioxide	B	212, 234, 256, 296, 337.5	4.05, 4.30, 3.74, 4.31, 4.08
2-Ethoxy-3-methyl-	A	214, 277 (sh), 292.5	3.94, . . ., 3.75
2-Methoxy-3,6-dimethyl-	A	214, 295	3.93, 3.87
2-Ethoxy-3,6-dimethyl-[d]	A	216, 297	3.97, 3.89
3-Ethoxy-2-methyl-, 1-oxide	A	217, 264, 302.5, 306	4.22, 3.97, 3.54
3-Ethoxy-2,5-dimethyl-, 1-oxide	A	220, 262, 309	4.34, 4.01, 3.76
2-Ethoxy-3-pyrazylmethyl acetate	A	216, 294	4.04, 3.88
2-Ethoxy-3-pyrazinemethanol	B	215, 294	4.11, 3.90

[a] A = Spectro Grade methanol, B = water. [b] G. T. Newbold and F. S. Spring [*J. Chem. Soc.*, 373 (1947)] give λ_{max}^{EtOH} 227 mμ (log ϵ 3.88), 323 (3.56). [c] Ref. 10 gives λ_{max}^{EtOH} 225 mμ (log ϵ 4.18), 272 (3.79), 327 (3.68). [d] Ref. 10 gives λ_{max}^{EtOH} 298 mμ (log ϵ 3.92).

Anal. Calcd. for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.18; N, 14.30. Found: C, 54.59; H, 6.39; N, 16.14.[23]

2-Ethoxy-3-pyrazinemethanol.—A mixture of 6.2 g. (0.032 mole) of 2-ethoxy-3-pyrazylmethyl acetate and 32 ml. of 10% sodium hydroxide was allowed to stand over a weekend at room temperature, although the phases became homogeneous within 2 hr. The solution was extracted with ether; the extract was washed with water and dried. Removal of solvent and sublimation of the residue gave 2.7 g. (55%) of product, m.p. 43°. For analysis, the product was sublimed several times, which raised the melting point to 46-47°.

Anal. Calcd. for $C_7H_{10}N_2O_2$: C, 54.5; H, 6.5; N, 18.2. Found: C, 54.84; H, 6.57; N, 17.88.

3-Ethoxy-2,5-dimethylpyrazine 1-Oxide.—Heating under reflux a mixture of 3.2 g. (0.02 mole) of 3-chloro-2,5-dimethylpyrazine 1-oxide and 17.5 ml. of absolute ethanol containing 3.46 g. of potassium hydroxide for 4 hr. and working up the reaction as described above yielded 1.52 g. (45%) of crude product, m.p. 93-96°. One recrystallization from petroleum ether (b.p. 30-60°) brought the melting point to 96-97°; Baxter and associates[10] give m.p. 92-94°.

2-Ethoxy-3,6-dimethylpyrazine.—A solution of 8.6 g. (0.06 mole) of 2-chloro-3,6-dimethylpyrazine in 50 ml. of absolute ethanol containing 10.1 g. (0.18 mole) of KOH was heated for 16 hr. in a stainless steel bomb at 120°. Half the solvent was removed at reduced pressure, an equal quantity of water was added, and the product was extracted into ether. Removal of the solvent after drying and distillation of the residue afforded 6.1 g. (66.3%) of product, b.p. 96-98° (31 mm.), n^{26}_D 1.4920.

2-Methoxy-3,6-dimethylpyrazine.—Heating a solution of 8.6 g. (0.06 mole) of 2-chloro-3,6-dimethylpyrazine in 60 ml. of absolute methanol containing 10.1 g. of potassium hydroxide for 2 hr. under reflux and working up the mixture as described gave a total of 5.4 g. (65%) of methyl ether, b.p. 86° (22 mm.), n^{25}_D 1.5026.

Absorption Spectra.—Ultraviolet absorption spectra were determined on a Bausch and Lomb Spectronic 505 recording spectrophotometer, calibrated with both mercury emission spectrum and holmium oxide. Infrared absorption spectra were determined on a Perkin-Elmer Model 21 recording spectrophotometer calibrated against a polystyrene film. The ultraviolet absorption spectra are given in Table I.

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[23] This analysis, as well as the abrupt change in the boiling point on redistillation, showing the presence of material with a higher nitrogen content, indicates some deacetylation had occurred. The ease of hydrolysis of pyrazylmethyl acetates has been reported.[16]

Terpenes. XIV.[1] The Reaction of Pulegone with Lead Tetraacetate

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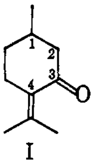
Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

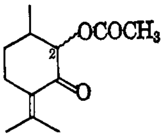
Received March 20, 1964

Pulegone (I) has been found to react with lead tetraacetate in benzene to yield predominantly *cis*- and *trans*-4-acetoxyisopulegone (IV) rather than 2-acetoxypulegone (II), the product of the reaction of pulegone with mercuric acetate.[3] Pyrolysis of IV gave menthofuran (III) in addition to the expected diene XII. The mechanisms involved in the formation of IV and its subsequent conversion to III are discussed.

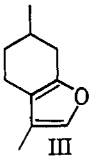
In a recent communication[3] we reported on the formation of *cis*- and *trans*-2-acetoxypulegone (II) in the reaction of pulegone (I) with mercuric acetate in acetic acid and the surprising pyrolysis of II to yield optically pure menthofuran (III). We have now investigated the reaction of pulegone with lead tetraacetate in benzene and find that under these conditions II is produced to only a minor extent and the major product is instead a mixture of *cis*- and *trans*-4-acetoxyisopulegone (IV).



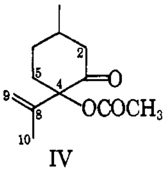
I



II



III



IV

Gas–liquid chromatography (g.l.c.) immediately showed that the product (IV) of the reaction of pulegone with lead tetraacetate had a lower retention time than

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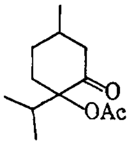
[1] Terpenes XIII: L. H. Zalkow and D. R. Brannon, *J. Chem. Soc.*, in press.

[2] National Institutes of Health Fellow, 1962-1964.

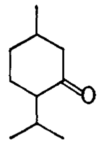
[3] L. H. Zalkow, J. W. Ellis, and M. R. Brennan, *J. Org. Chem.*, **28**, 1705 (1963).

II and its infrared spectrum showed carbonyl bands at 1745 and 1700 cm.$^{-1}$, indicating that an α,β-unsaturated carbonyl as in pulegone and in II was not present. In addition, IV gave no ultraviolet spectrum characteristic of α,β-unsaturated ketones. The n.m.r. spectrum of IV showed the C-10 methyl group at δ 1.74 and two acetoxy methyl signals of equal intensity appeared at δ 1.97 and 2.03 (*cis* and *trans*). In II (*cis* and *trans*) the isopropylidene methyl groups gave signals at δ 1.76 and 1.84, whereas the acetoxy signal appeared at δ 2.09. In the spectrum of IV the C-1 methyl signal appeared as a pair of doublets (J = 5.5 c.p.s.) of approximately equal intensity centered at δ 0.98 and 1.03 (*cis* and *trans*); in II the *cis* isomer showed the C-1 methyl signal as a doublet (J = 7 c.p.s.) centered at δ 0.96, whereas the *trans* isomer showed this doublet at δ 1.05. In the spectrum of II the C-2 proton of the *cis* isomer appeared as a doublet (J = 5.5 c.p.s.) at δ 5.10, whereas in the *trans* isomer the doublet was centered at δ 4.64; by contrast, the spectrum of IV showed a complicated multiplet in the region δ 4.95–5.20 integrating for two protons.

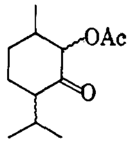
Hydrogenation of IV gave the dihydro derivative V and menthone (VI). The formation of VI indicated that no deep-seated skeletal rearrangement had taken place in the conversion of I to IV. G.l.c. showed that V had a lower retention time than VII, the dihydro derivative of II. The infrared spectrum of V showed two saturated carbonyl bands (1748 and 1725 cm.$^{-1}$) and its n.m.r. spectrum no longer showed the complicated multiplet at δ 4.95–5.20, present in the spectrum of IV; thus this multiplet arose from olefinic protons and not from protons attached to carbons bearing acetoxy groups as at C-2 in II and VII. This information suggested structure IV (*cis* and *trans*) for the product of the reaction of pulegone with lead tetraacetate. The band in the infrared spectrum usually found[4] for the olefinic protons of the isopropenyl group at 890 cm.$^{-1}$ was absent in the spectrum of IV, but other cases are known in which this band is absent.[5]



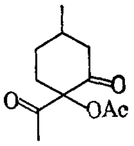
V



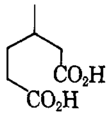
VI



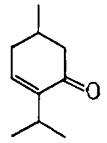
VII



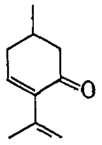
VIII



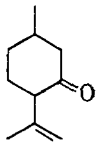
X



XI



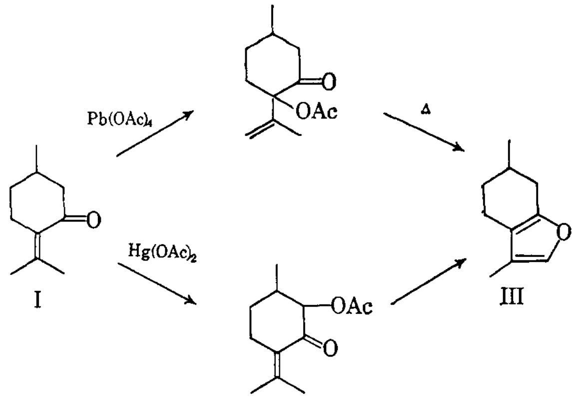
XII



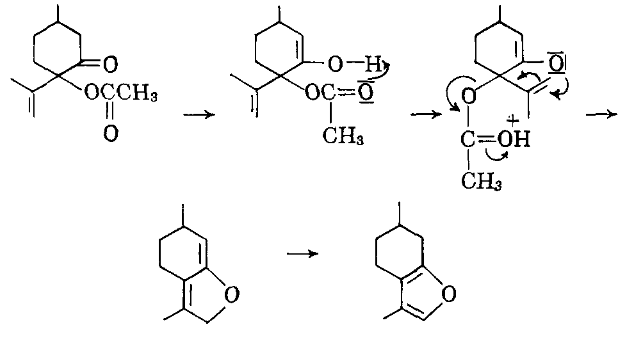
XIII.

That IV was indeed the correct structure was shown as follows. Ozonolysis of IV gave formaldehyde and a diketone VIII which gave a positive iodoform test but a negative ferric chloride test. The n.m.r. spectrum of VIII was consistent with the assigned structure. VIII was reduced with lithium aluminum hydride to give the triol IX which was oxidized with potassium permanganate to give β-methyladipic acid (X) identical with an authentic sample prepared from pulegone. Thus, the acetoxy group in IV could not have been located at C-2 or C-5, the positions of pulegone one might expect to be reactive toward lead tetraacetate. Additional evidence that the acetoxy group of IV was located at C-4 was found in the pyrolysis of V, which gave XI, shown not to be identical with pulegone (II) by infrared and n.m.r. spectra and by g.l.c.

SCHEME I

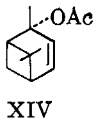


SCHEME II

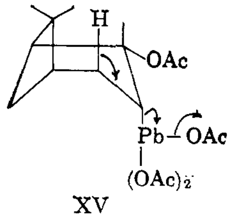


Pyrolysis of IV gave in addition to the expected product XII in 56% yield, menthofuran (III) in 44% yield. Thus, pyrolysis of both 2-acetoxypulegone and 4-acetoxyisopulegone give menthofuran (Scheme I). Menthofuran is apparently not produced from diene XII since repyrolysis of the initially formed mixture of XII and III did not change the ratio of the two products. It is suggested that III arises as shown in Scheme II. When isopulegone (XIII) was treated with lead tetraacetate under the identical conditions used in the reaction with pulegone, the g.l.c. of the product indicated it to be a complex mixture containing only a small amount of IV, thus suggesting that pulegone does not rearrange to isopulegone before reacting with lead tetraacetate.

Whitham[6] showed that the primary product of the reaction of α-pinene with lead tetraacetate in benzene is *cis*-2-acetoxy-3-pinene (XIV) which he suggested was



XIV



XV

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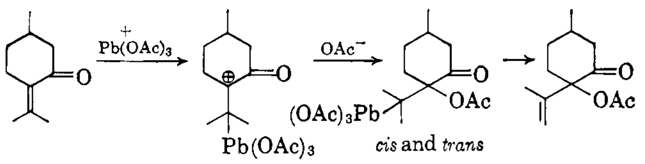
[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34.

[5] L. H. Zalkow and N. Burke, *Chem. Ind.* (London), 292 (1963).

[6] G. H. Whitham, *J. Chem. Soc.*, 2232 (1961).

formed in an ionic reaction involving attack of Pb$^+$(OAc)$_3$ on α-pinene from the side remote from the *gem*-dimethyl bridge to give an intermediate of the bromonium ion type followed by *cis* opening by acetate anion to form the intermediate XV, which then underwent elimination as shown to yield XIV and lead diacetate. If the Whitham mechanism were applicable in the reaction of pulegone with lead tetraacetate, as discussed in this article, then the initial electrophilic attack would have to be nonstereospecific to account for the formation of *cis* and *trans* IV. On the other hand, the formation of a classical-type carbonium ion intermediate as shown in Scheme III would readily explain the formation of *cis* and *trans* products.

Scheme III



Lead tetraacetate has often been used to introduce the acetoxy group α to a keto function in saturated compounds, particularly in the steroid field[7]; usually this is most efficiently done in acetic acid as solvent in the presence of a Lewis acid such as boron trifluoride. However, Cavill and Solomon[8] found that α-acetoxylation of cyclohexanone proceeded in much better yield but more slowly in benzene compared with acetic acid. These workers suggested that a free-radical mechanism was involved in the acetoxylation of ketones. Whatever the mechanism involved, it does appear that the enol form is the reactive intermediate.[9] Thus a number of questions remain to be answered regarding the mechanism of the reaction of lead tetraacetate with ketones and olefins.[10] It is hoped that further investigations underway in our laboratory will offer an explanation for the lack of reactivity of the C-2 position in pulegone in the reaction with lead tetraacetate in benzene as compared to the reactivity of this position with mercuric acetate in acetic acid.

Experimental

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-5 spectrometer; n.m.r. spectra were determined with the varian A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane as an internal standard (δ = 0). Gas chromatograms, unless otherwise indicated, were obtained with the Aerograph Hy-Fi gas chromatograph using a hydrogen flame detector and a column $^1/_8$ in. × 5 ft. of 5% SE-30 on acid-washed Chromosorb W, with hydrogen and nitrogen flow rates of 30 ml./min.

Preparation of 4-Acetoxyisopulegone (IV).—A solution prepared by adding 15.2 g. of pulegone and 55 g. of lead tetraacetate to 150 ml. of dry benzene was refluxed until it gave a negative starch-iodide test (~2 hr.). After cooling, the benzene solution was washed with water until the wash water was neutral to litmus paper and the benzene layer was then dried over magnesium sulfate and concentrated with a rotary evaporator. Fractional distillation of the residue gave (a) 6.6 g., b.p. 25–75° at 0.5 mm.; then (b) 5.41 g., b.p. 75–90° at 0.5 mm. Gas chromatography of b showed only about 5% of II. The retention times of II and IV were 3 and 2 min., respectively at 180°. Under the conditions used in the g.l.c., an authentic sample of II gave a double peak centered at 3 min., whereas IV gave a single sharp peak at 2 min. Several other g.l.c. columns also failed to resolve IV into its two components. However, the n.m.r. spectrum of IV showed that it was an approximately equal mixture of *cis* and *trans* isomers by the appearance of two acetoxy signals of almost equal intensity at δ 1.97 and 2.03 and by the appearance of a pair of doublets for the C-1 methyl group. Redistillation of fraction b gave the analytical sample of IV, b.p. 87° at 0.5 mm.; $\nu_{\max}^{\text{film}}$ 3095, 1745, 1700, 1648, 1239, and 895 (weak and broad) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.34; H, 8.86.

IV (0.5 g.) was added to a solution prepared by dissolving 1 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate in 10 ml. of water and ethanol was added until the turbid solution became clear. The solution was heated on the steam bath for 3 min., then cooled overnight. The solid precipitate was recrystallized from ethanol–water and gave m.p. 205–208° dec. The elemental analysis indicated that, in forming the semicarbazone, IV had lost the elements of acetic acid.

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27. Found: C, 63.37; H, 8.20.

Hydrogenation of IV. Preparation of VI.—IV (1 g.) in 30 ml. of absolute ethanol was hydrogenated in the presence of 0.1 g. of 10% palladium on charcoal at atmospheric pressure and room temperature until hydrogen uptake appeared to cease. The catalyst was removed by filtration and the solvent was removed with a rotary evaporator. Distillation gave a lower boiling fraction (bath temperature of 50–70° at 0.5 mm.) which was shown to be mostly menthone (VI) by g.l.c., and a higher boiling fraction (bath temperature of 80–95° at 0.5 mm.) which was rich in V. The analytical sample of V was obtained by preparative g.l.c. using an Aerograph Autoprep with a column $^1/_4$ in. × 10 ft. of 10% silicone rubber on Chromosorb P at 150° with a flow rate of 88 cc./min.; $\nu_{\max}^{\text{film}}$ 1748, 1724, and 1240 cm.$^{-1}$

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 68.13; H, 9.47.

II[3] was hydrogenated in a similar manner to give VII. G.l.c. comparisons of V and VII using a $^1/_4$ in. × 10 ft. Craig polyester succinate column at 130° with a thermal detector and a helium flow rate of 62 cc./min. showed that individually and on admixture V and VII had retention times of 12.3 and 14 min., respectively.

An authentic sample of l-menthone was prepared by Jones oxidation[11] of l-menthol (Mallinckrodt) and it was identical by infrared and g.l.c. with VI isolated as described above.

Pyrolysis of V.—A solution containing 0.2 g. of V in 10 ml. of benzene was forced through a 1.5 cm. × 17 cm. Vycor column packed with $^3/_{32}$-in. glass helices and heated to a temperature of 300° under nitrogen pressure (77 cc./min.). The crude pyrolysate was washed with 10% sodium bicarbonate, then water, and finally dried over anhydrous magnesium sulfate. Removal of the benzene with a rotary evaporator and distillation of the residue gave an impure product consisting mainly of an α,β-unsaturated ketone ($\nu_{\max}^{\text{film}}$ 1675 cm.$^{-1}$), presumably XI, which when compared by g.l.c. (100°, H_2 and N_2 flow rates of 20 cc./min.) with pulegone and menthone alone and on admixture gave the following retention times: 3.5 (VI), 3.8 (XI), and 4.7 min. (I). The n.m.r. spectrum of XI showed an olefinic proton at δ 6.61; carvone is reported to show its analogous vinylic proton β to the carbonyl group at δ 6.75, whereas piperitone shows its vinylic proton α to the carbonyl group at δ 5.87.[12]

Ozonolysis of IV. Conversion of IV to β-Methyladipic Acid (X).—A stream of oxygen containing ~3% ozone was passed through a solution prepared by dissolving 1.14 g. of IV in 15 ml. of methylene chloride at −70° until the characteristic blue color persisted. The solution was then stirred with 0.2 g. of zinc and 15 ml. of water at room temperature for 3 hr. After filtration, the organic layer was washed with water several times, a saturated methanolic solution of dimedone was added to the combined

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[7] Carl Djerassi, "Steroid Reactions—An Outline for Organic Chemists," Holden-Day, Inc., San Francisco, Calif., 1963, Chapter 13.

[8] G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955).

[9] R. C. Fuson, E. W. Maynert, T.-L. Tan, E. R. Trumbull, and F. W. Wassmundt, *J. Am. Chem. Soc.*, **79**, 1938 (1957).

[10] For a recent review of the new developments in oxidations by lead tetraacetate, see R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

[11] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem Soc.*, 2555 (1953).

[12] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

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.; $\nu_{\max}^{\text{film}}$ 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 hypoiodite.

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 ($\nu_{\max}^{\text{film}}$ 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. × 6 ft. column of 10% silicone rubber on 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 repyrolyzed 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. × 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.

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The Thermolysis of 5-Aryltetrazoles

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Rates of the thermal decomposition of 5-phenyltetrazole in several solvents and of 5-aryltetrazoles 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-aryltetrazoles has been known for some time.[2] During the past decade the thermolyses of both isomeric diaryltetrazoles and 5-aryltetrazoles have received renewed attention. The decomposition of 1,5-diaryltetrazoles 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 Seidel[5] 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-aryltetrazoles in which substituent and solvent effects are determined.

Experimental[6]

Materials.—All of the 5-aryltetrazoles 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

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(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).

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(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.

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