on the 5- and 2-carbons, respectively, and a sharp singlet at 10.01 p.p.m. owing to the acid proton. The integrations of these resonance absorptions were consistent with these assignments.

Diethylketene Acetal and 1,4-Dioxane.—A mixture consisting of 1,4-dioxane (132 g., 1.5 moles), diethylketene acetal (15.0 g., 0.13 mole), and *t*-butyl peroxide (1.5 g., 0.01 mole) was heated for 18 hr. at 120–130° in a stainless steel autoclave. Distillation of the resulting reaction mixture yielded 9.4 g. of ethyl 1,4-dioxylacetate which was collected at a boiling range of 85–108° at 2 mm., $n^{25}\text{D}$ 1.4400.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.15; H, 8.12. Found: C, 55.13; H, 8.04.

The infrared spectrum of this material had a strong carbonyl absorption at 5.75–5.80 μ. The n.m.r. spectrum showed a triplet centered at 1.25 p.p.m. owing to the methyl group and a complex absorption ranging from 3.0 to 4.3 p.p.m. owing to the ring protons and the methylene protons of the ethyl group. The peaks of a doublet centered at 2.3 p.p.m. owing to the α-methylene protons were split, presumably the result of coupling with the ring protons. The mass spectrum showed a parent peak at *m/e* 174 (calcd. mol. wt., 174). Prominent peaks in the mass spectrum were found at *m/e* 73, 87, 101, and 129 owing to $(CO_2C_2H_5)^+$, $(CH_2CO_2C_2H_5)^+$ and/or $(CH_2OCH_2CH_2OCH)^+$, $(CH_2OCH_2CH_2OCHCH_2)^+$, and $(CH_2OCH_2CH_2OCHCH_2CO)^+$ fragments, respectively.

Attempted Free-Radical Addition of 2-Propanol to Diethylketene Acetal.—A mixture of 2-propanol (60 g., 1.0 mole), diethylketene acetal (11.6 g., 0.10 mole), and *t*-butyl peroxide (1.46 g., 0.01 mole) was heated in sealed glass tubes at 125° for 18 hr. Distillation yielded a product (10.0 g., b.p. 45° at 10 mm.). The infrared spectrum of this material showed a very weak carbonyl absorption. Although not conclusively identified as such, the n.m.r. spectrum was consistent for that of diisopropyl ethyl orthoacetate.

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The Chemistry of Pyrazine and Its Derivatives. XI. The Pyrazylethylation of Certain Active Hydrogen Compounds

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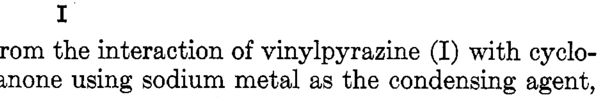
In an earlier publication[2] we indicated that a series of amines undergo conjugate addition (Michael condensation) with vinylpyrazine to give pyrazylethylated amines. We now report that four other types of active hydrogen compounds, RH, will undergo the Michael condensation with vinylpyrazine. The over-all reactions are indicated in the following equation.



I

From the interaction of vinylpyrazine (I) with cyclohexanone using sodium metal as the condensing agent, there was obtained 2-(2-pyrazylethyl)cyclohexanone in 67.5% yield. This is considerably lower than the 81% yield of the same product which was isolated from the interaction of the pyrrolidine enamine of cyclohexanone and vinylpyrazine followed by hydrolysis.[3] However, the latter method involves the prior formation of the enamine, and the reaction conditions are considerably more drastic than those used in the present study. When I was treated with cyclopentanone in the presence of metallic sodium, a mixture of products was obtained, *i.e.*, the desired product, 2-(2-pyrazylethyl)cyclopentanone (21.9%), and the self-condensed derivative of cyclopentanone, cyclopentylidenecyclopentanone (42.9%). Again, a very much higher yield (66%) was obtained by the pyrrolidine enamine of cyclopentanone–vinylpyrazine method.

The pyrazylethylation of acetophenone failed in the presence of sodium but was effected by sodamide in liquid ammonia to give low yields of two products: (a) phenyl 3-pyrazyl-1-propyl ketone (8.9%, monopyrazylethylated product), and (b) the bis Michael adduct, 1,5-dipyrazyl-3-benzoylpentane, 9.7%).

That the pyrazylethylation of ethyl phenylacetate gives ethyl 2-phenyl-4-pyrazylbutanoate and that phenylacetonitrile was pyrazylethylated to give 2-phenyl-4-pyrazylbutanenitrile was established by hydrolyzing a sample of each of these compounds to 2-phenyl-4-pyrazylbutanoic acid.

Finally, acetamide was pyrazylethylated on its nitrogen atom to give N-(2-pyrazylethyl)acetamide. The structure of the product was elucidated by subjecting a sample to basic hydrolysis to give 2-aminoethylpyrazine, which was identical in its properties with the compound that had been obtained earlier[2] by the direct pyrazylethylation of ammonia.

Experimental Section

Pyrazylethylation of Cyclohexanone.—A mixture of cyclohexanone (19.6 g., 0.2 mole), vinylpyrazine (10.6 g., 0.1 mole), and small pieces of sodium (0.1 g.) was stirred and heated at 90°. The reaction became exothermic and the temperature rose spontaneously to 160°. The reaction was allowed to cool to 100° and then was heated at 100–115° for 30 min. The mixture was cooled to room temperature, absolute ethanol (2 ml.) was added, and the mixture was poured onto ice. It was extracted with several portions of ether and dried over sodium sulfate, and, after removing the solvent at atmospheric pressure, the residue was distilled to give 2-(2-pyrazylethyl)cyclohexanone (13.8 g., 67.5%, b.p. 129–130° at 0.5 mm.). The product gave a semicarbazone, m.p. 176–177° alone and when mixed with a sample obtained from the product produced by the interaction of N-(1-cyclohexenyl)pyrrolidine with vinylpyrazine.[3]

Pyrazylethylation of Cyclopentanone.—A mixture of cyclopentanone (16.8 g., 0.2 mole), vinylpyrazine (10.6 g., 0.1 mole), and sodium (0.1 g.) was stirred and heated at 90°. The reaction became exothermic and the temperature rose spontaneously to 140°. The mixture was allowed to cool to 100°, heated at 100–105° for 30 min., and processed as described in the last experiment to give a mixture of 2-(2-pyrazylethyl)cyclopentanone (4.2 g., 21.9%, b.p. 139–140° at 1.5 mm.; semicarbazone, m.p. 185–186° alone and when mixed with a sample obtained from the product prepared by the enamine method[3]) and cyclopentylidenecyclopentanone (3.6 g., 42.9%, b.p. 85–86° at 1.3 mm.; semicarbazone, m.p. 216–217°[4] from 95% ethanol).

Pyrazylethylation of Acetophenone.—A solution of acetophenone (12.0 g., 0.1 mole in 25 ml. of anhydrous ether) was added over a 15-min. period to sodamide which was prepared from sodium metal (2.3 g., 0.1 g.-atom) in 100 ml. of liquid ammonia using a ferric nitrate catalyst,[5] and the mixture was stirred for 1 hr.

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[1] This work is based on part of the thesis submitted by G. M. S. to the Graduate Faculty of the University of Pittsburgh in partial fulfillment of the requirements of the Ph.D. degree.

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Vinylpyrazine (10.6 g., 0.1 mole in 25 ml. of anhydrous ether) was added and the mixture was stirred for an additional 30 min. Then, ammonium chloride (5.5 g.) and about 100 ml. of ether were added and the liquid ammonia was allowed to evaporate. The residue was poured onto ice and the phases were separated. The aqueous phase was extracted twice with ether and twice with chloroform. The combined organic phases were dried over sodium sulfate, the solvents were removed at atmospheric pressure, and the residue was distilled to give phenyl 3-pyrazyl-1-propyl ketone [2.0 g., 8.9%, b.p. 158–162° at 1.0 mm., m.p. 60–60.8° from petroleum ether (b.p. 60–70°) (*Anal.* Calcd. for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24. Found: C, 74.26; H, 6.33.); 2,4-dinitrophenylhydrazone, m.p. 173.8–174.6° from 95% ethanol (*Anal.* Calcd. for $C_{20}H_{18}N_6O_4$: C, 59.12; H, 4.46. Found: C, 59.36; H, 4.23.)]. The distillation residue was extracted with boiling petroleum ether to give the bis Michael adduct, 1,5-dipyrazyl-3-benzoylpentane [1.6 g., 9.7%, m.p. 69–69.8° from petroleum ether (*Anal.* Calcd. for $C_{20}H_{20}N_4O$: C, 72.26; H, 6.06. Found: C, 72.57; H, 5.92.)].

Pyrazylethylation of Ethyl Phenylacetate.—A mixture of ethyl phenylacetate (16.4 g., 0.1 mole), vinylpyrazine (10.6 g., 0.1 mole), and sodium (0.1 g.) was refluxed for 90 min., cooled to room temperature, and then processed as described in the first experiment above except that chloroform was used in place of ether to give ethyl 2-phenyl-4-pyrazylbutanoate [14.7 g., 54.5%, b.p. 171–172° at 1.15 mm. (*Anal.* Calcd. for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71. Found: C, 71.30; H, 6.57.); styphnate, m.p. 114–115° from 95% ethanol (*Anal.* Calcd. for $C_{22}H_{21}N_5O_{10}$: C, 51.28; H, 4.11. Found: C, 51.46; H, 4.25.)]. Hydrolysis of a sample of the product with 20% sodium hydroxide gave 2-phenyl-4-pyrazylbutanoic acid, m.p. 105.8–106.6° (from water) (*Anal.* Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.82. Found: C, 69.44; H, 5.64.).

Pyrazylethylation of Phenylacetonitrile.—A mixture of phenylacetonitrile (23.4 g., 0.2 mole), vinylpyrazine (10.6 g., 0.1 mole), and sodium (0.1 g.) was stirred and heated at 120–130° for 20 min., allowed to cool to room temperature, and processed as described in the preceding experiment to give 2-phenyl-4-pyrazylbutanenitrile: 13.3 g., 59.8%, b.p. 150–151° at 0.12 mm. (*Anal.* Calcd. for $C_{14}H_{13}N_3$: C, 75.31; H, 5.87. Found: C, 75.40; H, 5.71.). A sample of this nitrile was hydrolyzed with 10% hydrochloric acid to give 2-phenyl-4-pyrazylbutanoic acid, m.p. 105.5–106.5° alone and when mixed with the acid obtained in the preceding experiment.

Pyrazylethylation of Acetamide.—A mixture of acetamide (11.8 g., 0.2 mole), vinylpyrazine (10.6 g., 0.1 mole), and sodium (0.1 g.) was allowed to react under the conditions described in the preceding experiment to give N-(2-pyrazylethyl)acetamide: 7.1 g., 43.0%, b.p. 150–154° (0.54 mm.) (*Anal.* Calcd. for $C_8H_{11}N_3O$: C, 58.16; H, 6.71. Found: C, 58.22; H, 6.66.). A mixture of the product (6.0 g., 0.037 mole) and 70 ml. of 20% sodium hydroxide solution was refluxed for 1 hr., cooled to room temperature, and extracted with several portions of chloroform. After removing the solvent at atmospheric pressure, the residue was distilled to give 2-aminoethylpyrazine [2.7 g., 60.5%, b.p. 102–103° at 9.0 mm.[2]; phenylthiourea derivative, m.p. 82–83° (from benzene) alone and when mixed with an authentic sample].[2]

Synthesis of Trifluoromethyl Hypofluorite[1]

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Until the present time the reported syntheses of trifluoromethyl hypofluorite (CF_3OF) and other fluoroxy compounds were performed by the fluorination of oxygen-containing compounds with fluorine and/or silver difluoride.[2-8] The reaction of dioxygen difluoride (O_2F_2) with tetrafluoroethylene(C_2F_4) to produce CF_3OF has also been described.[9] The only previously reported formation of a hypofluorite from oxygen difluoride (OF_2) resulted from a reaction between OF_2 and sulfur trioxide (SO_3) which gave a compound containing a primary fluorine and an OF group (FSO_2-OOF).[10] Ruff and Menzel[11] reported that methane (CH_4) and OF_2 exploded when ignited by a spark, but they did not indicate the nature of the products.

Discussion

Equimolar mixtures of CHF_3 and OF_2 at pressures between 20 and 100 mm. do not react spontaneously at room temperature in the absence of light. Strong irradiation of these mixtures with a high-pressure quartz mercury vapor light results in a slow reaction in which hydrogen fluoride (HF), carbon tetrafluoride (CF_4), carbon dioxide (CO_2), carbonyl fluoride (COF_2), and silicon tetrafluoride (SiF_4) (from HF and glass) are formed. Products capable of oxidizing iodide to iodine were not observed in the light-induced reactions. A gas phase explosion occurs when an electric spark is used to initiate the reaction of an equimolar mixture of CHF_3 and OF_2 at pressures above 25 mm. At 25 mm. or less, the detonation does not propagate. At pressures of 100 mm. or more, the products are again only HF, CF_4, CO_2, COF_2, and SiF_4. At a pressure of 50 mm., a 15% yield of CF_3OF is observed in addition to the products previously mentioned. Compounds such as perfluoroethane (C_2F_6), perfluorodimethyl ether $(CF_3)_2O$, and perfluorodimethyl peroxide $(CF_3O)_2$ are not observed.

Mixtures of CH_4 and OF_2 from 1:4 to 1:10 were allowed to react at total pressures ranging from 6 to 60 mm. As with CHF_3–OF_2, a spontaneous reaction was not observed at room temperature. When the reaction mixtures were exposed to sparks, explosive reactions occurred. These explosive reactions occurred at pressures as low as 6 mm. with 1:4 CH_4:OF_2 mixtures. The lower pressure limit of this explosive reaction was not determined. The products obtained in this reaction were CF_3OF, CO_2, HF, SiF_4, and small amounts of COF_2. Trace amounts of CF_4 (<1%) were also present. Yields of up to 50% CF_3OF were obtained. This compound was present in all of the reactions with CH_4 and OF_2.

The reactions can be pictured schematically as shown. At this time, knowledge of there action

$$CHF_3 + OF_2 \longrightarrow CF_3OF + HF$$

$$CH_4 + 4\,OF_2 \longrightarrow CF_3OF + 4HF + {}^3/_2O_2$$

kinetics of these reactions is insufficient to determine if the reaction mechanism is a concerted single-step reaction or a multistep recombination of radicals produced

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(1) This work was supported by the Office of Naval Research under Contract Nonr 3597(00).

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