means of pressure from a tank of prepurified nitrogen), a solution of 33 g. of freshly distilled cyclopentadiene in 150 cc. of dry ether was added dropwise with stirring over a period of 30 min.

After being stirred another hour at room temperature, the suspension of cyclopentadienyllithium (V) was forced under nitrogen pressure in a slow, steady stream into a cooled, stirred solution of 100 g. of *p*-toluenesulfonyl azide in 300 cc. of dry ether. The reaction became deep yellow almost immediately and gradually turned reddish-brown. A precipitate appeared during the addition which required one hr. Rapid filtration separated the mixture into a solid phase (A) and a red ether solution which was extracted twice with 100-cc. portions of water, dried over anhydrous sodium sulfate and concentrated. Distillation of the residue through a short Vigreux column gave 16 g. (35% of theory) of red diazocyclopentadiene, b.p. 52–53° at 50 mm. The material was best purified by crystallization first from alcohol and then from pentane, both at −70°. The heavy yellow needles melted at −23 to −22° to a red liquid, n^{25}D 1.6150, $d^{29}{}_{25}$ 1.059.

Anal. Calcd. for $C_5H_4N_2$: mol. wt., 92.1. Found: mol. wt. (cryoscopic in benzene), 93.1.

Anal. Calcd. for $C_5H_4N_2$: C, 65.2; H, 4.4; N, 30.4. Found: C, 65.2; H, 4.3; N, 30.5.

The solid (A) was dissolved in water, treated with activated charcoal, filtered and acidified with hydrochloric acid. The colorless precipitate was filtered and dried to give 25.3 g. of *p*-toluenesulfonamide, m.p. 135–136° after one recrystallization and infrared spectroscopically identical with an authentic sample.

Catalytic Reduction of Diazocyclopentadiene.—Diazocyclopentadiene (2.0 g.) in 50 cc. of ether rapidly absorbed 3.0 molar equivalents of hydrogen over Adams platinum catalyst. Removal of the ether and distillation of the residue gave 1 cc. of colorless material; b.p. 42–43° at 2 mm., n^{25}D 1.5058.

Authentic **cyclopentanone hydrazone** was prepared from 50 g. of 85% hydrazine hydrate in 100 cc. of 95% ethanol, to which 30 g. of cyclopentanone was added with shaking. The mixture was refluxed for 30 min. and, after standing at 4° overnight, was concentrated on the steam-bath and distilled at 2 mm. There was obtained 9 g. of hydrazone; b.p. 45–45.5° at 1 mm., $n^{25.5}$D 1.5083.

Anal. Calcd. for $C_5H_{10}N_2$: C, 61.2; H, 10.2; N, 28.6. Found: C, 61.0; H, 10.5; N, 28.5.

The infrared spectrum of the reduction product was identical with that of the authentic cyclopentanone hydrazone. Furthermore, when treated with 2,4-dinitrophenylhydrazine, a derivative, m.p. 137–139°, was obtained which melted at 139–140° in admixture with authentic cyclopentanone 2,4-dinitrophenylhydrazone of m.p. 140–141°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Preparation and Condensation of Polymethylol Compounds

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Several polymethylol compounds were prepared and their relative rates of condensation and thermal decomposition were compared.

Introduction

Sprung and Gladstone[1] have reported that the initial uncatalyzed rate of reaction of saligenin with phenol at 99° is 10 mole % per hour. In a continuation of this study it was of interest to compare reactivities of several other methylol compounds. It has now been found that the rate of reaction of 1-allyloxy-2,4,6-trimethylolbenzene with phenol is very nearly equal to that of saligenin while 2,4,6-trimethylolphenol reacts at a much greater rate. The rates of condensation were derived from measurements of changes in the concentrations of methylol groups determined by means of analytical acetylation.[2] In the absence of catalyst and at 99° a mixture of 1-allyloxy-2,4,6-trimethylolbenzene and three equivalents of phenol gave an initial rate of reaction of about 9 mole % per hour whereas the rate of a similar mixture of 2,4,6-trimethylolphenol and phenol was about 60 mole % per hour. At 60° in the presence of 1% (by weight) of *d*-camphorsulfonic acid, 1-allyloxy-2,4,6-trimethylolbenzene and phenol reacted at an initial rate of about 50 mole % per hour whereas the reaction of 2,4,6-trimethylolphenol was exceedingly rapid under the same conditions.

The decreasing order of thermal stability of the pure compounds is: 1-allyloxy-2-methylolbenzene, 1-allyloxy-2,4,6-trimethylolbenzene, saligenin, 2,4,-6-trimethylolphenol. After two hours at 120° a pure sample of 1-allyloxy-2-methylolbenzene lost 3% of its methylol groups, 1-allyloxy-2,4,6-trimethylolbenzene lost 9%, saligenin lost 81%, and 2,4,6-trimethylolphenol polymerized to an insoluble gel. In thermal decompositions both 2,4,6-trimethylolphenol and 1-allyloxy-2,4,6-trimethylolbenzene evolved formaldehyde.

1-Allyloxy-2,4,6-trimethylolbenzene was reported by Martin[3] to be a light tan liquid (*n* 1.575–1.579, *d* 1.20–1.21). In the course of the present investigation the 1-allyloxy-2,4,6-trimethylolbenzene of Martin was further purified and isolated as a colorless crystalline solid (m.p. 86.0–86.2°). In addition the following three compounds were prepared: 1-allyloxy-2-methylolbenzene, 1-allyloxy-2,4,6-tristrimethylsiloxymethylbenzene and 1-allyloxy-2,4-bistrimethylsiloxymethylbenzene.

2,4,6-Trimethylolphenol was prepared from sodium 2,4,6-trimethylolphenate by two methods: partial acidification[4] and by isolation and hydrolysis of the trimethylsilyl ether.[5] It was found that 2,4,6-trimethylolphenol exists in two polymorphic forms (m.p. 76 and 82°; mixed m.p. 82°). Previous workers have reported a diversity of melting points, 74–75°,[4] 76–78°[6] and 84°,[5] for this compound. Freeman[4] found that 2,6-dimethylolphenol also exhibits polymorphism.

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(1) M. M. Sprung and M. T. Gladstone, THIS JOURNAL, **71**, 2907 (1949).

(2) R. E. Burnett, *Anal. Chem.*, in press.

(3) R. W. Martin, U. S. Patent 2,579,330 (December 18, 1951).

(4) J. H. Freeman, THIS JOURNAL, **74**, 6257 (1952).

(5) R. W. Martin, *ibid.*, **74**, 3024 (1952).

(6) A. T. Carpenter and R. F. Hunter, *J. Appl. Chem.*, **1**, 217 (1951).

Experimental

1-Allyloxy-2-methylolbenzene.—A solution containing saligenin (124 g., 1.0 mole) and allyl bromide (121 g., 1.0 mole) in acetone (300 ml.) was heated at reflux temperature for 5 hours in the presence of potassium carbonate (138 g., 1.0 mole). The reaction mixture was filtered, washed with water and the resulting oil was taken up in ethyl ether and washed repeatedly with dilute sodium hydroxide. The crude reaction product was distilled to yield 122 g. (75%) of 1-allyloxy-2-methylolbenzene. Redistillation yielded pure material, b.p. 97.5–98.0° at < 1 mm., n^{20}D 1.5441.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.3; H, 7.3; hydroxyl equiv., 164. Found: C, 72.8; H, 7.3; hydroxyl equiv., 162.8.

1-Allyloxy-2,4,6-trimethylolbenzene.—A suspension of sodium trimethylol phenate (190 g., 0.92 mole) and potassium carbonate (40 g., 0.29 mole) in acetone (500 ml.) was treated with an excess of allyl bromide (120 g.; 1.0 mole) over a period of 7 hours. The reaction mixture was filtered and solvents were removed to leave 101 g. of a viscous oil I. An aliquot of this oil (20 g.) was dissolved in ethyl acetate (100 ml.), seeded and allowed to stand at 0°. From this solution was obtained 10.5 g. (26%) of 1-allyloxy-2,4,6-trimethylolbenzene, m.p. 86.0–86.2° (uncor., from ethyl acetate).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.3; H, 7.2; mol. wt., 224; hydroxyl equiv., 74.7. Found: C, 64.6; H, 7.4; mol. wt. (in dioxane), 206; hydroxyl equiv., 74.3.

The infrared spectrum of the compound is not inconsistent with the proposed structure.

1-Allyloxy-(2 and 4)-methylolbenzene.—A second aliquot of the viscous oil I was dissolved in ethyl ether and the solution was extracted six times with 10% sodium hydroxide solution. The ether solution was dried (over Drierite) and the solvent was removed under vacuum giving an oil (8%) which, on distillation in a small Vigreux column, yielded 1-allyloxymethylolbenzene, b.p. 106–107° at 1 mm., n^{20}D 1.5450, 3% yield.

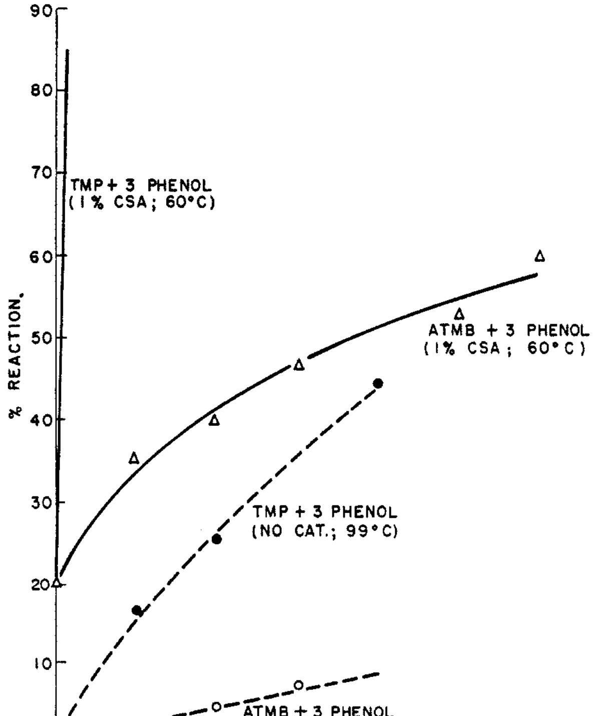

Fig. 1.—Rates of condensation reactions of trimethylol compounds with phenol: TMP, 2,4,6-trimethylolphenol; ATMB, 1-allyloxy-2,4,6-trimethylolbenzene; CSA, camphorsulfonic acid.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.3; H, 7.3; hydroxyl equiv., 164. Found: C, 72.8; H, 7.7; hydroxyl equiv., 170.

The infrared spectrum of this sample shows that it is a mixture of both *o*- and *p*-disubstituted aromatic compounds.

1-Allyloxy-2,4-bistrimethylsiloxymethylbenzene and 1-Allyloxy-2,4,6-tristrimethylsiloxymethylbenzene.—A third aliquot of the viscous oil I was allowed to react with an excess of trimethylchlorosilane in pyridine according to the procedure of Martin.[5] The salt and solvent were removed by filtration and vacuum distillation. The resulting product was subjected to a vacuum flash distillation, and this distillate was further purified by fractionation in a Vigreux column to yield two compounds: 1-allyloxy-2,4-bistrimethylsiloxymethylbenzene, b.p. 115–116° at < 1 mm. (0.04 mm.), n^{20}D 1.4832. *Anal.* Calcd. for $C_{17}H_{30}Si_2O_3$: C, 60.4; H, 8.9; Si, 16.6. Found: C, 60.3; H, 9.2; Si, 16.5.; and 1-allyloxy-2,4,6-tristrimethylsilyloxymethylbenzene, b.p. 143–146° at < 1 mm. (0.04 mm.), n^{20}D 1.4708. *Anal.* Calcd. for $C_{21}H_{40}Si_3O_4$: C, 57.2; H, 9.1; Si, 19.1; mol. wt., 440. Found: C, 57.1; H, 8.9; Si, 18.6; mol. wt. (in benzene), 421.

The infrared spectra of these two compounds are not inconsistent with their proposed structures.

Hydrolysis of 1-allyloxy-2,4,6-tristrimethylsiloxymethylbenzene in methanol followed by a vacuum evaporation of excess water and methanol gave crystalline 1-allyloxy-2,4,6-trimethylolbenzene.

1-Trimethylsiloxy-2,4,6-tristrimethylsiloxymethylbenzene.—A suspension of sodium 2,4,6-trimethylolphenate in pyridine was treated with an excess of trimethylchlorosilane, as above, and the crude reaction mixture was filtered and distilled to yield 1-trimethylsiloxy-2,4,6-tristrimethylsiloxybenzene, b.p. 120–125° at < 1 mm. (0.03 mm.), n^{20}D 1.4621. Martin[5] reported a boiling range of 135–145° (0.03–0.05 mm.) for this compound.

Anal. Calcd. for $C_{21}H_{44}Si_4O_4$: C, 53.3; H, 9.3; Si, 23.7. Found: C, 53.4; H, 9.6; Si, 24.1.

The hydrolysis of this compound to 2,4,6-trimethylolphenol, by the procedure of Martin,[5] was accompanied by considerable polymerization.

Reactions with Phenol and Thermal Decompositions.—The rates of condensation reactions of the methylol compounds with phenol were followed by changes in the concentration of methylol groups. Measurements were made by determinations of the total hydroxyl contents of samples by means of analytical acetylation.[2] The values for methylol hydroxyl were determined by subtraction of the known content of phenolic hydroxyl, which was assumed to remain constant, from the total hydroxyl content. Rate measurements, with or without catalyst, involved first the preparation of samples containing the trimethylol compound and three equivalents of redistilled phenol. Small (0.1 g.) aliquot samples were then taken from these stock solutions, which were maintained as liquids (at room temperature), and placed in small glass-stoppered test-tubes. The test-tubes containing the samples were maintained in a constant temperature bath for stated periods of time and analyzed by analytical acetylation. Several representative runs are presented in Fig. 1.

The measurements of thermal decompositions involved analyses for hydroxyl contents of pure samples of the methylol compounds which had been maintained at elevated temperatures for definite periods of time. The odor of formaldehyde was evident in the decompositions of 2,4,6-trimethylolphenol and 1-allyloxy-2,4,6-trimethylolbenzene.

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