trichlorosilane while the second step involves the addition of a molecule of trichlorosilane to vinyltrichlorosilane to give 1,2-bistrichlorosilylethane. The second step has been discussed in some detail in the previous publication.[1]

Additional evidence in support of the reactions as given in these equations has been obtained. A pentenyltrichlorosilane was isolated from the reaction of 1-pentyne and trichlorosilane in the presence of peroxide. There are two isomeric pentenyltrichlorosilanes which could be obtained in this reaction, however, from a consideration of the boiling point data and previous reactions that have been conducted under similar conditions, it is believed that the isolated compound is 1-pentenyl-1-trichlorosilane, $CH_3CH_2CH_2CH{=}CH$-$SiCl_3$.[2] Isolation of this substituted vinyl addition product indicates that equation (1) is one step of the reaction. Thus, it is reasonable to assume that the reactions as outlined by equations 1 and 2 are indeed the reactions whereby disubstituted products are formed from an alkyne and trichlorosilane in the presence of a peroxide.

This furnishes another method of preparing alkenyltrichlorosilanes. Vinyltrichlorosilane has been prepared by the direct reaction of vinyl chloride and silicon[3] or by dehydrohalogenation of a mixture of α- and β-chloroethyltrichlorosilanes with anhydrous quinoline.[3]

Experimental

1-Pentenyl-1-trichlorosilane.—A mixture of 271 g. (2.0 *M*) trichlorosilane and 12.1 g. (0.05 *M*) of finely divided benzoyl peroxide was placed in a glass-lined autoclave. To this was added 34 g. (0.5 *M*) of 1-pentyne (Farchan Research Laboratory) in 50 g. of trichlorosilane. The mixture was heated at 80° for fifty-two hours under its own vapor pressure. Distillation of the reaction mixture gave in addition to the unused trichlorosilane 10.8 g. of 1-pentenyl-1-trichlorosilane, b. p. 85° (80 mm.) and 11.9 g. of less pure 1-pentenyl-1-trichlorosilane. A residue of 18.2 g. was obtained.

Anal. Calcd. for $C_5H_9SiCl_3$: Si, 52.26; unsaturation, 1 double bond per 205 g. Found: Si, 51.6; unsaturation (reaction with Br_2), 1 double bond per 246 g.[4]

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(2) Sommer, Pietrusza and Whitmore [This Journal, **69**, 188 (1947); **70**, 484 (1948)] has shown that only 1-octyltrichlorosilane results from the addition of trichlorosilane to 1-octene in the presence of peroxide (99% yield).

(3) Hurd, *ibid.*, **67**, 1813 (1945).

(4) The author acknowledges the aid given by Dr. E. H. Winslow who determined the unsaturation.

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Viscosities of 2-Methyl-3-butyn-2-ol and 1,1-Dibutoxyethane

By Philip J. Elving,[1] Norman Alpert and Philip E. Tobias

The kinematic viscosities of 2-methyl-3-butyn-2-ol and 1,1-dibutoxyethane (acetaldehyde dibutyl acetal) were determined over the temperature range of 0 to 100°. A Fenske–Cannon–Ostwald viscosimeter (Series 50)[2] was used; distilled water was used to calibrate the viscosimeter. The accuracy of the data was limited by the constancy in temperature of the thermostat used, which was ±0.1°. The compounds were purified by careful rectification, and had these boiling point ranges and refractive indices: methylbutynol, 104 to 105°, n^{20}_{D} 1.4203; dibutoxyethane, 188 to 189°, 1.4080.

The viscosities were calculated from the equation $V = Ct$, where V is the kinematic viscosity in centistokes, C is the calibration constant for the viscosimeter, and t is the efflux time in seconds. The viscosity in centipoises equals the product of the viscosity in centistokes and the density; for methylbutynol, d^{20}_{20} 0.8628 and d^{25}_{25} 0.8588; for the dibutoxyethane, d^{20}_{20} 0.8335 and d^{25}_{25} 0.8300.

	Viscosity in centistokes	
Temp., °C.	Methylbutynol	Dibutoxyethane
0	10.83	1.927
25	3.43	1.239
50	1.54	0.871
75	0.891	0.668
100	0.539	0.492

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The Alkylation of Decalin with Ethylene[1,2]

By J. R. Dice and D. R. McKinney[3]

The alkylation of decalin[4] with ethylene in the presence of aluminum chloride produces a complex mixture of products. From this mixture we have isolated a fraction which apparently contains some 2-ethyldecalin. The evidence for this is based on the isolation of derivatives of 2-ethylnaphthalene from the dehydrogenation products of the given fraction. Since the dehydrogenation procedure employed[5] has been shown not to effect skeletal rearrangement in various similar methyl decalins and octalins, it is reasonable that no skeletal rearrangements occurred in this case. Derivatives of some other compounds were also isolated, but none could be identified. That some of the original products are aromatic in nature is shown by the colors obtained on adding picric acid and trinitrobenzene solutions and by the

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(1) Presented at the Fourth Annual Southwest Regional Meeting of the American Chemical Society, Shreveport, Louisiana, December 10, 1948.

(2) Most of the equipment used in this investigation was purchased from funds provided by the Research Institute of the University of Texas, Project 186.

(3) From the M. A. thesis of D. R. McKinney, the University of Texas, 1948.

(4) Pertinate references to the alkylation of cycloalkanes are: (a) Ipatieff, Komarewsky and Grosse, This Journal, **57**, 1722 (1935); and (b) Petrov, *Chimijatwerdogo Toplieva*, **5**, 632; *Chem. Zentr.*, **107**, I, 251 (1936).

(5) Linstead, Milledge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).

ultraviolet absorption spectra. The saturated hydrocarbon, presumably ethane, which was found in the exit gases apparently was formed by a reduction of ethylene with concomitant dehydrogenation of other substances in the reaction mixture.[4a]

Experimental

Reaction of Decalin and Ethylene.—To a three-necked flask fitted with a sealed stirrer, condenser and an inlet tube which reached almost to the bottom of the flask was added from 2 to 5 moles of decalin. Ethylene (Matheson Company, 95% pure), which had been washed with 25% sodium hydroxide and 95% sulfuric acid, was added until the decalin was saturated. After the addition of from 0.11 to 0.43 mole of anhydrous aluminum chloride, 1.0 to 1.5 moles of ethylene was added over a period of from seven to twelve hours at an approximately constant rate. The temperature was maintained at 50–60° throughout the reaction. The flow of ethylene was stopped for five minutes of each hour and dry hydrogen chloride was added to reactivate the catalyst. At three-hour intervals, portions of approximately one-third the initial amount of aluminum chloride were added. In the one experiment where the exit gases were collected, the rate of collection increased as the activity of the catalyst decreased.

When stirring was stopped, the mixture separated into two layers: an upper straw colored layer and a pasty red-dish-brown catalyst layer. The mixture was poured onto crushed ice and hydrochloric acid. The organic layer was dried over sodium sulfate after being washed with three portions of 6 *N* hydrochloric acid and three portions of water. After removing most of the unreacted decalin through a small packed column, the residue was fractionally distilled through a 60-cm. heated column with a wire spiral packing similar to one described by Cheronis.[6] The amounts of materials actually employed and the fractions obtained by distillation for a typical run are given in Table I.

TABLE I

ALKYLATION OF DECALIN WITH ETHYLENE. A.

Reagents used were 276.5 g. (2 moles) of decalin, 23.5 g. (0.171 mole) of anhydrous aluminum chloride (14.5 g. was added at the start of the reaction), and 28.0 g. (1 mole) of ethylene added during seven and one-half hours. Approximately 3200 cc. of exit gases were collected. Distillation fractions after removal of unreacted decalin were:

Fraction	Weight, g.	B. p., °C. (748 mm.)	$n^{25}D$
1	1.9	200–203	1.4710
2	1.4	203–207	1.4716
3	1.4	207–208	1.4717
4	3.2	209–212	1.4713
5	3.0	212–215	1.4705
6	4.5	215–220	1.4699
7	2.5	220–221	1.4691
8	1.6	221–222	1.4691
9	1.7	222	1.4691
10	5.8	Residue	1.4700

Analysis of Fractions 7 and 8, Table I.—Fractions 7 and 8 of Table I were combined and a 2.7-g. sample was dehydrogenated by the vapor phase method of Linstead and co-workers[5] at a temperature of 365–375°. Two passes were made over the catalyst and a total of 59% of the theoretical amount of hydrogen and 1.5 g. of pale yellow oil were obtained. A 0.5-g. sample of the oil was dissolved in absolute alcohol and treated with 0.57 g. of picric acid in hot absolute alcohol. A yellow complex precipitated which gave yellow needles which melted at 74–78° after four recrystallizations from methyl alcohol. A mixture with the picric acid complex of known 2-ethyl-naphthalene (m. p. 77–78°) melted at 76–78°. A 1,3,5-trinitrobenzene complex formed in the same manner and recrystallized from methyl alcohol had a melting point of 85.5–86.0°. After mixing with the 1,3,5-trinitrobenzene complex of 2-ethylnaphthalene (m. p. 87.5°), the melting point was 87°.

Analysis of Fraction 10, Table I.—Addition of 0.5 g. of the oil to saturated solutions of picric acid and 1,3,5-trinitrobenzene in absolute alcohol gave an orange color and a yellow color, respectively. These color changes did not occur when decalin or 1- or 2-ethyldecalin was added to alcoholic solutions of the nitro compounds.

Using a Model DU Beckman Spectrophotometer with a 1.000 mm. cell, a solution of 1.2 g. of Fraction (10), Table I in 1 liter of purified cyclohexane gave a broad absorption maximum in the region 260–275 $m\mu$ (optical density approximately 0.500 to 0.600).

Analysis of the Exit Gases.—A 2770-cc. sample of the exit gas was shaken with saturated bromine water to remove unreacted ethylene. Analysis of the residual gas (730 cc.) in a modified Orsat gas analysis apparatus showed 3.25% of combustible material. The percentage of combustible material in the original exit gas was calculated to be 0.96%.

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[6] Cheronis, "Semimicro and Macro Organic Chemistry," Thomas Y. Crowell Company, New York, N. Y., 1942, pp. 74–75.

Steric Effects in the Ultraviolet Absorption Spectra of 2,4,6-Trimethylbenzoic Acid and Methyl Ester

BY EDWARD A. FEHNEL

In connection with our studies of the spectra of substituted phenyl sulfones,[1] it seemed desirable to have available for comparison the spectra of certain substituted benzoic acids, particularly *o*-substituted derivatives in which steric strain might be expected to modify the benzene–carboxyl group interaction. Although the effects of steric inhibition of resonance on the ultraviolet absorption spectra of *o*-dialkyl ketones,[2] anilines,[3] nitrobenzenes,[4] phenols,[5] phenyl ethers,[6] and phenyl sulfides[7] have been investigated, no spectroscopic data seem to have been reported previously for *o*-dialkyl benzoic acids or esters. The ultraviolet spectra of several chlorobenzoic acids have recently been described by Ross,[8] who attributes the decreased absorption observed in the case of the *o*-dichloro acids to suppression of the resonance interaction between the carboxyl group and the benzene ring. The absorption spectra of 2,4,6-trimethylbenzoic acid and methyl 2,4,6-trimethylbenzoate have now been determined and are likewise found to exhibit the expected modifications due to steric effects.

The spectra of benzoic acid and its 2,4,6-trimethyl derivative in ethanol and in 0.01 *N* sodium

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[1] Fehnel and Carmack, THIS JOURNAL, **72**, 1292 (1950).

[2] O'Shaughnessy and Rodebush, *ibid.*, **62**, 2906 (1940).

[3] Remington, *ibid.*, **67**, 1838 (1945); Klevens and Platt, *ibid.*, **71**, 1714 (1949).

[4] Brown and Reagan, *ibid.*, **69**, 1032 (1947).

[5] Coggeshall and Lang, *ibid.*, **70**, 3283 (1948).

[6] Fehnel and Carmack, *ibid.*, **71**, 2932 (1949).

[7] Fehnel and Carmack, *ibid.*, **71**, 2889 (1949).

[8] Ross, *ibid.*, **70**, 4039 (1948).