Discussion

The Si–Cl bond lengths in the chloromethyl silanes are: 2.09 ± 0.03 Å. in $Si(CH_3)_3Cl$, 1.99 ± 0.03 Å. in $Si(CH_3)_2Cl_2$,[5] 2.01 ± 0.02 Å. in $SiCH_3Cl_3$[5] and 2.02 ± 0.02 Å. in $SiCl_4$.[7] The distances in the chlorosilanes are (in the same order): 2.06 ± 0.05 Å.,[8] 2.02 ± 0.03 Å.,[7] 2.01 ± 0.03 Å.[9] and 2.02 ± 0.02 Å. In both series of compounds the chlorine bond is longer when only one chlorine is attached to the silicon than when two or more chlorine atoms occur in the same molecule. This observation is similar to the effect found in the C–F bonds in fluorocarbons, where the available data are far more extensive. On the basis of the Si–Cl distances reported we should expect the two monochlorosilanes to react more readily than the polychlorosilanes in reactions involving the removal of chlorine.

The Si–C distance reported in $Si(CH_3)_3Cl$ (1.89 ± 0.03 Å.) is intermediate between the values reported in $Si(CH_3)_4$ (1.93 ± 0.03 Å.) and in $Si(CH_3)_2Cl_2$ (1.83 ± 0.06 Å. with a regular tetrahedral angle assumed for C–Si–C).

(7) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

(8) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(9) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).

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An Improved Synthesis of Glutaconic Ester

BY H. L. LOCHTE AND P. L. PICKARD[1]

Considerable quantities of glutaconic ester were required in connection with a synthetic problem, and previously described methods[2,3,4] were found tedious and expensive. A synthesis starting with citric acid was developed and found to give an over-all yield of 24%, based on the citric acid used. The citric acid was converted to acetonedicarboxylic ester, which was hydrogenated by Raney nickel to the hydroxy ester. This was dehydrated by thionyl chloride in pyridine. It was found that the hydrogenation either fails completely or proceeds very slowly except with a freshly prepared catalyst.

Diethyl Glutaconate.—One hundred grams of acetonedicarboxylic ester, prepared by the well-known method,[5] and about 1 g. of freshly prepared Raney nickel were hydrogenated at 1500 lb. pressure and 150°. Reduction was complete in four hours when the catalyst was very active, but in case of catalyst which had been stored under ethanol for long periods of time, or which had not been carefully prepared, hydrogenation either failed completely or was very slow. The catalyst was filtered off and discarded and the filtrate distilled at 2 mm. pressure. Seventy-seven grams (76%) of β-hydroxyglutaric ester was obtained, b. p. 105–107° (2 mm.), 133° (8 mm.), n^{20}_D 1.4381. This ester was dehydrated by the method of Gidvani[6] to yield 62 g. (88%) of glutaconic ester, b. p. 115° (4 mm.), n^{20}_D 1.4465. Saponification equivalent: found, 92.8; calculated, 93.1.

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[1] General Aniline Fellow, 1944–1945.

[2] Conrad and Gutzeit, *Ber.*, **15**, 2841 (1882).

[3] Pechman and Jenisch, *ibid.*, **24**, 3250 (1891).

[4] Blaise, *Bull. soc. chim.*, [3] **29**, 1014, 1028 (1903).

[5] "Organic Syntheses," Coll. Vol. 1, **1941**, John Wiley and Sons, Inc., New York, N. Y., 10, 237.

(6) Gidvani, *J. Chem. Soc.*, 2666 (1932).

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The Standard Free Energy of Formation and Entropy of the Aqueous Magnesium Ion

BY C. C. STEPHENSON

Improved calculations of the standard free energy of formation and entropy of the aqueous magnesium ion are made possible by recent thermodynamic data concerning some magnesium compounds.

The standard free energy of solution of $MgCl_2 \cdot 6H_2O$ is given by the equation $\Delta F° = -RT \ln 4(\gamma m)^3 a_1^6$, in which γ, the activity coefficient[1] of magnesium chloride in the saturated solution at 25° is 32.2, the solubility is 5.84 *m* and the activity of the water is 0.3296; hence, $\Delta F°_{298.1} = -6{,}180$ cal. The free energies of formation of $MgCl_2 \cdot 6H_2O$,[2] H_2O and the chloride ion are −505,410 ± 320 cal., − 56,693 cal. and −31,340 cal., respectively; from these values and the standard free energy of solution, the standard free energy of formation of the aqueous magnesium ion at 25° is −108,760 cal. The corresponding electrode potential is 2.358 volts.

The standard heat of formation of the magnesium ion may be calculated from the heats of formation[3] of $Mg(NO_3)_2$ −188,770 cal., and $Mg(NO_3)_2 \cdot 6H_2O$, −624,410 cal., and the standard heats of solution,[4] −21,530 cal. and 4,340 cal., respectively. The heats of formation of the nitrate ion,[5] −49,320, and water, −68,318 cal., are consistent with the heats of formation of the solids. The heat of formation of the magnesium ion is −111,660 cal. calculated from the heat of formation and solution of $Mg(NO_3)_2$ and −111,520 cal. is obtained from the corresponding data for $Mg(NO_3)_2 \cdot 6H_2O$. With the latter value and the free energy of formation, $\Delta S°_{298.1} = -9.3$ is calculated for the reaction $Mg + 2H^+ = Mg^{++} + H_2$, and the standard entropy of the magnesium ion is −32.7 cal. deg.$^{-1}$ mole^{-1}.

Additional values for the entropy and free energy of formation of the magnesium ion, derived from the solubility products of $Mg(OH)_2$, $MgCO_3$ and $Mg(NO_3)_2 \cdot 6H_2O$, are in good agreement, although less accurate. From a considera-

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(1) R. H. Stokes, *Trans. Faraday Soc.*, **41**, 642 (1945).

(2) K. K. Kelley and G. E. Moore, THIS JOURNAL, **65**, 2340 (1943).

(3) F. E. Young, *ibid.*, **66**, 773 (1944).

(4) W. W. Ewing, E. Klinger and J. D. Brandner, *ibid.*, **56**, 1053 (1934).

(5) W. R. Forsythe and W. F. Giauque, *ibid.*, **64**, 48 (1942).

tion of all the data, the free energy given above is probably accurate to 300 cal. and the entropy to one unit.

CAMBRIDGE, MASSACHUSETTS RECEIVED JANUARY 8, 1946

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p-Cyanostyrene

BY C. G. OVERBERGER AND R. E. ALLEN[1]

In a recent communication[2] a method of dehydrating *p*-cyanophenylmethylcarbinol to *p*-cyanostyrene was described. It has now been found that a much better yield can be obtained by first converting the carbinol to the acetate and then cracking the acetate by dropping it onto hot glass beads. The new method works best on quantities of less than 100 g.; with larger quantities polymerization during the deacetylation becomes serious.

Acetate of *p*-Cyanophenylmethylcarbinol.—Into a 200-cc. round-bottomed flask equipped with a condenser was placed 50 g. (0.34 mole) of *p*-cyanophenylmethylcarbinol and 70 g. (0.687 mole) of acetic anhydride. The mixture was treated for four hours under very gentle reflux and the contents of the flask were transferred to a 200-cc. distilling flask. The excess acetic anhydride and acetic acid were removed by distillation under water-pump pressures. The residue was then distilled through a helices-packed column. The product boiled at 154° (6 mm.); $n^{20}\mathrm{D}$ 1.5156, d^{4}_{20} 1.0972. The yield was 58 g. (0.307 mole) or 90.3% of the theoretical amount.

Anal.[3] Calcd. for $C_{11}H_{11}O_2N$: C, 69.82; H, 5.86. Found: C, 70.08; H, 5.82.

***p*-Cyanostyrene.**—Through a vertical fifteen inch, 20-mm. Pyrex tube, packed with solid glass beads heated to 575–600° by means of an electric furnace, was dropped 58 g. (0.307 mole) of the acetate of *p*-cyanophenylmethylcarbinol to which had been added a gram of *p*-*t*-butylcatechol, at the rate of one drop per second. The distillate was collected in an ice-cooled receiver, washed twice with 100 cc. of water and twice with 100-cc. of a 10% solution of sodium bicarbonate and dried over anhydrous sodium sulfate to which was added a small amount of *p*-*t*-butylcatechol. The product was distilled through a six-inch column packed with short pieces of glass rod. The yield was 30 g. (75.8%) b. p. 92–93° (3 mm.); $n^{20}\mathrm{D}$ 1.5772.

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(1) The work described in this note was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945).

(3) Microanalyses by Mr. H. S. Clark, Illinois State Geological Survey.

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The Hindered Phenols

BY GORDON H. STILLSON

In an article entitled "The Hindered Phenols," by Stillson, Sawyer and Hunt,[1] an unfortunate misstatement was made. On page 304, at the conclusion of the paragraph which begins on page 303, it was stated that 2,6-di-*t*-butyl-4-methylphenol " . . . is insoluble in aqueous or alcoholic alkali of any strength." The statement intended was " . . . is insoluble in Claisen solution or in aqueous alkali of any strength." However, upon examining the latter statement critically, it occurred to us that the term "Claisen solution" does not accurately define this solvent. Claisen's directions call for dissolving 350 g. of potassium hydroxide in 250 g. of water, and making this up to 1 liter with methanol.[2] Frequently[3] Claisen used a solution consisting of 350 g. of potassium hydroxide dissolved in 400 g. of water, made up to 1 liter with methanol. Niederl[4] defines Claisen solution as "a mixture of equal parts of methanol and 50% aqueous potassium hydroxide solution." Neither author specifies the purity of the methanol used.

Now it has been found that the solubility of the hindered phenols in Claisen solution is strongly influenced by the proportion of water in the methanol which is added to the aqueous potassium hydroxide solution. Recent experiments have shown that 2,6-di-*t*-butyl-4-methylphenol is soluble to the extent of 6 g. per liter in fresh Claisen solution made up with absolute methanol. When 90 parts absolute methanol to 10 parts of water by weight is employed, the solubility drops off to only 2.7 g. per liter. 2,4,6-Tri-*t*-butyl-phenol is soluble in the amount of 2.3 g. per liter in absolute Claisen solution and 1.7 g. per liter in Claisen solution made up with 90% methanol. This solubility probably can be attributed entirely to the methanol present. The addition of water to these alcoholic alkali solutions precipitates the hindered phenols; when dilute hydrochloric acid is added to the clear filtrates from such precipitations, no further separation takes place.

On the other hand, when the isomer of 2,6-di-*t*-butyl-4-methylphenol, the so-called "cryptophenol" 2,4-di-*t*-butyl-6-methylphenol, is dissolved in Claisen solution (absolute) at its limiting concentration of 20 g. per liter, the addition of water causes negligible precipitation. The subsequent acidification with dilute hydrochloric acid brings about complete precipitation of the alkylphenol. Thus it appears that the solubility of the cryptophenol in Claisen solution comes as a result of alkali solubility rather than alcohol solubility. This Note is submitted with the approval of the co-authors.

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(1) Stillson, Sawyer and Hunt, THIS JOURNAL, **67**, 303 (1945).

(2) Claisen, *Ann.*, **418**, 96 (1919).

(3) Claisen, *ibid.*, **442**, 210 (1925).

(4) Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

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Failure of the Doebner Reaction with 2-Chloro-5-aminopyridine. Synthesis of a Pyrrolidine Derivative[1]

BY MARTIN J. WEISS AND CHARLES R. HAUSER

Aniline, benzaldehyde and pyruvic acid may undergo either the Doebner cyclization, involving

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(1) The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Duke University.