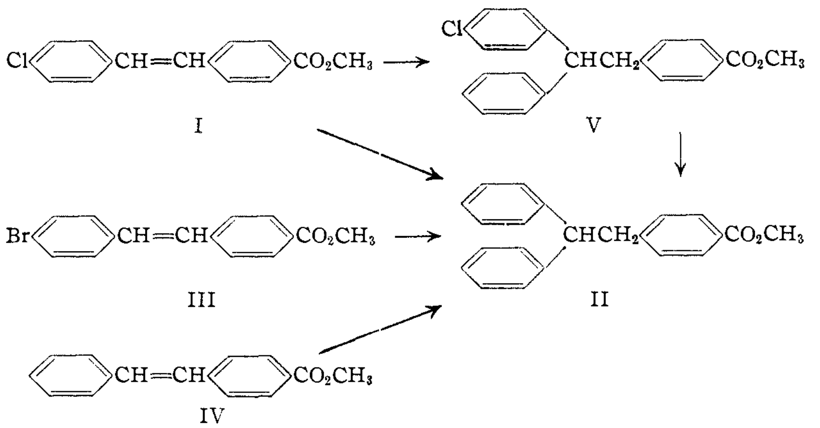
line when treated with benzene and aluminum chloride.[3] That the addition of the benzene was selective and did not affect the attachment of the quinoline nucleus was attributed to the fact that the ethylenic linkage is part of a heteroconjugated system.

Similar results have now been obtained with a phenyl radical bearing a carbomethoxyl group. A study of the action of benzene and aluminum chloride on *p*-carbomethoxystilbenes, in which the central ethylenic linkage is conjugated (through a benzene ring) with the carbomethoxy group, has shown that benzene adds reversibly to the lateral double bond. The addition takes place in the manner characteristic of heteroconjugated systems and is selective; the entering phenyl radical is joined to the carbon atom remote from the benzoate nucleus.

4-Chloro-4'-carbomethoxystilbene (I) reacts with benzene to yield a chlorine-free product, 1,1-diphenyl-2-*p*-carbomethoxyphenylethane (II). The phenyl group must become attached to the carbon atom adjacent to the chlorophenyl radical in order to eliminate chlorobenzene from the molecule. It was assumed that in the second step benzene was added in the same sense. This assumption was confirmed by oxidative degradation, which produces benzophenone.



The same product (II) was obtained from 4-bromo-4'-carbomethoxystilbene (III) and from 4-carbomethoxystilbene (IV). An indication of the course of the reactions with the halogen compounds was obtained by interrupting the condensation process after a short time. In this way it was shown that the chloro ester (I) condenses with benzene to yield initially 1-phenyl-1-*p*-chlorophenyl-2-*p*-carbomethoxyphenylethane (V). Oxidation of this product produces *p*-chlorobenzophenone. Although chlorobenzene was not isolated as a product of the conversion of V to II, its formation seems certain in view of the results reported for analogous transformations.[4]

Experimental

4-Chloro-4'-carbomethoxystilbene[5] and Benzene.—A solution of 2.5 g. of the stilbene in 100 ml. of dry benzene was saturated with dry hydrogen chloride. Four grams of aluminum chloride was added and the mixture shaken for five hours in a stoppered flask. Decomposition with ice and hydrochloric acid yielded a benzene solution of 1,1-diphenyl-2-*p*-carbomethoxyphenylethane. The solvent was distilled and the ethane recrystallized from methanol; m.p. 113–114°; yield 76%.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.55; H, 6.38. Found: C, 83.75; H, 6.47.

The foregoing preparation was repeated with the reaction time diminished to one hour. The product was 1-phenyl-1-*p*-chlorophenyl-2-*p*-carbomethoxyphenylethane (V). It was recrystallized from methanol; m.p. 107–108°; yield 62%.

Anal. Calcd. for $C_{22}H_{19}O_2Cl$: C, 75.61; H, 5.50. Found: C, 75.53; H, 5.71.

Further treatment of the chloroethane (V) under the conditions outlined above converted it to the chlorine-free ethane (II); melting point and mixed melting point 113–114°; yield 55%.

The same ethane was obtained in a 63% yield by subjecting 4-carbomethoxystilbene to the action of benzene, hydrogen chloride and aluminum chloride. When 4-bromo-4'-carbomethoxystilbene was used and the reaction allowed to continue for five hours, the bromine-free ethane (II) was produced in a 75% yield.

Oxidation of 1-phenyl-1-*p*-chlorophenyl-2-*p*-carbomethoxyphenylethane (V) produced *p*-chlorobenzophenone, which was isolated as the 2,4-dinitrophenylhydrazone; m.p. 192–194°. Grieve and Hey[6] reported a melting point of 184–185°. The 2,4-dinitrophenylhydrazone of a known sample of *p*-chlorobenzophenone was found to melt at 195–196° and gave the following analytical values:

Anal. Calcd. for $C_{19}H_{13}O_4N_4Cl$: C, 57.50; H, 3.30; N, 14.12. Found: C, 57.69; H, 3.36; N, 14.19.

A mixture of this compound and that from the oxidation melted at 192–195°.

1,1-Diphenyl-2-*p*-carbomethoxyethane (II) was oxidized by a method similar to that used by Böeseken and Bastet[7] in the oxidation of 1,1,2-triphenylethane. A mixture of 1 g. of the ethane, 2 g. of chromic anhydride and 50 ml. of glacial acetic acid was heated on a steam-bath for 20 hours. It was poured into 200 ml. of water containing 2 g. of sirupy phosphoric acid, and an excess of ammonium hydroxide was added. Ether extraction of this mixture yielded an oil which reacted with 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazone of benzophenone; melting point and mixed melting point 237–239°.

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RECEIVED MARCH 3, 1951

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(3) R. C. Fuson, L. L. Alexander, E. Ellingboe and A. Hoffman, *ibid.*, **58**, 1979 (1936).

(4) R. C. Fuson, A. P. Kozacik and J. T. Eaton, *ibid.*, **55**, 3799 (1933).

(5) For the preparation of the carbomethoxystilbenes see R. C. Fuson and H. G. Cooke, Jr., *ibid.*, **62**, 1180 (1940).

(6) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

(7) J. Böeseken and M. C. Bastet, *Rec. trav. chim.*, **32**, 184 (1913).

Complex Formation between Nickel Ion and Hydrazine in Solution

BY E. C. GILBERT AND WM. H. EVANS[1]

When hydrazine is added to a solution of a nickel salt, a deep blue color is formed, followed shortly by the precipitation of a red-violet solid complex salt if the solution is at all concentrated. This is of course accompanied by the disappearance of the blue color. If nickel sulfate is used the precipitation occurs at a very low concentration. The limited solubility of these nickel hydrazine complexes has been used to prepare a considerable number of them, including the sulfate, acetate,

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(1) Abstracted from Ph.D. thesis of Wm. H. Evans, 1947.

benzoate, chloride, bromide, pyrophosphate, oxalate and cyanide. By the use of nickel nitrate however a much more intense color may be secured in the solution before precipitation occurs. This is probably due both to the variation in the stability of any complexes formed with the change in ionic strength occasioned by the change in anion, and to greater solubility of the complex nitrate.

Franzen and Mayer[2] prepared a complex with nickel nitrate containing $Ni(N_2H_4)_3^{++}$. This was a red violet solid and appears to be the precipitate that forms when nickel nitrate and hydrazine solutions are allowed to stand. Sommer and Weise,[3] however, report the preparation of a deep blue hydrated nickel sulfate containing but one molecule of hydrazine, and Curtius and Schrader,[4] prepared a sulfate complex containing $Ni(N_2H_4)_2^{++}$.

This behavior indicates that there might occur stepwise addition of hydrazine to the nickel ion, with the monohydrazine nickel ion as an intermediate step in the formation of di- or trihydrazine complexes. It would be of interest to know what complexes are capable of existence in solution, their relative stability, and proportions if soluble enough to be detected.

Experimental

A spectrophotometric study of the system nickel nitrate–hydrazine hydrate was made with monochromatic light in bands of 100 Å. width over the spectral range of 4000–7200 Å. using a Cenco-Sheard Photelometer, with 1 cm. Corex absorption cells. Solutions (0.02 molal) were made from Baker C.P. nickel nitrate low in cobalt, and Edwal 100% hydrazine hydrate, in the ratio of $1Ni{:}1N_2H_4$, $1Ni{:}2N_2H_4$, $1Ni{:}3N_2H_4$. Higher ratios were not experimentally feasible as they caused precipitation of the insoluble trihydrazine nickel salt. The optical density log I_0/I (where I_0 is the intensity of light transmitted by a reference solution of sodium nitrate of the same ionic strength as that used in the nickel solutions) was plotted against wave length as shown in Fig. 1. It would appear from first inspection of these that only one complex was present (even in solutions concentrated enough for precipitation to take place). This could be due to absorption by different complexes in the same spectral region, or such low solubility that they did not affect the absorption.

Recourse was to Job's principle of continuous variation.[5] The method has been extended by Vosburgh.[6] A series of solutions 0.02 $(1-x)$ M in nickel nitrate and $0.02x$ M in hydrazine was prepared with x varying from 0.0 to 0.75 and the absorption determined for the wave lengths 5800, 6000 and 6200 Å. These results are shown in Fig. 2 where it is apparent that there is good evidence for maxima at $x = 0.5$ and $x =$ *ca.* 0.66 indicating the formation of two complexes $Ni(N_2H_4)^{++}$ and $Ni(N_2H_4)_2^{++}$. It is generally assumed that the divalent nickel ion is hexacovalent. It is probable therefore that in solution these complexes with hydrazine are also partially hydrated. There is no evidence for this from the present experiment, so simple formulas are used.

The stability constant of the monohydrazinate was next approximated by the use of a series of solutions $0.04(1-x)$ M in nickel nitrate and $0.08x$ M hydrazine where the absorption was again measured at 5800, 6000 and 6200 Å., results being shown in Fig. 3. The maximum value oc-

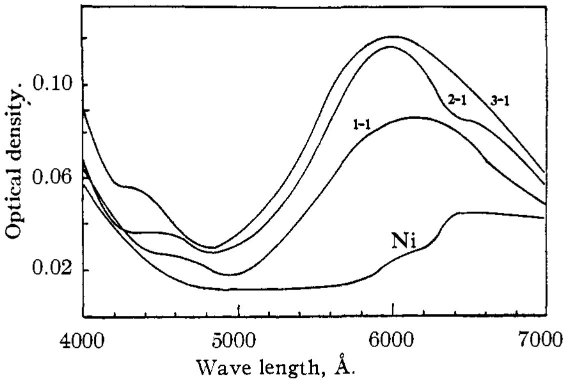

Fig. 1.—Absorption spectra of 0.02 M nickel nitrate solutions with various ratios of added hydrazine.

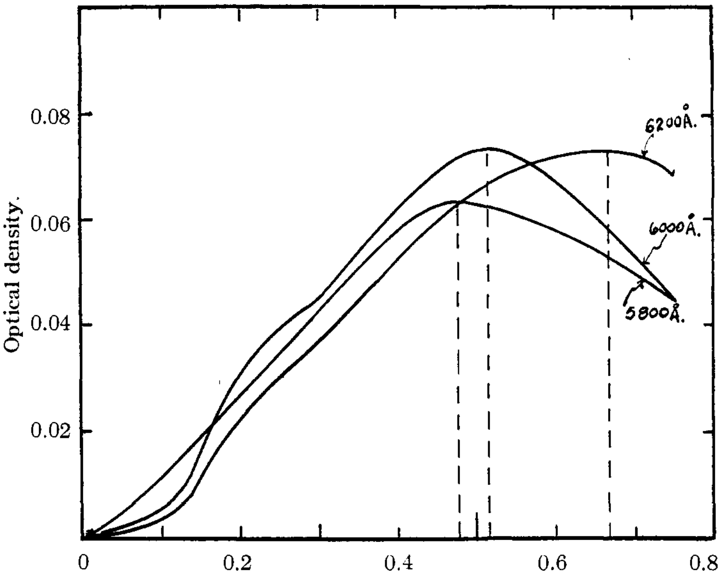

Fig. 2.—Absorption of $(1-x)$ liters of 0.02 M nickel nitrate and x liters of 0.02 M hydrazine.

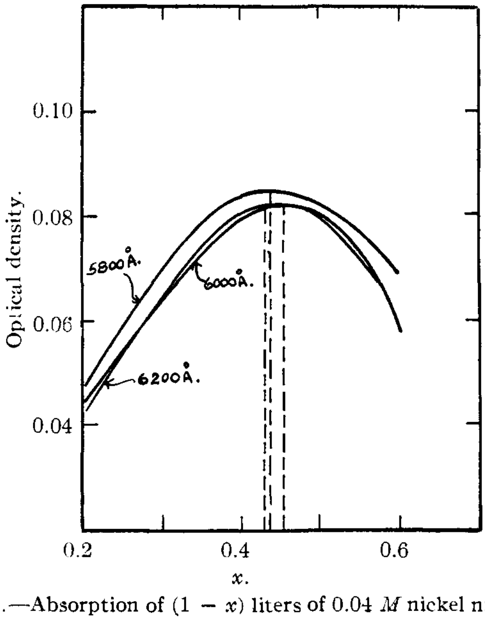

Fig. 3.—Absorption of $(1-x)$ liters of 0.04 M nickel nitrate and x liters of 0.08 M hydrazine.

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(2) H. Franzen and O. von Mayer, *Z. anorg. Chem.*, **60**, 247 (1908).

(3) F. Sommer and K. Weise, *ibid.*, **94**, 51 (1916).

(4) T. Curtius and F. Schrader, *J. prakt. Chem.*, [2] **50**, 341 (1894).

(5) (a) P. Job, *Compt. rend.*, **180**, 928 (1925); (b) *Ann. chim.*, [10] **9**, 113 (1928); (c) [11] **6**, 97 (1936).

(6) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941); W. C. Vosburgh and R. K. Gould, *ibid.*, **64**, 1630 (1942).

curred at $x = 0.443$. Substitution in the appropriate equation (ref. 5b, equation 7) gives 0.1 for $K = ([Ni^{++}][N_2H_4])/([Ni(N_2H_4)^{++}])$. The stability constant of the dihydrazinate could not be determined because of the interfering absorption of the first complex in the same region. In addition precipitation prevented sufficiently high concentrations. The evidence is therefore only quantitative for the existence of the monohydrazine nickel(II) ion in solution.

DEPARTMENT OF CHEMISTRY
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CORVALLIS, OREGON
RECEIVED DECEMBER 26, 1950

Perfluorinated Grignard Derivatives

BY ALBERT L. HENNE AND WILLIAM C. FRANCIS

Since the recent disclosure by Haszeldine[1] that we had obtained perfluorinated Grignard derivatives, we have received repeated requests for experimental directions. The following general procedure, while not yet optimum, will permit others to proceed with practical results.

We have made our Grignard derivatives from iodides, $C_nF_{2n+1}I$, and most of the work was done with C_3F_7I. Contrary to a general impression, the formation of C_3F_7MgI is exceedingly easy; its stability is, however, so poor that complete decomposition occurs promptly at room temperature.

A clue to this behavior was obtained when the Grignard was prepared in an atmosphere of dry carbon dioxide. Under these conditions $C_3F_7CO_2H$ resulted in 6 to 10% yield. When the reaction was carried out in a nitrogen atmosphere and later carbonated, little or no acid was obtained. At 0°, the Grignard is still unstable, but it is possible to form it in ether solution at this temperature, drop it promptly into water or a slurry of Dry Ice in ether[2] and isolate C_3F_7H or $C_3F_7CO_2H$, respectively, in 5 to 7% yields. These experiments show that perfluorinated Grignard reagents exist as such, and appear to react normally.

If Grignard formation is carried out at about −80° in an ether solution of C_3F_7I containing a suspension of magnesium and Dry Ice, a 45% yield of $C_3F_7CO_2H$ is easily obtained, presumably improvable by refining the mechanical handling.

Reaction in a carbon dioxide atmosphere using the "extreme dilution" procedure usually applied to allylic halides appears promising, but at the present time the recommended procedure is the low-temperature reaction just described.

Pilot tests have shown that these procedures can be extended to reaction with the carbonyl function, and acetone gives the expected carbinol. More detailed information will be presented later.[3]

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(1) R. N. Haszeldine, *Nature*, **167**, 139 (1951).

(2) A. S. Hussey, THIS JOURNAL, **73**, 1364 (1951).

(3) In a preprinted abstract for the New York Meeting of the A.C.S., September, 1951, Haszeldine states that perfluorinated Grignard Reagents appear to condense normally with a series of conventional functions (private communication).

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS, OHIO
RECEIVED MAY 9, 1951

The Synthesis of 4-Chloro-3-indoleacetic Acid

BY CORWIN HANSCH AND JOHN C. GODFREY

4-Chloro-3-indoleacetic acid has been synthesized by the procedure of Snyder and Pilgrim[1] for assessment as a plant growth-regulator. This substance has been tested by the avena test as part of a program[2] to correlate plant growth activity with chemical structure. The compound was found by Dr. Robert Muir of the State University of Iowa to be active in promoting plant growth; his complete results will be published elsewhere. The starting point for the synthesis of the 4-substituted acid was 4-chloroindole[3] a generous sample of which was supplied by Dr. F. C. Uhle of Harvard University.

Experimental

4-Chlorogramine.—To 1.42 ml. of 25% aqueous dimethylamine cooled in an ice-bath was added 1 g. of cold acetic acid and 0.58 g. of cold 40% formalin. This solution was then poured onto 1.12 g. of 4-chloroindole, the beaker being rinsed with $^1/_3$ ml. of water. The mixture was allowed to come to room temperature and after some shaking all of the chloroindole dissolved. This solution was allowed to stand overnight and then heated to 30–40° for 2 hours after which 1.35 g. of KOH in 10 ml. of water was added. The oil which separated crystallized quickly and after standing in an ice-bath 2 hours, the crystals were separated and dried. Dilution of the filtrate with the wash water caused more crystals to separate. Yield of crude chlorogramine was 1.4 g., m.p. 135–143°. After crystallization from acetone the m.p. was 147.6–148.4°.

Anal.[4] Calcd. for $C_{11}H_{13}N_2Cl$: C, 63.31; H, 6.24. Found: C, 63.40; H, 6.50.

The picrate was prepared in ethanol solution and recrystallized from the same solvent; m.p. 157.4–158.6°.

Anal. Calcd. for $C_{17}H_{16}N_5O_7Cl$: C, 46.63; H, 3.66. Found: C, 46.60; H, 4.10.

4-Chloro-3-indoleacetic Acid.—To 0.91 g. of potassium cyanide dissolved in 1.7 ml. of water and 5.4 ml. of 95% ethanol was added 0.57 g. of 4-chlorogramine. This mixture was heated under reflux for 98 hours and then diluted with 12 ml. of water. The resulting precipitate (presumably amide of 4-chloroindoleacetic acid) was removed by filtration (no free 4-chloroindoleacetic acid was obtained from this filtrate on acidification) and hydrolyzed by boiling with 2 *N* KOH for 4 hours. Acidification of the KOH solution caused a considerable precipitate of silicic acid and chloroindoleacetic acid. This precipitate and solution was evaporated to dryness and the residue extracted with ether. After evaporation of the ether the residue was crystallized from alcohol and ethylene chloride; yield 0.1 g., m.p. 179–180°.

Anal. Calcd. for $C_{10}H_8O_2NCl$: C, 57.28; H, 3.82. Found: C, 56.90; H, 4.30.

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(1) H. R. Snyder and F. J. Pilgrim, THIS JOURNAL, **70**, 3770 (1948).

(2) C. Hansch and R. M. Muir, *Plant Physiol.*, **25**, 389 (1950).

(3) F. C. Uhle, THIS JOURNAL, **71**, 761 (1949).

(4) All analyses were made by C. F. Geiger of Chaffey College, Ontario, California.

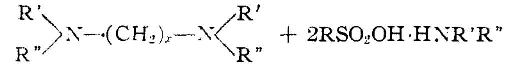
DEPARTMENT OF CHEMISTRY
POMONA COLLEGE
CLAREMONT, CALIF.
RECEIVED FEBRUARY 26, 1951

Preparation of N,N,N',N'-Tetrasubstituted Diamines

BY THOMAS M. LAAKSO AND DELBERT D. REYNOLDS

Recent investigations in our laboratory required the use of certain N,N,N',N'-tetrasubstituted diamines. A general method for their preparation is not described in the literature.

The method described here involves the reaction of glycol disulfonates with secondary amines as indicated by



$$RSO_2O{-}(CH_2)_x{-}OSO_2R + 4R'R''NH \longrightarrow (R')(R'')N{-}(CH_2)_x{-}N(R')(R'') + 2RSO_2OH{\cdot}HNR'R''$$

R may be alkyl, aryl, and so forth; R′ and R″ may