

0.100 g. (0.000356 mole) of *d,l*-dihydroanisoin, 0.070 g. (70% yield), m.p. 118–120°, was reisolated.

Saponification of *meso*- and *dl*-Dihydroanisoin Bis-*m*-bromobenzoates.—To 10 ml. of 20% aqueous methanol containing 1.0 g. of potassium hydroxide was added 0.420 g. (0.000657 mole) of *meso*-dihydroanisoin bis-*m*-bromobenzoate. While allowing nitrogen to pass through the solution, the reaction mixture was brought to reflux for 5 hr. The reaction mixture was diluted with 30 ml. of water and cooled to room temperature. The precipitate, 0.1723 g. (96% yield), m.p. 164–169°, was collected. This substance was identified as the *meso*-dihydroanisoin by infrared spectrum and mixture melting point. The aqueous basic solution was acidified and extracted with methylene chloride. After drying over magnesium sulfate and removal of the solvent at reduced pressure, 0.197 g. (75% yield), m.p. 140–150°, of *m*-bromobenzoic acid was obtained.

Hydrolysis of the *dl*-di-ester required a reaction time of 12 hr. By extraction of the reaction mixture with methylene chloride and drying of the extract, 0.115 g. (84% yield), m.p. 112–118°, of *d,l*-dihydroanisoin was isolated, identified by mixture melting point and infrared spectrum. The aqueous solution was acidified and extracted with chloroform. After drying over magnesium sulfate and evaporation of the solvent, 0.150 g. (74% yield), m.p. 145–155°, of *m*-bromobenzoic acid was obtained.

Galvinoxyl was prepared by a modification of the procedure of Coppinger.¹⁵ A solution of 42.4 g. (0.1 mole) of 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxydiphenylmethane in 500 ml. of benzene was deaerated by passing a stream of nitrogen through the solution for 2 hr. With stirring under nitrogen, 108 g. (0.45 mole) was isolated. On repeated recrystallization from benzene or *n*-pentane under nitrogen atmosphere, 1.0 g. of material was obtained of dec. pt. 158° (dependent on rate of heating); λ_{max} in benzene, 434 m μ (ϵ 145,000), 530 m μ (broad shoulder ϵ 1020), 775 m μ (ϵ 580). Galvinoxyl obeys Beer's law at the wave lengths examined. An iodometric titration of galvinoxyl (see below) showed that it was $97 \pm 1.0\%$ pure. The infrared spectrum was missing the bands at 3670 and 1519 cm.⁻¹; however, a faint shoulder at 1620 cm.⁻¹ was detected. Since these bands are due to hydrogalvinoxyl, it seems probable that no more than 5% hydrogalvinoxyl is present as an impurity in the galvinoxyl.

Iodometric Titration of Galvinoxyl.—Into a clean, dry 125-ml. stoppered erlenmeyer flask was weighed a sample of galvinoxyl. The galvinoxyl was dissolved in 2 ml. of chloroform or 3 ml. of benzene. To this solution 13 ml. of acetic

acid (anal. reagent) was added and the solution was degassed by adding crushed Dry Ice. After the solution reached room temperature, approximately 1 g. of solid sodium iodide (anal. reagent) was added. The entire sample was diluted with 45 ml. of deaerated water and placed in the dark for 5 min. The solution was titrated with standard sodium thiosulfate solution until near the end-point. Starch indicator (2 ml.) was added and the sample titrated until the blue starch-iodine color just disappeared. A 35.1-mg. sample of galvinoxyl required 7.95 ml. of 0.01 *N* thiosulfate, indicating a purity of 95.5%.

Stability of the Dimethoxystilbenes to Galvinoxyl.—A degassed benzene solution of galvinoxyl at 45° underwent 2.5% decrease in the 775 m μ band in 90 hr. A degassed benzene solution of galvinoxyl (0.00095 *M*) and *p,p'*-dimethoxy-*trans*-stilbene (0.01 *M*) at 45° underwent 3.5% decrease in the 775 m μ (galvinoxyl) band and 1% increase in the 329 m μ (olefin) band in 90 hr. A degassed benzene solution of the galvinoxyl (0.002 *M*) and the *cis*-olefin (0.002 *M*) underwent no change at 434 m μ (galvinoxyl) and no increase at 329 m μ (*i.e.*, no isomerization of *cis*- to *trans*-olefin) in 24 hr.

Kinetic Method. Titrimetric and Spectrophotometric Determination of Rates of Reaction of Peroxides and Olefins.—All kinetic runs were degassed on the vacuum line to at least 0.1 mm. pressure by the method described in the product studies. The tubes were placed in a constant temperature bath, removed at intervals, and quenched in a water-ice mixture. An aliquot was removed and added to a solution of sodium iodide in acetic acid, degassed with Dry Ice. The titration procedure was that described above for galvinoxyl. For spectrophotometric determinations, an aliquot of the kinetic solution was removed by a lambda-pipet, diluted with the solvent to the desired concentration, and the optical density measured on a Beckman DU spectrophotometer at the desired wave length. Average deviation in rate constants by both titrimetric and spectrophotometric procedures was about 2–3%. A sample run, including galvinoxyl, is shown in Table V. The results are summarized in Tables I, III and IV.²⁰

Acknowledgment.—We wish to thank the Ethyl Corporation for a generous sample of 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxydiphenylmethane.

(39) All of the original kinetic data are reported in the doctoral thesis of W. Adam, M.I.T., February, 1961.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

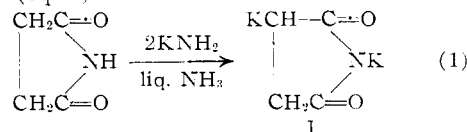
Condensations at the α -Carbon of Succinimide Through its Dipotassio Salt Prepared by Means of Potassium Amide

BY DAVID R. BRYANT¹ AND CHARLES R. HAUSER

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Three types of condensations were effected at the α -carbon of succinimide through its dipotassio salt, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. They involved benzylation with benzyl chloride, aroylations with aromatic esters, and aldol condensations with benzophenone and anisaldehyde. These preferential reactions at the carbanion of the dipotassio salt rather than at its imide anion resulted in new products or furnished new routes for synthesis of known compounds.

This paper describes three types of condensations at the α -carbon of succinimide through its dipotassio salt I, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia (eq. 1).



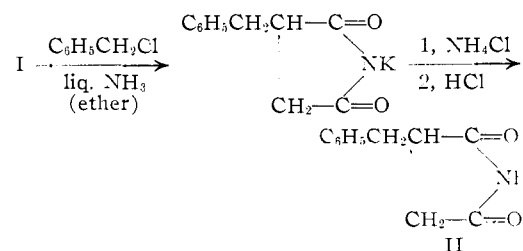
These condensations are similar to those observed recently² with the dipotassio salts of certain

(1) National Science Foundation Predoctoral Fellow, 1958–1961.

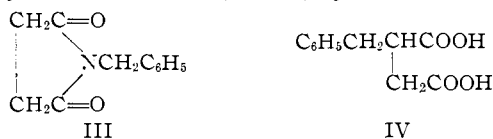
(2) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958), and T. M. Harris and C. R. Hauser, *ibid.*, **81**, 1160 (1959).

β -diketones such as acetylacetone, to which succinimide is related as a cyclic nitrogen analog.

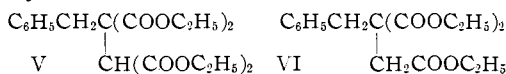
Benylation of dipotassio salt I was effected with benzyl chloride to form the C-benzyl derivative II in 16–29% yield (eq. 2).



That the product was II, not the possible N-benzyl derivative III, was indicated by its solubility in 5% sodium hydroxide, a band in its infrared spectrum at 3.23 μ for the N-H group³ and by its melting point which agreed satisfactorily with that reported for II when prepared by other methods.^{4,5} The structure of II was confirmed by acid-catalyzed hydrolysis to form the known 2-benzylsuccinic acid (IV) in 94% yield.

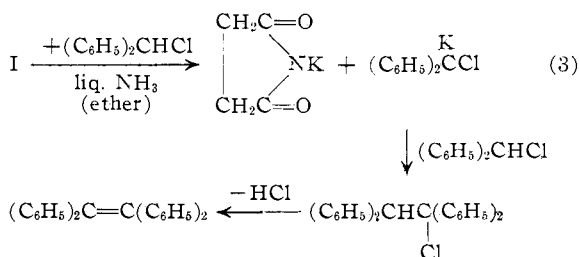


Although the yield of II was only fair, the present direct method (eq. 2) appears more convenient than earlier indirect methods,^{4,5} the last step of which involved the thermal cyclization of the diammonium salt of IV. Diacid IV was prepared either by the benzylation of diethyl 2,3-dicarbethoxysuccinate to form V⁴ or by the alkylation of 2-benzylmalonic ester with ethyl bromoacetate to give VI,⁵ with subsequent hydrolysis and decarboxylation.



Two benzylation procedures were employed in the present study. One involved the addition of benzyl chloride to I, and the other the addition of I to excess benzyl chloride in liquid ammonia. The latter inverse addition procedure afforded the better yield of II. Both procedures produced considerable amounts of higher boiling material, which appeared to consist of higher C-benylation products since it was soluble in 5% sodium hydroxide but not in bicarbonate. The introduction of two alkyl groups at the same or at another carbanion has been observed with the dialkali salts of certain β -diketones under similar conditions.⁶ In certain experiments a small amount of stilbene was isolated. This product arose through the self-condensation of benzyl chloride, a type of reaction realized in high yield with alkali amides in liquid ammonia.⁷

When the benzylation of I was effected in refluxing ether or in toluene on a steam-bath, the product appeared to consist largely of higher C-benylation material. None of II was isolated.



(3) See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 221.

(4) A. Baeyer and W. H. Perkin, *Ber.*, **17**, 449 (1884).

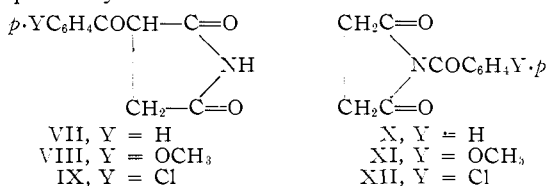
(5) Ramart-Lucas and M. Z. Papadakis, *Ann. chim.*, [10] **18**, 32 (1932).

(6) R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **25**, 158 (1960).

(7) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

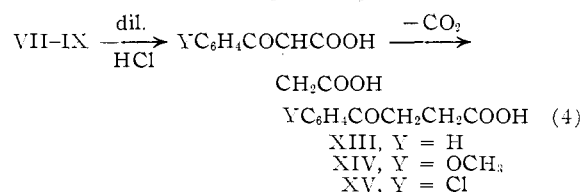
In contrast to benzyl chloride, benzhydryl chloride failed to alkylate dipotassium salt I. Instead, this halide underwent self-alkylation to produce tetraphenylethylene⁷ (97%) and presumably regenerated succinimide (eq. 3).

Aroylations of dipotassium salt I were effected with the methyl esters of benzoic, anisic and *p*-chlorobenzoic acids to form the C-royl derivatives VII-IX in yields of 44-71, 33-44 and 5-14%, respectively.

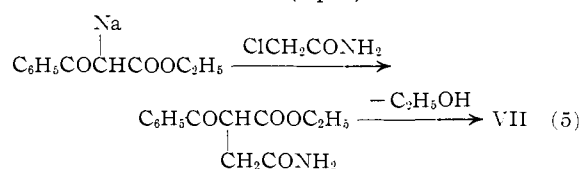


That the products were the C-royl derivatives VII-IX, not the possible N-royl derivatives X-XII, was indicated by their solubility in 5% sodium hydroxide solution, by positive enol tests with ethanolic ferric chloride, and by their infrared spectra, which gave bands in the region 3.1-3.2 μ indicative of the N-H group.³ None of these properties is characteristic of the N-royl derivatives X-XII, which were prepared for comparison.⁸

Structures VII-IX were established by acid-catalyzed hydrolysis, accompanied by decarboxylation, to form the known acids XIII-XV in yields of 64, 83 and 62%, respectively (eq. 4).



Structure VII was further confirmed by an independent synthesis from sodio ethyl benzoylacetate and α -chloroacetamide (eq. 5).⁹



The 3-roylsuccinimides VII-IX appeared to exist largely in the keto form, since they produced the maximum enol colors only on standing. This conclusion was supported by their infrared spectrum which had no characteristic broad enol band in the 6.0-6.5 μ region.¹⁰

Compounds VII-IX reacted with copper acetate solution, but the products appeared to consist of mixtures of the corresponding chelates and the nitrogen-copper salts. A small amount of a copper derivative of VII was isolated having a satisfactory analysis for the corresponding chelate, but the analysis obtained for the copper derivative from VIII did not correspond to that of the chelate.

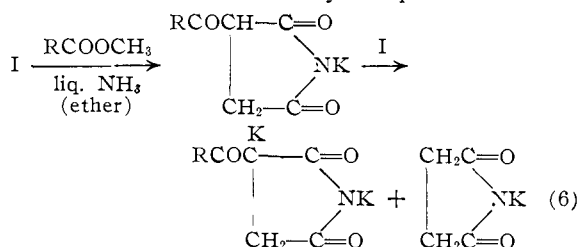
In the aroylations of I, two different proportions of the reactants were employed. In one, the ratio

(8) See A. W. Titherley, *J. Chem. Soc.*, **85**, 1673 (1904).

(9) See J. Champlon, *Ann. chim.*, [12] **9**, 647 (1954).

(10) See ref. 3, p. 142.

of ester to I was 1:2 (method B); in the other, molecular equivalents of ester, I, and potassium amide were used (method A). In the former method the extra equivalent of, I, was presumably neutralized in converting the product to its dipotassio salt (eq. 6), whereas in method A this last step may be considered to be effected by the potassium amide.



Proportions of reactants similar to those of methods A and B have been employed in the related aroylations of sodio ketones¹¹ and of dipotassio- β -diketones¹² to form β -diketones and 1,3,5-triketones, respectively. Although the succinimide regenerated as its monopotassio salt according to eq. 6 was not isolated, practically all of the ketone and β -diketone regenerated in similar aroylations of sodio ketones and dipotassio- β -diketones by method B have been recovered.^{11,12}

In Table I are summarized the yields of aroyl derivatives VII-IX obtained in methods A and B. In the former method the yields were based on the ester and in the latter on succinimide (or ester).

TABLE I
YIELDS OF AROYLATION PRODUCTS FROM I AND AROYL ESTERS

Method	Time, hr.	Product	Yield, %
Methyl benzoate			
B	1	VII	44-48
B	4	VII	71
A	1	VII	44 ^a
Methyl anisate			
B	1	VIII	33-38
B	4	VIII	47 ^b
A	1.25	VIII	47 ^c
Methyl <i>p</i> -chlorobenzoate			
B	5 min.	IX	11
B	0.5 or 3	IX	13-14 ^d
A	1	IX	5

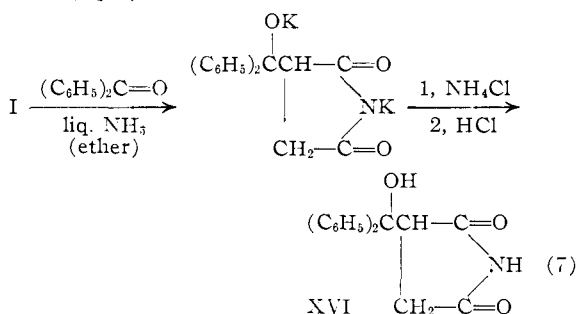
^a Benzoic acid (14%) also obtained. ^b Anisic acid (18%), anisamide (1%) and unchanged ester (3%) also obtained. ^c Anisic acid (17%) and anisamide (12%) also obtained. ^d Obtained also *p*-chlorobenzoic acid (20%).

Besides these products, appreciable amounts of the corresponding carboxylic acids (14-20%) were obtained. Since the esters should not have been hydrolyzed under the conditions employed, the origin of these acids is not clear. As might be expected, some of the corresponding amide was formed in method A. In the reaction with the *p*-chloro ester, the benzyne type of reaction might have occurred to some extent.¹³ In general, ethereal solu-

tions of the reaction products were first extracted with sodium bicarbonate solution (or sodium acetate) to remove the carboxylic acid and then with dilute sodium hydroxide to remove the aroyl derivatives VII-IX.

At least for the preparation of VII, the direct aroylation of I (see eq. 6) is superior to the indirect method employed as an independent synthesis (eq. 5) in which the over-all yield of VII was only 2%. However, an attempt to effect the propionylation of I with methyl propionate was unsuccessful; apparently an α -hydrogen of this ester underwent preferential ionization. Even when succinimide was treated with two molecular equivalents of lithium amide in liquid ammonia followed by an equivalent of ethyl acetate, none of the corresponding 3-acetylsuccinimide was isolated.¹⁴ Champion⁹ has reported a 60% yield of the latter compound from sodio ethyl acetoacetate and α -chloroacetamide (see eq. 5).

Aldol Condensations of Dipotassio Salt I.—Dipotassio salt I underwent an addition reaction with benzophenone to form the hydroxyimide XVI (eq. 7).



A 66% yield (94% conversion yield) of XVI was obtained when the reaction mixture was poured onto a suspension of ammonium chloride in liquid ammonia. This inverse neutralization procedure may have prevented some reversion of the condensation, since XVI was realized in 52% yield when ammonium chloride was added directly to the reaction mixture.

Structure XVI was supported by its analysis and its infrared spectrum, which showed a medium band at 2.89 μ for the hydroxyl group¹⁵ and appropriate bands for the nitrogen-hydrogen and carbonyl groups. This structure was established by dehydration to form XVII (89%), the infrared spectrum of which showed a strong band at 6.14 μ for the conjugated carbon-carbon double bond¹⁶ and appropriate bands for the nitrogen-hydrogen and conjugated carbonyl groups. The structure of XVII, and consequently of XVI, was confirmed by hydrolysis to form diacid XVIII, which was independently synthesized employing the Stobbe reaction (Scheme A).

The conversion yield of diacid XVIII from XVII was 32%; no other product was isolated. Incidentally, imide XVII failed to undergo appreciable

(11) See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 63.

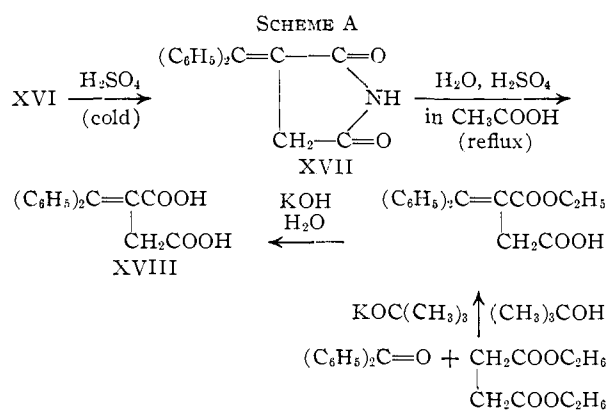
(12) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 538 (1960).

(13) See J. D. Roberts, H. Simmons, Jr., L. Carlsmith and C. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

(14) The analogous extension of aroylations of β -diketones to an acylation with methyl propionate by the use of lithium amide instead of potassium amide has been realized in fair yield; unpublished results of S. D. Work, R. J. Light and C. R. Hauser.

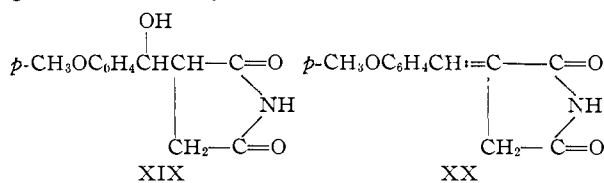
(15) See ref. 3, p. 96.

(16) See ref. 3, p. 136.

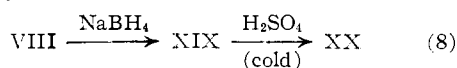


hydrolysis on refluxing in aqueous hydrochloric acid or acidic aqueous dioxane for ten hours.

Similarly, dipotassio salt I reacted with anisaldehyde to form hydroxyimide XIX in 32% yield. The structure of this product was supported by analysis, infrared spectrum and dehydration to give XX in 76% yield.



The structure of XX, and consequently of XIX, was confirmed by an independent synthesis involving the reduction of 3-anisoylsuccinimide (VIII), followed by dehydration (eq. 8).



This relationship between the aroylsuccinimide VIII and the aldol product XIX is interesting, although the over-all yield of the dehydration product XX from VIII was only 2%. An attempt to effect the reverse transformation, involving an Oppenauer oxidation of aldol XIX using aluminum isopropoxide and cyclohexanone, was unsatisfactory.

It is to be noted that, while the Stobbe reaction may be chosen for the synthesis of an unsaturated diacid such as XVIII (see Scheme A), the present aldol process furnishes a convenient method for the synthesis of not only hydroxyimides XVI and XIX but also of the unsaturated imides XVII and XX.

Experimental¹⁷

Preparation of Dipotassiosuccinimide (I).—To a stirred suspension of 0.2 mole of potassium anide in 500 ml. of commercial, anhydrous liquid ammonia² contained in a 1-l. three-necked flask was added 9.9 g. (0.1 mole) of finely powdered succinimide from an erlenmeyer flask through Gooch tubing fitted with a standard taper joint. The resulting pale yellow suspension was stirred for 15–25 min. before using as described below; this reagent was assumed to contain 0.1 mole of dipotassiosuccinimide (I).

Benylation of Dipotassio Salt I. (A). Direct Addition Procedure.—To a stirred suspension of 0.1 mole of I in 500 ml. of liquid ammonia was added during 1 minute 12.7 g. (0.1 mole) of benzyl chloride in an equal volume of anhy-

drous ether. The yellow color of I faded to leave a gray suspension. After stirring for 15 min., excess finely powdered ammonium chloride was added. The liquid ammonia was then evaporated on a steam-bath as an equal volume of ether was added. The resulting ethereal suspension was added to a mixture of 20 ml. of 12 *N* hydrochloric acid and 100 g. of crushed ice. After stirring to dissolve solids, the layers were separated. The ethereal layer was combined with two ethereal extracts of the aqueous layer, and the solution was washed a few times with saturated sodium bicarbonate solution. The ethereal solution then was extracted with 5% sodium hydroxide until the extracts were essentially colorless; the combined alkaline extract was acidified with 12 *N* hydrochloric acid. The resulting oil was removed by extraction with ether. The ethereal solution was washed with saturated sodium bicarbonate solution and then dried over magnesium sulfate. The solvent was distilled on a steam-bath, the last portion being removed with a water aspirator. The residual oil was distilled *in vacuo* through a 1.5 × 10 cm. Vigreux column to give 3-benzylsuccinimide (II), b.p. 155–160° at 0.5 mm., m.p. 92.5–95°; one recrystallization from absolute ethanol-hexane gave 3.1 g. (16%) of II, m.p. 95–96.5° and 97.5–98° after another recrystallization, reported⁵ m.p. 98°. The pot residue (4.3 g.) was chromatographed through an alumina column to give 0.7 g. more of II for an over-all yield of 20%.

The ethereal layer containing neutral reaction products was worked up to give 0.6 g. (6%) of stilbene, which was identified by the mixture melting point method and by infrared spectra employing an authentic sample. Some (2 g.) of the benzyl chloride was recovered.

(B) Inverse Addition Procedure.—To 100 ml. of liquid ammonia in a 1-l. three-necked flask fitted with a mechanical stirrer and air condenser was added a solution of 25.3 g. (0.2 mole) of benzyl chloride in an equal volume of anhydrous ether. To this mixture was added immediately, with stirring during 10 min., a suspension of 0.1 mole of dipotassio salt I in 400 ml. of liquid ammonia (from a flask having a stopcock at the bottom). After stirring for 10 min. longer, excess ammonium chloride was added, and the ammonia was replaced by ether. The resulting ethereal suspension was worked up essentially as described above. There was obtained 11.7 g. of a residual light yellow oil, which was distilled to give a fraction, b.p. 162–165° at 0.4 mm. Recrystallization of this material from absolute ethanol-hexane gave 5.19 g. (27%) of II, m.p. 96–97°. A second crop (0.43 g., 2%) was obtained, m.p. 93.5–94.2°. The pot residue weighed 3.13 g.

Hydrolysis of II.—A 0.5-g. sample of 3-benzylsuccinimide (II) was refluxed with 5 ml. of 12 *N* hydrochloric acid and 15 ml. of water for 4 hr. The solution then was cooled in an ice-bath and extracted with three 10-ml. portions of ether. The combined ethereal solution was extracted with three 10-ml. portions of saturated sodium bicarbonate solution. The combined bicarbonate solution was acidified with 12 *N* hydrochloric acid to precipitate (on cooling) 0.33 g. (60%) (94% conversion yield) of 2-benzylsuccinic acid, m.p. 159–161°. One recrystallization from a mixture of absolute ethanol and hexane raised the m.p. to 160–161°, reported¹⁸ m.p. 162°. There was recovered 0.18 g. (36%) of unchanged II, m.p. and mixed m.p. 96.5–97°.

Treatment of I with Benzhydryl Chloride.—A solution of 20.3 g. (0.1 mole) of benzhydryl chloride in 100 ml. of anhydrous ether was added during 5 min. to a stirred suspension of 0.1 mole of dipotassio salt I in 500 ml. of liquid ammonia. The yellow color of I was changed to orange, then faded after 0.5 hr., at which time the reaction mixture was neutralized with ammonium chloride and worked up to give 16.1 g. (97%) of 1,1,2,2-tetraphenylethane, m.p. 222.5–225° and 225–226° after two recrystallizations from ethanol-toluene. Admixture with an authentic sample of tetraphenylethane showed no depression; the infrared spectra of the two samples were identical. The benzhydryl derivative of succinimide was not found.

Aroylations of Dipotassio Salt I (Table I).—The general procedure in method B involved the addition of a solution of 0.05 mole of the aroyl ester in 100 ml. of anhydrous ether to a stirred suspension of 0.1 mole of dipotassio salt I in 500 ml. of liquid ammonia during 2–5 min. After stirring

(17) Melting points were taken with a Mel-Temp capillary melting point apparatus. Infrared spectra were produced with a Perkin-Elmer Infracord by the potassium bromide pellet method. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(18) J. A. McRae and L. Marlon, *Can. J. Research*, **15B**, 480 (1937).

for the appropriate time (see Table I), 10.7 g. (0.2 mole) of ammonium chloride was added, and the liquid ammonia was replaced by ether. To the resulting ethereal suspension was added a mixture of 25 ml. of 12*N* hydrochloric acid and 150 g. of cracked ice. After stirring to dissolve solids, the layers were separated. The ethereal layer was combined with several ethereal extracts of the aqueous layer, and the ethereal solution was extracted three times with 25-ml. portions of saturated sodium bicarbonate solution. The ethereal solution was then extracted with 5% sodium hydroxide solution until the alkaline layer was nearly colorless. The alkaline extracts were combined, washed with ether, cooled in an ice-bath and acidified with 12 *N* hydrochloric acid. The resulting oil or precipitate was removed by extraction with ether or by filtration. The ethereal solution was washed with sodium bicarbonate solution and dried over magnesium sulfate. If colored, Norite was used. The solvent was removed by means of a steam-bath and water aspirator, leaving the product as an oil or solid.

The general procedure in method A involved the addition of 0.05 mole of the ester to a mixture of 0.05 mole each of dipotassium salt I and potassium amide in 500 ml. of liquid ammonia. This reagent was prepared from 0.05 mole of succinimide and 0.15 mole of potassium amide. The reaction mixture was worked up essentially as described above.

Details for typical experiments employing the various aroyl esters are given below.

(A) **With Methyl Benzoate.**—The reaction of I with this ester by method B produced a brown suspension, which was worked up after 1 hour to give 4.4–4.9 g. (44–48%) of 3-benzoylsuccinimide (VII), m.p. 134–137° and 137.5–138° after several recrystallizations from methanol.

Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.93; H, 4.57; N, 6.79.

Significant infrared bands appeared at 3.11, 5.68, 5.85 and 5.98 μ . Admixture of VII with a sample of *N*-benzoylsuccinimide (m.p. 129–129.7°) prepared as described below, depressed the m.p. to 105–108°.

When the reaction period was 4 hr., the yield of VII was 7.2 g. (71%), a sample of which melted at 132–134°. This product was not as pure as that obtained in 48% yield after the 1-hour period.

The reaction of I with methyl benzoate in the presence of potassium amide (method A) gave 4.5 g. (44%) of VII, m.p. 133.5–135° and 135.5–137.2° after one recrystallization from water. Acidification of the combined sodium bicarbonate extract of the original reaction precipitated 0.87 g. (14%) of benzoic acid, m.p. 117–119° and 121–122° after one recrystallization from water. The melting point was not depressed on admixture with an authentic sample of benzoic acid.

Treatment of methanolic and ethanolic solutions of VII with ethanolic ferric chloride produced, on standing, purple and wine colors, respectively.

Treatment of a solution of 1.00 g. of VII in 10 ml. of ethanol with 150 ml. of hot, filtered saturated copper acetate solution produced almost immediately a precipitate which, after heating on a steam-bath for 0.5 hr., was collected and washed with water, ethanol, and finally a little ether to give 1.26–1.30 g. of green solid (vacuum dried). A sample was recrystallized twice from boiling ethanol (much undissolved solid being removed) to give a small amount of green chelate, m.p. 245° dec. (became tan at 238°).

Anal. Calcd. for $C_{22}H_{16}N_2O_6Cu$: C, 56.47; H, 3.45; N, 5.99; Cu, 13.58. Found: C, 56.15; H, 3.84; N, 6.17; Cu, 13.39.

Its infrared spectrum had peaks at 3.10, 5.73 and 5.85 μ . A suspension of a sample of the chelate in ether was shaken thoroughly with 12 *N* hydrochloric acid to regenerate VII, m.p. 135–136°.

Hydrolysis of VII (2.0 g.) was effected with a mixture of 25 ml. of 12 *N* hydrochloric acid and 25 ml. of water (refluxed 7 hr.). After standing overnight, the resulting white crystals were collected and washed twice with small portions of water to give 1.12 g. (64%) of 3-benzoylpropionic acid (XIII), m.p. 116.2–116.8°, reported¹⁹ m.p. 116°; neut. equiv. calcd. 178.18, found 176 and 179. The identity of XIII was confirmed by the mixture m.p. method and comparison of its infrared spectrum with that of an authentic sample.

(19) E. Buecker, *Ann. chim.*, [5] **26**, 435 (1882).

Independent synthesis of VII was accomplished by adaptation of the method of Champion³ for the corresponding acetyl compound. Sodium ethoxide (0.4 mole) in 250 ml. of absolute ethanol was prepared using 9.2 g. of sodium; ethyl benzoacetate (76.9 g., 0.4 mole) then was added. After stirring for 0.3 hr., a solution of 18.7 g. (0.2 mole) of α -chloroacetamide in 200 ml. of warm absolute ethanol was added rapidly, and then the mixture was heated at 80° for 4 hr. The precipitate, produced on cooling, was collected and acidified with 5% hydrochloric acid to give 0.8 g. (2%) of red solid, which, on recrystallization from ethanol-water using Norite, gave crystals of VII, m.p. 138–138.5°. This sample was shown to be identical with that obtained from dipotassium salt I by the mixture melting point method and by comparison of the infrared spectra.

(B) **With Methyl Anisate.**—The reaction of I with this ester by method B produced an orange suspension, which was worked up after 1 hour to give 3.8–4.4 g. (33–38%) of 3-(4-methoxybenzoyl)-succinimide (VIII), m.p. 127.2–129.5° and 128.4–129.2° after several recrystallizations from ether. The infrared spectrum of VIII had significant bands at 3.26, 5.69, 5.86 and 6.03 μ .

Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.79; H, 4.75; N, 6.01. Found: C, 61.75; H, 4.69; N, 5.96.

When the reaction period was 4 hr., there was obtained 5.5 g. (47%) of VIII, m.p. 119–126°. Acidification of the bicarbonate extracts precipitated 1.4 g. (18%) of anisic acid, m.p. 183.2–185°, identified by mixture melting point method. There was also isolated 0.08 g. (1%) of anisamide and 0.26 g. (3%) of recovered methyl anisate.

The reaction of I with methyl anisate for 1.25 hr. in the presence of potassium amide (method A) gave 5.49 g. (47%) of VIII, m.p. 116–121° and 125–126° after one recrystallization from ether. Acidification of the bicarbonate extract gave 1.26 g. (17%) of anisic acid, m.p. 183.2–185.5°. Removal of the solvent from the original ether layer gave a neutral residue, from which was isolated 0.91 g. (12%) of anisamide, 166.5–167.5°, and a trace of recovered methyl anisate.

Treatment of methanolic and ethanolic solutions of VIII with ethanolic ferric chloride produced, on standing, green and wine colors, respectively.

Treatment of a solution of VIII in ethanol with aqueous copper acetate produced a green precipitate that was not sufficiently soluble in the more common solvents to be recrystallized satisfactorily. A sample of this precipitate melted at 245.5–246° dec. After washing with hot ether, water, and ethanol, it was analyzed.

Anal. Found: C, 50.34; H, 4.13; N, 4.90; Cu, 15.93.

Hydrolysis of VIII (0.500 g.) was effected with a mixture of 7 ml. of 12 *N* hydrochloric acid and 7 ml. of water (refluxed 8 hr.). After standing overnight, the resulting silky white crystals were collected and washed with small portions of cold water to give 0.373 g. (83%) of 3-(4-methoxybenzoyl)-propionic acid (XIV), m.p. 143–145.5° and 147.8–148.2° after one recrystallization from ethanol-water, reported²⁰ m.p. 146–147°; neut. equiv. calcd. 208.2, found 208.

(C) **With Methyl *p*-Chlorobenzoate.**—The reaction of 0.076 mole of I with 0.038 mole of this ester in 50 ml. of anhydrous ether (method B) produced a brown suspension, which was worked up after 5 min. to give 3.67 g. of yellow product, m.p. 120–180°. After stirring with three successive 100-ml. portions of 20% sodium acetate solution, filtering each time, and recrystallizing the final solid from a mixture of absolute ethanol and hexane, there was obtained 0.98 g. (11%) of 3-(*p*-chlorobenzoyl)-succinimide (IX), m.p. 162.5–163°. Significant infrared bands were found at 3.20, 5.63, 5.72 and 5.94 μ .

Anal. Calcd. for $C_{11}H_8ClNO_3$: C, 55.59; H, 3.39; Cl, 14.92; N, 5.90. Found: C, 55.67; H, 3.50; Cl, 14.85; N, 5.90.

Acidification of the sodium acetate filtrates precipitated 0.75 g. (13%) of *p*-chlorobenzoic acid, m.p. 235–239°, identified by comparison of melting point and infrared spectra with an authentic sample.

The reaction of I with methyl *p*-chlorobenzoate in the presence of potassium amide (method A) produced IX, m.p. 161–162°, in 5% yield. Acidification of the bicarbo-

(20) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **58**, 2314 (1936).

nate extracts precipitated 3.1 g. (20%) of *p*-chlorobenzoic acid.

Treatment of methanolic and ethanolic solutions of IX with ethanolic ferric chloride produced on standing purple and wine colors, respectively.

Treatment of an ethanolic solution of IX with aqueous copper acetate produced a precipitate, from which there was obtained a small amount of green powder, m.p. 165–165.5° dec.

Hydrolysis of IX (0.5 g.) was effected with a mixture of 7 ml. each of 12 *N* hydrochloric acid and water (refluxed 24 hr.). Cooling precipitated 0.275 g. (62%) of 3-(*p*-chlorobenzoyl)-propionic acid (white crystals), m.p. 131–131.5°, reported²¹ m.p. 131°; neut. equiv. calcd. 212.6, found 214 and 216.

N-Aroylsuccinimides X–XII.—*N*-benzoylsuccinimide (X) was prepared in 80% yield from succinimide and benzoyl chloride in pyridine as described by Titherley.⁸ It melted at 129–129.7°, reported⁸ m.p. 129–130°.

Similarly, *N*-anisoylsuccinimide (XI) and *N*-(*p*-chlorobenzoyl)-succinimide (XII) were synthesized from succinimide and the corresponding aroyl chloride in yields of 85 and 86%, respectively. Compound XI melted at 130–131.5° and at 134.5–135.2° after three recrystallizations from ethanol. Some carbonyl infrared bands were found at 5.60, 5.80 and 5.94 μ .

Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.79; H, 4.75; N, 6.01. Found: C, 61.94; H, 4.24; N, 6.08.

Compound XII melted at 212–214° and at 213–214° after one recrystallization from ethanol. Carbonyl infrared bands were located at 5.57, 5.80 and 5.88 μ .

Anal. Calcd. for $C_{11}H_9ClNO_3$: C, 55.59; H, 3.39; Cl, 14.92; N, 5.90. Found: C, 55.65; H, 3.39; Cl, 15.00; N, 5.85.

Aldol Condensation of Dipotassio Salt I. (A) with Benzophenone.—To a stirred suspension of 0.1 mole of I in 500 ml. of liquid ammonia was added, during 5 min., 18.2 g. (0.1 mole) of benzophenone in 125 ml. of anhydrous ether. A blue color was produced. After 3.25 hr., the reaction mixture was poured into 10.7 g. of finely powdered ammonium chloride in 100 ml. of liquid ammonia. The blue color was discharged leaving a gray suspension. The resulting reaction mixture was transferred back to the original reaction flask in which some of the reaction product had remained. The ammonia was removed on a steam-bath as an equal volume of ether was added. The resulting ethereal suspension was stirred with 300 ml. of water, and then the mixture was filtered. The light tan solids collected were washed with water to give on drying crude 3-(α -hydroxy- α , α -diphenylmethyl)-succinimide (XVI), m.p. 194–198° dec. The ethereal layer of the filtrate was dried and the solvent removed to leave 9.4 g. of residue, from which was recovered 5.7 g. (31%) of benzophenone, m.p. 41.5–43°.

The crude product XVI was dissolved in 200 ml. of 5% sodium hydroxide. After washing with ether, the alkaline solution was acidified with 12 *N* hydrochloric acid. The resulting precipitate was collected, washed with water and vacuum dried to give 18.4 g. (66%, 94% conversion yield) of XVI, m.p. 196–200°. After two recrystallizations from a mixture of absolute ethanol and hexane, the crystals melted at 200–201° when heated from room temperature in a capillary tube. The instantaneous melting point determined by dropping portions on a hot Fisher–Johns block was 210°. Infrared bands were found at 2.89, 5.62 and 5.82 μ .

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.40; H, 5.36; N, 5.20.

In another experiment the reaction mixture was neutralized by the direct addition of solid ammonium chloride to give XVI in 52% yield.

Dehydration of XVI (6 g.) was effected by shaking it with 80 g. of cold 18 *M* sulfuric acid in a flask cooled in an ice-bath. As soon as the sample had dissolved (within about 10 min.), the solution was poured onto 60 g. of crushed ice. The resulting precipitate was collected on a funnel and washed well with cold water to give 5.3 g. (89%) of 3-(diphenylmethylidene)-succinimide (XVII) (yellow), m.p. 238–243° and 247–248° (white) after one recrystallization

from absolute ethanol. Its infrared spectrum had bands at 5.68, 5.88 and 6.14 μ .

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.52; H, 4.81; N, 5.44.

Hydrolysis of XVII was effected by refluxing a 1-g. sample of it in a mixture of 50 ml. of glacial acetic acid, 10 ml. of water and 5 ml. of concentrated sulfuric acid for 24 hr. After cooling, solvent was removed with a rotary evaporator until crystals appeared, the residue then being poured into 400 ml. of water from which the organic products were isolated by continuous extraction with ether (16 hr.). The ethereal solution was extracted with saturated sodium bicarbonate solution; the bicarbonate extracts were combined and then acidified with 12 *N* hydrochloric acid. The resulting yellow oil was extracted with ether. The ethereal extracts were dried over magnesium sulfate. After distillation of the solvent, the residue was washed with hexane to give 0.22 g. (32% conversion yield) of 2-(diphenylmethylidene)-succinic acid (XVIII), m.p. 165.5–166.5° and 166.2–166.8° after one recrystallization from absolute ethanol–hexane, reported²² 168–169°. The m.p. was not depressed on admixture with an authentic sample.

The ethereal solution remaining after the bicarbonate extracts was dried and the solvent distilled to give, after washing with 10 ml. of cold ether, 0.36 g. of unchanged imide XVII.

Independent synthesis of XVIII was effected by refluxing 0.3 g. of potassium hydroxide, 20 ml. of water and 0.32 g. of β -carbethoxy- γ , γ -diphenylvinylacetic acid which had been prepared according to the procedure of Johnson.²³ The mixture was refluxed for 2 hr., cooled, acidified with dilute hydrochloric acid, and the resulting precipitate collected. On drying, 0.21 g. (74%) of 2-(diphenylmethylidene)-succinic acid (XVIII), m.p. 165.0–165.8°, was obtained, reported²³ m.p. 168–169°.

(B) **With Anisaldehyde.**—To a stirred suspension of 0.2 mole of I in 500 ml. of liquid ammonia was added, during 5 min., 27.2 g. (0.2 mole) of freshly distilled anisaldehyde in 100 ml. of anhydrous ether. The resulting clear brown solution was stirred for 1.5 hr., then 200 ml. of anhydrous ether was added to produce a pink suspension. After stirring for 2 hr. longer, excess ammonium chloride was added, and the ammonia was replaced by ether. To the resulting ethereal suspension was added a mixture of 25 ml. of 12 *N* hydrochloric acid and 250 g. of crushed ice. The layers were separated, several ethereal extracts of the aqueous layer being combined with the ethereal layer. The ethereal solution was extracted several times with saturated sodium bicarbonate solution and then with 5% sodium hydroxide. Acidification of the combined bicarbonate extract afforded anisic acid (1.7 g., 6%), m.p. and mixed m.p. 183–185°. Acidification of the combined sodium hydroxide extract afforded an oil, which was taken up in ether. After drying over magnesium sulfate, the solvent was removed from the ethereal solution to leave 15 g. (32%) of XIX as a yellow glass. Eight grams of this glass was allowed to sit in an open beaker for 2 months. The crystalline material obtained was filtered and washed with a small portion of ethanol to give 3.3 g. of 3-(α -hydroxy-4-methoxybenzyl)-succinimide (XIX), m.p. 118.5–118.8° and 119.2–120.0° after one recrystallization from absolute ethanol–hexane. Significant infrared bands were found at 3.09, 3.25, 5.73 and 5.93 μ .

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.26; H, 5.57; N, 5.95. Found: C, 61.30; H, 5.28; N, 5.68.

In another experiment the reaction mixture was neutralized by the direct addition of ammonium chloride to give XIX in about the same yield.

Dehydration of XIX (0.5 g.) was effected by dissolving it in cold concentrated sulfuric acid and pouring the resulting red solution onto crushed ice. The precipitate was collected, washed with water and a little cold ethanol to give 0.348 g. (76%) of 3-(4-methoxybenzylidene)-succinimide (XX), m.p. 246.6–247.2° after two recrystallizations from acetone. Infrared bands were found at 3.22, 5.74 and 5.90 μ .

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.34; H, 5.08; N, 6.46.

(21) H. Stobbe, *Ann.*, **308**, 89 (1899).

(22) C. F. H. Allen, J. B. Normington and C. V. Wilson, *Can. J. Research*, **11**, 382 (1934).

(23) W. S. Johnson, J. W. Petersen and W. R. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

Independent synthesis of XX was effected by rapidly adding a solution of 2.33 g. (0.01 mole) of 3-anisoylsuccinimide VIII in 70 ml. of hot isopropyl alcohol to a stirred suspension of 1.52 g. (0.04 mole) of sodium borohydride in 50 ml. of warm isopropyl alcohol (98–99%). After stirring for 5 hr. and cooling to room temperature, the solvent was removed to leave a white solid, which was dissolved in

dilute sodium hydroxide solution. Acidification of the solution afforded 1.28 g. of an oil, which was dehydrated with sulfuric acid to give 0.04 g. (2%) of XX, m.p. 242–243° and 244–245° after one recrystallization from acetone. The m.p. was not depressed on admixture with a sample of XX obtained as described above. The infrared spectra of the two samples were identical.

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

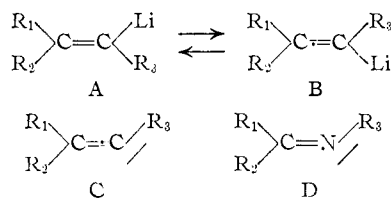
Effects of Structural Changes on the Interconversion of Stereoisomeric Imines. Isoelectronic Models for Vinyl Anions¹

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cis-p-Chlorobenzophenone methylimine (*cis*-I) and *trans-p*-nitrobenzophenone methylimine (*trans*-II) have been obtained as crystalline solids and found to rearrange to the equilibrium mixtures of *cis* and *trans* isomers in cyclohexane solution at room temperature and above. The first-order rate constants for the isomerizations have been measured. Examination of available infrared data suggests that the position of the monosubstituted phenyl absorption in the 700 cm.⁻¹ region may be used to make configurational assignments to properly constituted olefins, imines, oximes and azo compounds, the absorption frequency of the monosubstituted phenyl ring being as much as 5–9 cm.⁻¹ higher when the ring is *cis* to a substituent on the adjacent doubly bound carbon or nitrogen atom. Preliminary evidence indicates that N-arylimines such as *p*-methoxy-*p'*-nitrobenzophenone *p*-tolylimine (*cis*-VI) crystallize as a single stereoisomer but that *cis-trans* isomerization occurs very rapidly in solution even at room temperature and below. Attempts to verify the previous report²⁹ of the isolation of stable *cis* and *trans* isomers of 2-nitrofluorene *p*-tolylimine have not been successful.

Studies^{3,4} of the factors affecting the steric stability of *cis*- and *trans*-vinyl lithium compounds of type A and B have suggested^{4c} that carbanions C probably in a state of aggregation are prime intermediates. Because of the complexities of these systems it was desired to have model compounds which might be used to obtain information about the effects of structural changes on configurational stability of species related to the carbanions C. For this purpose imines D were of particular interest and a study of their stereochemical behavior was therefore undertaken.



The first substances selected for study were the *p*-chlorobenzophenone methylimines (*cis*- and *trans*-I) and *p*-nitrobenzophenone methylimines (*cis*- and *trans*-II).⁵ Reaction of *p*-chlorobenzophenone dichloride with methylamine led to an oil which crystallized on standing at room temperature for a two-week period. The resulting solid could be obtained free from the carbonyl absorption characteristic of the starting ketone, melted sharply

and gave correct analytical values for the desired imines I. Absorption at 1620 cm.⁻¹ assigned to the carbon-nitrogen double bond⁶ and a single sharp absorption at 693 cm.⁻¹ attributed to the monosubstituted phenyl group⁶ were observed when the infrared spectrum of a freshly prepared solution was measured. On standing, the solution showed no marked change in the absorption at 1620 cm.⁻¹, but a lowering of intensity of the absorption at 693 cm.⁻¹ and development of a second band at 701 cm.⁻¹ were observed. Further, a sharp infrared absorption at 827 cm.⁻¹ in the spectrum of the freshly dissolved solid (attributed to the deformation of hydrogens in the *p*-chlorophenyl ring⁶) decreased in intensity when the solution was allowed to stand and a new absorption at 837 cm.⁻¹ developed. The n.m.r. spectra of freshly prepared solutions of the imine showed, in addition to absorption due to the protons of the aromatic rings, a single N-CH₃ proton resonance at about 6.76τ (in deuteriochloroform) which, however, was unchanged when the solution was allowed to stand. It was concluded from these and other results to be discussed that the crystalline form is a single stereoisomer. Consideration of the infrared absorption in the 700-cm.⁻¹ region permits a configurational assignment to be made. Examination of the infrared spectra of a number of olefins suggests that the position of the hydrogen deformation frequency is generally higher in that isomer with another atom or group *cis* to the monosubstituted phenyl ring. The available data are summarized in Table I. It will be seen that the difference between the two isomers is generally 5–9 cm.⁻¹, although the α -methyl- β -bromostyrenes did not show an experimentally observable difference. In no case were the relative positions of the monosubstituted phenyl absorptions reversed. A similar difference seems to be present

(1) Supported in part by the National Science Foundation (G4467). Taken from the Ph.D. Thesis of Jack Walter Hausser, University of Illinois, 1960, available on microfilm from Univ. Microfilms, Ann Arbor, Mich.

(2) Rohm and Haas Fellow, 1958–1959.

(3) A. N. Nesmeyanov, A. E. Borilov and N. A. Vol'kenau, *Izvest. Akad. Nauk. (U.S.S.R.), Otdel. Khim. Nauk*, 992 (1954).

(4) (a) D. Y. Curtin, H. W. Johnson, Jr., and E. G. Stelner, *J. Am. Chem. Soc.*, **77**, 4566 (1955); (b) D. Y. Curtin and J. W. Crump, *ibid.*, **80**, 1922 (1958); (c) W. J. Koehl, Jr., and D. Y. Curtin, Abstracts of 138th Meeting, Amer. Chem. Soc., New York, N. Y., 1960, p. 52P.

(5) Throughout this paper the designations "*cis*" and "*trans*" will be used to describe the relative positions of the *p*-substituted phenyl ring and the methyl or aryl substituent on the imine nitrogen.

(6) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Company, London, 2nd Ed., 1958.