The silver chloride is wet by the nitrobenzene and remains at the boundary between the two layers and this avoids the necessity of filtering it off. The benzene layer was washed carefully twice with 10-ml. portions of distilled water, and the three aqueous layers containing the excess silver nitrate were combined for analysis. The excess silver nitrate was determined by titration with potassium thiocyanate. The normal Volhard technique of using ferric alum as indicator was not sensitive enough to give good results. The end-point could be found much more accurately potentiometrically with a silver electrode in the titration cell and a standard calomel electrode connected by a salt bridge filled with potassium chlorate.

A typical rate run with equal concentrations of benzoate ion and 2,4-dinitrochlorobenzene is shown in Table II.

TABLE II

RATE CONSTANTS FOR REACTION OF POTASSIUM BENZOATE WITH 2,4-DINITROCHLOROBENZENE IN 60% DIOXANE AT 93°

Time increment, min.	$k \times 10^5$, l. mole^{-1} sec.$^{-1}$
720	4.27
960	4.37
1440	4.20
1680	4.21
2760	4.30
7650	4.03
Average	4.23

A second run was made with samples containing 0.1 *M* benzoic acid (concentration of the two reactants, 0.05 *M*) in order to test the possibility that the attacking reagent was the hydroxide ion produced by hydrolysis of benzoate. The rate constant obtained (3.67×10^{-5} l. mole^{-1} sec.$^{-1}$) was close enough to that obtained with no benzoic acid added to establish the fact that benzoate is the principal attacking species. To further establish this point a run was made with the concentration of potassium benzoate twice that of the substrate. The rate constant, 4.23×10^{-5} l. mole^{-1} sec.$^{-1}$, was the same as that obtained in the first run. The concentrations used and the rate constants obtained are summarized in Table III.

TABLE III

RATE CONSTANTS FOR REACTION OF POTASSIUM BENZOATE WITH 2,4-DINITROCHLOROBENZENE WITH VARYING CONCENTRATIONS OF REACTANTS

Run	Concn. potassium benzoate, mole/liter	Concn. of dinitrochlorobenzene, mole/liter	Concn. benzoic acid, mole/liter	$K_{93} \times 10^5$, l. mole^{-1} sec.$^{-1}$
1	0.0500	0.0500		4.23
2	.0500	.0500	0.1000	3.67
3	.0667	.0333		4.23

The reactions of potassium *p*-methoxybenzoate and *p*-nitrobenzoate with 2,4-dinitrochlorobenzene were carried out in an identical manner with that described above for the potassium salt of the unsubstituted benzoic acid. The rate constants are summarized in Table I.

Investigation of Reaction Products.—When the reaction mixture was poured into a separatory funnel containing water and benzene, the aqueous layer was colored a distinct yellow. The addition of acid followed by shaking almost completely removed the color from the aqueous layer. The behavior led us to suspect that 2,4-dinitrophenol was formed by hydrolysis of the expected ester product during the reaction.

A sample of 2,4-dinitrophenyl benzoate was prepared by heating stoichiometric amounts of 2,4-dinitrophenol and benzoyl chloride in an oil-bath at 180° for two hours. The product was recrystallized from benzene to give a pale yellow crystalline material, m.p. 132–133°. Solutions of this ester in 60% dioxane were heated with potassium benzoate at 93° for 12 hours. The solutions became a darker yellow with heating and when poured into a separatory funnel containing benzene and water the same color changes described above were noted. Evaporation of the aqueous layer (not acidified) yielded a considerable amount of the potassium salt of 2,4-dinitrophenol. These results indicate that the replacement of halogen from activated aromatic positions would not be a good method of preparing the corresponding phenyl esters.

The Displacement of Iodide from Methyl Iodide by Benzoate Ions.—The reaction conditions and method of analysis were identical with those in the preceding section. It was unnecessary to use nitrobenzene to wet the silver halide since silver iodide does not interfere with Volhard determinations.[6] The reaction was run at 93° in sealed ampules and proceeded to completion in a few hours. A sample without the benzoate attacking agent showed a considerable amount of displaced iodide after a few hours of heating at 93°. This was attributed to hydrolysis at the high temperature. The reaction then was run at a lower temperature of 25.5° where hydrolysis is much slower but still not negligible. Corrections for the amount of hydrolysis were applied by running blanks.[7] The rate constants obtained are listed in Table I.

---

[6] H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 185.

[7] It has been pointed out by a referee that the blank does not necessarily correct the bimolecular displacement by hydroxide ion produced by the hydrolysis of the benzoate ions. One could seek an explicit demonstration that this side reaction is unimportant by applying the same test as was reported above in the case of displacements on the activated aryl halides. This was not deemed necessary in the case of the methyl iodide reaction since the relative importance of reaction by the benzoate ions and hydroxide can be estimated readily by the method of Swain and Scott.[8] The *n* value for hydroxide is 4.2 and that for benzoate ions cannot be a great deal less than 2.7, the value for acetate. The *s*-value for methyl iodide is 1.15[9] so the value of log ($k_{OH^-}/k_{RCO_2^-}$) must be of the order of 1.7 to 2.0. In water the hydrolysis of benzoate (K_i for benzoic acid is 6.8×10^{-5}) in a 0.1 *N* solution would produce hydroxide ion at a concentration of less than 10^{-5} *M*. This means that $k_{RCO_2^-}[RCO_2^-]$ would exceed $k_{OH^-}[OH^-]$ by about two orders of magnitude. In the dioxane–water mixture the hydrolysis would be still less extensive and the rate difference would become still larger.

[8] C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

[9] M. F. Hawthorne, G. S. Hammond and B. M. Graybill, *ibid.*, **77**, 486 (1955).

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

The Synthesis of α-Methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$ butenolide and its Reduction with Lithium Aluminum Hydride

BY FAUSTO RAMIREZ AND MORDECAI B. RUBIN[1]

RECEIVED DECEMBER 15, 1954

During an investigation[2] into the possibility of effecting partial reduction of γ-aryl-$\Delta^{\alpha,\beta}$- and γ-aryl-$\Delta^{\beta,\gamma}$-butenolides with lithium aluminum hydride, α-methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$-butenolide (I) was prepared from α-methyl-β-(2-naphthoyl)-propionic acid (III). The $\Delta^{\alpha,\beta}$-butenolide I resulted from the keto-acid III upon treatment with a few drops of sulfuric acid in an acetic acid–acetic anhydride mixture. The isomeric $\Delta^{\beta,\gamma}$-butenolide could not be obtained under conditions which yielded the $\Delta^{\beta,\gamma}$-butenolide from β-benzoyl-α-methylpropionic acid.[2] The similarity between the course of reduction of α-methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$-butenolide (I) and α-methyl-γ-phenyl-$\Delta^{\alpha,\beta}$-butenolide[2] with lithium aluminum hydride is indicated by the considerable similarity of the infrared spectra obtained from the crude reaction products in each case. No partial reduction to γ-hydroxy-α,β-unsaturated aldehyde was achieved.

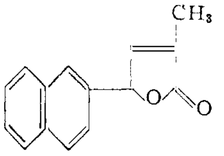
---

[1] Union Carbide and Carbon Fellow, 1952–1953. From part of the Ph.D. Thesis of M.B. Rubin.

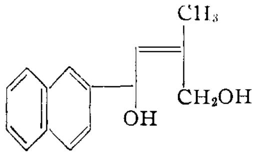
[2] F. Ramirez and M. B. Rubin, THIS JOURNAL, **77**, in press (1955).

With excess hydride in diethyl ether at room temperature only a 30% yield of 2-methyl-4-(2-naphthyl)-2-butene-1,4-diol[3] (II) could be realized from the butenolide (I).

The required α-methyl-β-(2-naphthoyl)-propionic acid (III) was prepared from 2-acetonaphthone (IV) by a sequence of reactions involving: (1) base-catalyzed condensation of IV and acetaldehyde in methanol solution to 2-(β-methoxybutyro)-naphthone (V), (2) elimination of methanol from the β-methoxy-ketone V at 150° under the influence of zinc chloride to yield 2-crotononaphthone (VI), (3) addition of cyanide to VI with formation of α-methyl-β-(2-naphthoyl)-propionitrile (VII) and (4) hydrolysis of the nitrile VII to the keto-acid III. Although the yield of step (1) was low, the sequence of reactions can be performed conveniently without isolation of the intermediates, purification being effected readily at the keto-acid III stage.[4]



I



II

Experimental[5]

2-(β-Methoxybutyro)-naphthone (V).[6]—To a mixture of 2-acetonaphthone (IV, 319 g.), acetaldehyde (112 g.) and anhydrous methanol (500 ml.), cooled in an ice–salt-bath, was added dropwise a solution of sodium methoxide in methanol (from 9 g. of sodium and 180 ml. of methanol). The mixture was kept ice-cold for 36 hours, treated with acetic acid (24 g.) and concentrated until salts began to precipitate. Water (500 ml.) was added, the oil which separated was extracted with ether and the ether was removed.[7] From the oil thus obtained, some unreacted 2-acetonaphthone (75 g.) was removed by steam distillation. The residue from the steam distillation gave, on fractional distillation through a short column at 0.1 mm.: (1) 38 g. of material, b.p. 129–133° (2-acetonaphthone); (2) 16 g. of a fraction, b.p. 135–140°; (3) 64 g. of 2-(β-methoxybutyro)-naphthone (V), b.p. 155–159°, $n^{24}\text{D}$ 1.6046; (4) some higher boiling material not further investigated. A sample from fraction 3 gave on redistillation compound V, b.p. 149–152° (0.1 mm.), $n^{27}\text{D}$ 1.5998, $d^{27}{}_{27}$ 1.110; $[R]^{27}\text{D}$. Found: 70.2, calculated 69.9.

Treatment of V with a solution of 2,4-dinitrophenylhydrazinium sulfate in aqueous methanol containing excess sulfuric acid gave the **2,4-dinitrophenylhydrazone** of **2-crotononaphthone**, m.p. 203–204° (from ethyl acetate–methanol, $\lambda_{\text{max}}^{\text{Chl.}}$ 390 mμ (ε 32,900)).

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: C, 63.8; H, 4.3; N, 14.9. Found: C, 63.7; H, 4.2; N, 14.6.

2-Crotononaphthone (VI).—A mixture of 2-(β-methoxybutyro)-naphthone (V, 10 g.) and freshly fused zinc chloride (0.1 g.) was placed in a distillation apparatus attached to a receiver, cooled in a Dry Ice–acetone-bath. The flask was heated for 30 minutes at 150° while the pressure was being reduced to 30 mm. The distillate (1.2 ml.) was shown to be methanol by preparation of the 3,5-dinitrobenzoate, m.p. 107–109°, and comparison with an authentic sample.

The residue was evaporatively distilled at 100° (0.01 mm.) to yield 6 g. of low melting 2-crotononaphthone (VI). A sample recrystallized from petroleum ether had m.p. 57.5–59°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.7; H, 6.2. Found: C, 85.9; H, 6.4.

The 2,4-dinitrophenylhydrazone prepared from VI had m.p. 214.4–214.8° (from ethyl acetate–ethanol), $\lambda_{\text{max}}^{\text{Chl.}}$ 390 mμ (ε 31,200).

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: C, 63.8; H, 4.3; N, 14.9. Found: C, 63.5; H, 4.2; N, 15.0.

This derivative does not appear to be identical with the previously mentioned derivative prepared directly from 2-(β-methoxybutyro)-naphthone (V), which may be due to geometrical isomerism.

α-Methyl-β-(2-naphthoyl)-propionitrile (VII).—To a stirred solution containing 5 g. of 2-crotononaphthone (VI), 50 ml. of ethanol and 1.7 ml. of glacial acetic acid kept at 50° was added dropwise a solution of 3.8 g. of potassium cyanide in 10 ml. of water. After 3 hours the mixture was cooled and the precipitated solid was filtered; yield 4.3 g. A sample recrystallized from ethanol had m.p. 93.8–94.8°.

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.7; H, 5.9; N, 6.3. Found: C, 80.8; H, 5.9; N, 6.3.

α-Methyl-β-(2-naphthoyl)-propionic Acid (III). (a).—A mixture of keto-nitrile VII (1.3 g.) and 15% aqueous potassium hydroxide (20 ml.) was refluxed for 2 hours. The cold solution was poured into cold, dilute hydrochloric acid. The recrystallized product (0.8 g.) had m.p. 169–170° (from chloroform), $\lambda_{\text{max.}}^{\text{Chl.}}$ 5.90, 5.99 μ and broad band in the 2.9–3.5 μ region; reported for α-methyl-β-(2-naphthoyl)-propionic acid (III)[4] m.p. 166–167°.

(b) **From 2-Acetonaphthone without Purification of Intermediates.**—The crude oil obtained from the condensation between 2-acetonaphthone and acetaldehyde is treated directly with zinc chloride as described. The crude residue so obtained is taken up in ethanol–acetic acid and treated with potassium cyanide as described. The crude nitrile can be hydrolyzed without further purification. The over-all yield of α-methyl-β-(2-naphthoyl)-propionic acid (III), m.p. 166.2–167.2°, is 8.2% based on 2-acetonaphthone.

α-Methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$-butenolide (I).—A mixture containing 1 g. of keto-acid III, 4 ml. of acetic anhydride, one drop of concd. sulfuric acid and 4 ml. of acetic acid was kept on the steam-bath for 2 hours. The crystalline solid obtained upon cooling was filtered and washed with acetone; yield 0.45 g., m.p. 253–255°. The analytical sample was obtained from chloroform–carbon tetrachloride, m.p. 255.0–256.6°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 80.2; H, 5.3.

When the butenolide I was refluxed with 10% aqueous alcoholic potassium hydroxide the salt of the original keto-acid was formed. Acidification yielded the keto-acid III. No precipitate was formed when compound I was treated with 2,4-dinitrophenylhydrazine reagent. No hydrogen uptake by I was observed in ethanol solution at atmospheric pressure in the presence of PtO_2.

2-Methyl-4-(2-naphthyl)-2-butene-1,4-diol (II).—A mixture of 1.5 g. of butenolide I and 74 ml. of a 0.11 *M* solution of lithium aluminum hydride in ether was kept at room temperature for 3 hours. Moist ether was added and the solid formed was removed by filtration. Removal of the ether gave 0.5 g. of white powder from which no pure compound could be isolated. The solid residue obtained by filtration was suspended in chloroform and treated with 5% hydrochloric acid. From the chloroform solution 0.9 g. of white solid was obtained. One recrystallization from chloroform–carbon tetrachloride gave 0.5 g. of II, m.p. 155–158°. The analytical sample melted at 159.1–159.5° (from ethyl acetate–hexane).

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 78.7; H, 7.2.

A sample of the unsaturated diol II (200 mg.) was oxidized with chromium trioxide–pyridine. α-Methyl-γ-(2-naphthyl)-$\Delta^{\alpha,\beta}$-butenolide (80 mg.), m.p. 255.2–255.8°, was the only isolable product.

---

(3) Presumably of *cis* configuration by analogy with the previously studied case (ref. 2).

(4) R. D. Haworth (*J. Chem. Soc.*, 1125 (1932)) prepared α-methyl-β-(2-naphthoyl)-propionic acid (III) in 17% yield from benzene and α-methylsuccinic anhydride. The keto-acid III had to be separated from about 18% of the isomeric α-methyl-β-(1-naphthoyl)-propionic acid also formed in the Friedel–Crafts reaction.

(5) Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

(6) C. Dufraisse and M. Demontvignier, *Bull. soc. chim. France*, **41**, 842 (1927), condensed acetophenone with acetaldehyde in this manner.

(7) As described below, this crude oil can be used directly in the next step.

α-Methyl-γ-(2-naphthyl)-butyrolactone.—The keto-acid III (1 g.) was dissolved in aqueous sodium hydroxide and reduced with 0.12 g. of sodium borohydride at room temperature. Acidification gave 0.75 g. of lactone, m.p. 93–95°. α-Methyl-γ-(2-naphthyl)-butyrolactone melted at 93.0–93.6°, $\lambda_{\max}^{\text{chl.}}$ 5.55 μ.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.6; H, 6.2. Found: C, 79.6; H, 6.4.

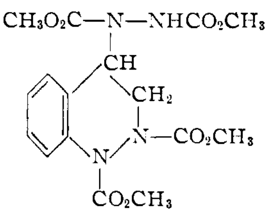
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, N. Y.

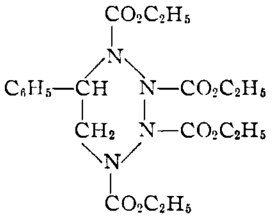
The Reaction of Ethyl Azodicarboxylate with Some Chlorostyrenes

BY NORMAN RABJOHN AND H. M. MOLOTSKY[1]

RECEIVED DECEMBER 14, 1954

Diels and Alder[2] and Ingold and Weaver[3] have reported that esters of azodicarboxylic acid react with styrene in the ratio of two moles of the ester to one of the unsaturated compound. The former workers[2] assigned structure I to the product obtained from the condensation of methyl azodicarboxylate with styrene. Ingold and Weaver[3] suggested structure II for the substance they isolated from the reaction of ethyl azodicarboxylate with styrene. The present note describes a short study of the reaction of ethyl azodicarboxylate with three chlorostyrenes.


I


II

It has been found that *o*-chlorostyrene and *p*-chlorostyrene form adducts with ethyl azodicarboxylate in benzene solution, whereas 2,6-dichlorostyrene fails to react under the same conditions. The latter result might be expected on the basis of a structure such as I.

Experimental[4]

Materials.—*o*-Chloro-, *p*-chloro- and 2,6-dichlorobenzaldehyde were supplied generously by the Heyden Chemical Corporation. These aldehydes were converted to the corresponding chlorophenylmethylcarbinols by treatment with methylmagnesium iodides. The carbinols were dehydrated to the substituted styrenes by means of potassium bisulfate according to the method of Brooks.[5] The following physical properties were observed for these materials: *o*-chlorostyrene, b.p. 106–108° (70 mm.), $n^{20}D$ 1.5637 (lit.[6] b.p. 60–61° (4 mm.), $n^{20}D$ 1.5648); *p*-chlorostyrene, b.p. 85–87° (14 mm.), $n^{20}D$ 1.5640 (lit.[6] b.p. 53–54° (3 mm.), $n^{20}D$ 1.5658) and 2,6-dichlorostyrene, b.p. 70–72° (5 mm.), $n^{25}D$ 1.5722 (lit.[6] b.p. 64–65° (3 mm.), $n^{20}D$ 1.5752).

The ethyl azodicarboxylate was prepared[7] from hydrazine and ethyl chloroformate in 66% over-all yield; b.p. 115–120° (20 mm.), $n^{25}D$ 1.4222.

Reaction of Ethyl Azodicarboxylate with the Chlorostyrenes.—A mixture of 36.3 g. (0.21 mole) of ethyl azodicarboxylate, 55 ml. of benzene and 14.8 g. (0.107 mole) of freshly prepared *p*-chlorostyrene was allowed to stand at room temperature for 40 days after which a part of the solvent was removed by evaporation. The semi-solid mass was filtered and there resulted 29.8 g. of a white, amorphous material which melted at 111–122°. The filtrate was evaporated to give a sticky residue which formed an oil readily. The latter was redissolved in benzene and passed down a column of aluminum oxide. The solution which passed through the column was evaporated to give a further 8.8 g. (75% total yield) of product. The adduct was recrystallized from an ethyl acetate–methanol mixture; m.p. 129.5–131°.

Anal. Calcd. for $C_{20}H_{27}O_8N_4Cl$: C, 49.33; H, 5.58. Found: C, 49.22; H, 5.51.

A mixture of 22.5 g. (0.13 mole) of ethyl azodicarboxylate, 75 ml. of benzene and 9.3 g. (0.067 mole) of freshly prepared *o*-chlorostyrene was caused to react under the same conditions as described in the previous experiment. After removing the solvent, a very viscous liquid was obtained which could not be induced to crystallize. It was dissolved in benzene and passed through a column packed with aluminum oxide. The solution which passed through the column was evaporated to give 11.2 g. (35%) of a glassy mass, which when scraped with a spatula formed a colorless, crystal-like substance. It melted at 52–54° after being dried for several hours at reduced pressure.

Anal. Calcd. for $C_{20}H_{27}O_8N_4Cl$: C, 49.33; H, 5.58. Found: C, 49.48; H, 5.46.

A mixture of 22.5 g. (0.13 mole) of ethyl azodicarboxylate, 25 ml. of benzene and 10.5 g. (0.06 mole) of 2,6-dichlorostyrene was allowed to stand at room temperature for 25 days during which time there had been no perceptible change in color. A sample (3.3 g.) of the reaction mixture, from which the solvent had been removed, was twice distilled to yield 0.95 g. (42% recovery) of ethyl azodicarboxylate; b.p. 117–119° (20 mm.), $n^{25}D$ 1.4215. A small amount of undistillable material remained.

A further indication that no reaction had occurred between ethyl azodicarboxylate and 2,6-dichlorostyrene was obtained by following the viscosity of a mixture which contained 0.054 mole of the ester and 0.027 mole of the dichlorostyrene in 75 ml. of benzene. No significant change was observed after 14 days at 35 ± 0.5°.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI

---

[1] Abstracted in part from the M.A. Thesis of H. M. Molotsky, 1949.

[2] O. Diels and K. Alder, *Ann.*, **450**, 237 (1926).

[3] C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, **127**, 378 (1925).

[4] All melting points are uncorrected. The authors are indebted to Mr. Y. N. Lee for the semi-micro carbon and hydrogen analyses.

[5] L. A. Brooks, THIS JOURNAL, **66**, 1295 (1944).

[6] C. S. Marvel, C. G. Overberger, R. E. Allen, H. W. Johnston, J. H. Saunders and J. D. Young, *ibid.*, **68**, 861 (1946).

[7] N. Rabjohn, *Org. Syntheses*, **28**, 58 (1948).

Preparation of Organomagnesium Compounds of Substituted Silicon Esters[1]

BY SANDERS D. ROSENBERG AND EUGENE G. ROCHOW

RECEIVED NOVEMBER 20, 1954

During the course of some research at this Laboratory, it became necessary to prepare an active organometallic intermediate of a silicon compound which contained two hydrolyzable groups in the molecule. The report of Frisch and Shroff[2] that the Grignard reagent of trimethyl-*p*-bromophenoxysilane was prepared in an 83% yield pointed the way.

It was thought that an ester such as methyl-*p*-bromophenyldiphenoxysilane would have a good chance to form a reasonably stable Grignard. The Grignard was characterized by reaction with trimethylchlorosilane.

$$CH_3Si(OC_6H_5)_2C_6H_4MgBr \xrightarrow{(CH_3)_3SiCl} (CH_3)_3SiC_6H_4Si(CH_3)(OC_6H_5)_2$$

---

[1] This research was supported by the Rubber and Plastics Branch, Wright Air Development Center.

[2] K. C. Frisch and P. D. Shroff, THIS JOURNAL, **75**, 1249 (1953).