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.

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The Reaction of Ethyl Azodicarboxylate with Some Chlorostyrenes

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

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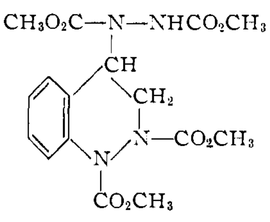
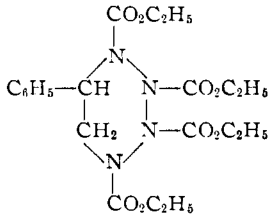
Diels and Alder[2] and Ingold and Weaver[3] have reported that esters of azodicarboxylic acid react with styrene in the ratio of two moles of the ester to one of the unsaturated compound. The former workers[2] assigned structure I to the product obtained from the condensation of methyl azodicarboxylate 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.[5] 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.[5] 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°.

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[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

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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.

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

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[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).

The yield of methyl-*p*-trimethylsilylphenyldiphenoxysilane isolated by this procedure was 14%.

In order to minimize the self-destruction of the Grignard, methyl-*p*-bromophenyldi-*o*-cresoxysilane was substituted for the phenoxysilane. The position of the methyl group *ortho* to the silicon–oxygen bond helped to improve the yield of the ester, methyl-*p*-trimethylsilylphenyldi-*o*-cresoxysilane, to 41.5%, by hindering the attack of the Grignard upon the silicon–oxygen bond.

The preparations of methyl-*p*-dimethylaminophenyldichlorosilane (32%) and methyl-*p*-dimethylaminophenyldimethoxysilane (31%) also are described, along with that of methyl-*p*-bromophenyldichlorosilane (28%). The latter compound was used as an intermediate in the preparation of the silicon esters.

Experimental

Methyl-*p*-dimethylaminophenyldichlorosilane.—*p*-Dimethylaminophenyllithium (0.27 mole) in 225 ml. of ethereal solution was added to 80.0 g. (0.54 mole) of methyltrichlorosilane in 500 ml. of ether dropwise and with good stirring. The mix was then refluxed for 0.5 hour, cooled and filtered under nitrogen. Fractional distillation of the filtrate led to the isolation of 20.0 g. (32.0%) of methyl-*p*-dimethylaminophenyldichlorosilane distilling at 106–110° (0.7 mm.), m.p. 41.5°.

Anal. Calcd. for $C_9H_{13}Cl_2NSi$: Cl, 30.22; N, 5.99. Found: Cl, 29.20; N, 6.30.

Methyl-*p*-dimethylaminophenyldimethoxysilane.—*p*-Dimethylaminophenyllithium (0.25 mole) in 225 ml. of ethereal solution was added to 68.0 g. (0.50 mole) of methyltrimethoxysilane in 500 ml. of ether. Treatment as above led to the recovery of 20.0 g. (58.8%) of methyltrimethoxysilane, b.p. 98–100° (760 mm.), and the isolation of 15.4 g. (31.3%) of methyl-*p*-dimethylaminophenyldimethoxysilane distilling at 88–90° (0.3 mm.).

Anal. Calcd. for $C_{11}H_{19}O_2NSi$: C, 58.75; H, 8.51; N, 6.23. Found: C, 58.78; H, 8.41; N, 7.22.

Methyl-*p*-bromophenyldichlorosilane.—To a rapidly stirred solution of 112 g. (0.75 mole) of methyltrichlorosilane in 750 ml. of ether was added 0.5 mole of *p*-bromophenylmagnesium bromide in 500 ml. of ethereal solution. The mix was then refluxed for 2.0 hr., allowed to stand overnight and filtered under nitrogen. The ether and excess methyltrichlorosilane were distilled and the residual oil carefully fractionated under reduced pressure.

Cut 1 distilled at 89–91° (0.7 mm.). The distillate partially solidified on cooling. The liquid portion was decanted and redistilled. A forerun, which solidified on reaching the water condenser, distilling at 64–68° (0.3 mm.) and a liquid fraction distilling at 65–68° (0.3 mm.) were obtained. The solid was combined with that previously isolated. The liquid fraction was then subjected to vacuum sublimation; the liquid was maintained at 100° and 0.2 mm., and the solid which sublimed was caught on the walls of a cold finger condenser. Cut 2 distilled at 94–174° (0.7 mm.). This fraction was redistilled to yield a solid forerun distilling at 58–60° (0.3 mm.) and a liquid fraction distilling at 67–70° (0.3 mm.).

The combined solid was crystallized from ethanol to yield 3.0 g. of *p*-dibromobenzene melting at 83–85°. The two liquid fractions were combined to give a total of 37.1 g. (27.5%) of methyl-*p*-bromophenyldichlorosilane.

Anal. Calcd. for $C_7H_7BrCl_2Si$: C, 31.13; H, 2.58. Found: C, 31.41; H, 2.73.

Methyl-*p*-bromophenyldiphenoxysilane.—In a 1-l. flask were placed 57.9 g. (0.213 mole) of methyl-*p*-bromophenyldichlorosilane, 23 g. (0.25 mole) of triethylamine and 250 ml. of ether. To this was added 40.0 g. (0.426 mole) of phenol and 22 g. (0.25 mole) of triethylamine in 250 ml. of ether, dropwise and with good stirring. The mix was refluxed for 4 hours, cooled and filtered. The ether was distilled and the residue was fractionally distilled under reduced pressure.

Cut 1 distilled at 56–90° (3.0 mm.) as a semi-solid with a pronounced phenol-like odor. Cut 2 distilled at 190–206° (1.1 mm.) as a viscous yellow oil, wt. 58.9 g. This material was redistilled to yield 43.5 g. (54.4%) of methyl-*p*-bromophenyldiphenoxysilane distilling at 183–185° (0.9 mm.), m.p. 43–44°.

Anal. Calcd. for $C_{19}H_{17}BrO_2Si$: C, 59.23; H, 4.45. Found: C, 57.63; H, 4.55.

The Methyl-*p*-bromophenyldi-*o*-cresoxysilane.—Crude methyl-*p*-bromophenyldichlorosilane was prepared by the addition of 0.70 mole of *p*-bromophenylmagnesium chloride (from 165.2 g. (0.7 mole) of *p*-dibromobenzene and 17.0 g. (0.7 g. atom) of magnesium) in 750 ml. of ether to 1.4 moles of methyltrichlorosilane in 2 l. of ether; the ethereal solution was filtered, and the ether and excess methyltrichlorosilane removed by distillation. To the crude material was added 71.0 g. (0.7 mole) of triethylamine and 1 l. of ether. A solution of 151.0 g. (1.4 moles) of *o*-cresol and 71.0 g. of triethylamine in 250 ml. of ether was added to the reaction solution in a thin stream with good stirring. The mix was then stirred overnight, filtered and the solvent distilled. The residue was then distilled under reduced pressure.

Cut 1 distilled at 60–140° (1.3 mm.). When this was redistilled at 1 atm., 44.1 g. (29.2%) *o*-cresol was recovered. Cut 2 distilled at 170–285° (1.3 mm.). This was redistilled to give a small forerun and 66.5 g. (22.3%) of methyl-*p*-bromophenyldi-*o*-cresoxysilane distilling at 196–200° (1.0 mm.).

Anal. Calcd. for $C_{21}H_{21}BrO_2Si$: C, 61.10; H, 5.12. Found: C, 61.05; H, 5.10.

Methyl-*p*-trimethylsilylphenyldiphenoxysilane.—In a 100-ml. flask were placed 14.3 g. (0.037 mole) of methyl-*p*-bromophenyldiphenoxysilane, 0.9 g. (0.37 g. atom) of magnesium turnings, 8.0 g. (0.074 mole) of trimethylchlorosilane and 50 ml. of ether. The reaction was initiated by the addition of 0.5 ml. of ethyl bromide, and was stirred and refluxed for 3.5 hr. On cooling, the mix was filtered, the ether removed by distillation and the residue distilled under reduced pressure. One fraction distilling at 156–180° (1.0 mm.) was obtained. This was redistilled to yield 2.0 g. (14.0%) of methyl-*p*-trimethylsilylphenyldiphenoxysilane distilling at 172° (1.0 mm.).

Anal. Calcd. for $C_{22}H_{26}O_2Si_2$: C, 69.80; H, 6.93. Found: C, 70.12; H, 6.12.

Methyl-*p*-trimethylsilylphenyldi-*o*-cresoxysilane.—In a 300-ml. flask were placed 31.5 g. (0.076 mole) of methyl-*p*-bromophenyldi-*o*-cresoxysilane, 16.5 g. (0.152 mole) of trimethylchlorosilane, 3.4 g. (0.15 g. atom) of magnesium turnings and 100 ml. of ether. The reaction was initiated by the addition of 4.3 g. (0.04 mole) of ethyl bromide and was then stirred and refluxed for 6 hr. The mix was cooled, filtered, the ether removed by distillation and the residue distilled under reduced pressure. After a small forerun, the fraction distilling at 175–200° (1.0 mm.) was collected. This was carefully redistilled to yield 12.8 g. (41.5%) of methyl-*p*-trimethylsilylphenyldi-*o*-cresoxysilane distilling at 182–185° (0.6 mm.).

Anal. Calcd. for $C_{24}H_{30}O_2Si_2$: C, 70.90; H, 7.44. Found: C, 72.94; H, 7.03.

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Low and High *p*H Effects in Serum Albumin[1]

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Serum albumin exhibits various anomalies in its reactivity with hydrogen ions[2] and other low molecular weight ions and molecules[3] at low and high *p*H. The cause of these anomalies would be better understood if information were available about the configuration of serum albumin over the

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[1] The part of this work carried out at Cornell University was supported by the Office of Naval Research and Eli Lilly and Co.

[2] C. Tanford, *Proc. Iowa Acad. Sci.*, **59**, 206 (1952); Abstracts of September 1954 ACS meeting, p. 77C.

[3] I. M. Klotz and J. Ayers, *Disc. Faraday Soc.*, **13**, 189 (1953).