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]

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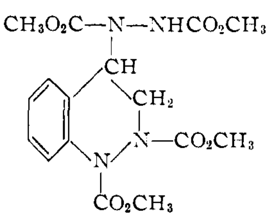
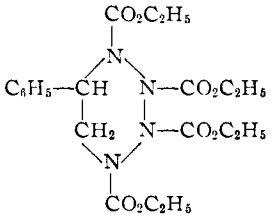
Diels and Alder[2] and Ingold and Weaver[3] have reported that esters of azodicarboxylic acid react with styrene in the ratio of two moles of the ester to one of the unsaturated compound. The former workers[2] assigned structure I to the product obtained from the condensation of methyl azodicarboxylate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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI
COLUMBIA, MISSOURI

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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**, 278 (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).

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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).