[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

The Use of Liquid Phase Oxidation for the Preparation of Nuclearly Substituted Styrenes. IV.[1] *m*-Chlorostyrene

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m-Chlorostyrene has been prepared by heating *m*-chlorophenylmethylcarbinol with potassium bisulfate at reduced pressure[3,4,5] in yields as high as 83%.[4] The carbinol was prepared by treating *m*-chlorobenzaldehyde with methylmagnesium iodide[4,5] or by treating acetaldehyde with *m*-chlorophenylmagnesium bromide.[3]

We have found that chlorobenzene can be alkylated with ethylene in the presence of aluminum chloride to give *m*-chloroethylbenzene in 37% conversion and 80% yield. Oxidation of *m*-chloroethylbenzene with air at 100 p. s. i. pressure in the presence of a chromium oxide catalyst gave *m*-chloroacetophenone in 26% conversion and 76% yield. This ketone was hydrogenated to *m*-chlorophenylmethylcarbinol in 94% yield by means of hydrogen and copper chromite. While this preparation of the carbinol from chlorobenzene involves three steps, the yields are good and the use of such difficultly available intermediates as *m*-chlorobenzaldehyde and *m*-chlorobromobenzene is avoided. The 84% yield of *m*-chlorostyrene, obtained by dehydrating *m*-chlorophenylmethylcarbinol in the vapor phase over alumina, is comparable to the 83% reported for the potassium bisulfate method.[4]

A still better method of synthesis was found to involve the chlorination of *m*-chloroethylbenzene in the presence of light and a phosphorus trichloride catalyst to give α,*m*-dichloroethylbenzene in 44% conversion and 91% yield. When the vapors of the latter compound, together with steam, were passed over a calcium sulfate catalyst, *m*-chlorostyrene was obtained in 93% yield.

Experimental

***m*-Chloroethylbenzene.**—Chlorobenzene was treated with ethylene in the presence of aluminum chloride in an autoclave equipped with a stirrer and gas inlet. The charge consisted of 3178 g. of chlorobenzene, 45.4 g. of ethyl chloride and 90.8 g. of anhydrous aluminum chloride. While the temperature was held at 100°, 454 g. of ethylene was introduced over a two-hour period. The mixture was then cooled, removed from the autoclave and poured into 5 kg. of ice water containing 100 cc. of concentrated hydrochloric acid. After the complex had decomposed, the organic layer was separated, dried over anhydrous potassium carbonate and distilled. In this way there was obtained 1702 g. (53.7% recovery) of chlorobenzene, b. p. <68° at 14 mm., $n^{25}\mathrm{D}$ 1.5213–1.5201; 1478 g. (37.3% conversion and 80.2% yield) of *m*-chloroethylbenzene, b. p. 68–74° at 14 mm.,[6] $n^{25}\mathrm{D}$ 1.5181–1.5160 (1103 g., b. p. 68–72° at 14 mm., $n^{25}\mathrm{D}$ 1.5171–1.5168); and 361 g. (7.6% calculated as chlorodiethylbenzene) of more highly alkylated material. The residue was 21 g.

***m*-Chloroacetophenone.**—Into a stirred autoclave equipped with a reflux condenser and gas outlet, thermowell and air inlet there was placed 500 g. of *m*-chloroethylbenzene and 5 g. of chromium oxide. While this mixture was stirred at a temperature of 140–155°, 3 cu. ft./hr. of air at 100 p. s. i. was introduced for a six-hour period. After cooling, the autoclave was opened, and the reaction mixture removed and filtered. By washing the solution with aqueous alkali and acidifying the extract there was obtained 8.1 g. (1.4%) of *m*-chlorobenzoic acid. The organic layer was distilled to obtain 331.5 g. (66.2% recovery) of *m*-chloroethylbenzene, b. p. 65–69° at 13 mm., $n^{25}\mathrm{D}$ 1.5181–1.5161, and 140.6 g. (25.6 % conversion and 76.0% yield) of *m*-chloroacetophenone, b. p. 76–92° at 3 mm., $n^{25}\mathrm{D}$ 1.5462–1.5491. The tarry residue weighed 13.7 g. (2.5%).

***m*-Chlorophenylmethylcarbinol.**—A standard American Instrument Company hydrogenation autoclave was charged with 100 g. of *m*-chloroacetophenone and 10 g. of copper chromite. The initial hydrogen pressure was 980 p. s. i. at 27°. Hydrogenation was conducted at 140° for seven hours. After the catalyst was removed by filtration, the product was distilled to give 94.9 g. (94%) of *m*-chlorophenylmethylcarbinol, b. p. 85–89° at 2 mm. (102–104° at 3 mm.),[4] $n^{25}\mathrm{D}$ 1.5418 ($n^{20}\mathrm{D}$ 1.5438).[4]

***m*-Chlorostyrene.**—A pyrolysis tube[7] was packed with activated alumina. Over a forty-minute period 74 g. of *m*-chlorophenylmethylcarbinol, together with some steam, was passed through the tube at 90 mm. pressure and 313–340°. Upon cooling, the tube was washed out with benzene and the distillate extracted with the same solvent. The combined washings and extracts were distilled from a trace of sulfur and hydroquinone to give 55 g. (84%) of *m*-chlorostyrene, b. p. 75–79° at 15 mm. (62–63° at 6 mm.),[4] $n^{25}\mathrm{D}$ 1.5612 ($n^{20}\mathrm{D}$ 1.5619).[4]

α,*m*-Dichloroethylbenzene.—A 1-liter three-necked flask equipped with a stirrer, condenser, thermometer and gas inlet tube was charged with 562 g. of *m*-chloroethylbenzene and 3 g. of phosphorus trichloride. While the temperature was maintained at 10–15° by means of an ice-salt-bath and the flask was illuminated with ultraviolet light, chlorine was introduced until a gain of 85 g. was observed. Direct distillation of the reaction mixture yielded 292.6 g. (52.1% recovery) of *m*-chloroethylbenzene, b. p. 70° at 17 mm.–74° at 16 mm., $n^{25}\mathrm{D}$ 1.5172–1.5183 and 306.2 g. (43.6% conversion and 91.4% yield) of α,*m*-dichloroethylbenzene, b. p. 63–70° at 2 mm., $n^{25}\mathrm{D}$ 1.5401–1.5423. The tarry residue weighed 8.7 g. (1.0%).

***m*-Chlorostyrene.**—The pyrolysis tube was packed with calcium sulfate (Drierite). Over a one hundred sixty-minute period 250 g. of α,*m*-dichloroethylbenzene, together with about three (liquid) volumes of steam, was passed through the tube at 90 mm. pressure and 425–475°. Upon cooling, the tube was washed out with 50

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[1] For the preceding paper in this series see Emerson, Heyd, Lucas, Lyness, Owens and Shortridge, THIS JOURNAL, **69**, 1905 (1947).

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[3] Marvel and Schertz, THIS JOURNAL, **65**, 2054 (1943).

[4] Brooks, *ibid.*, **66**, 1295 (1944).

[5] Ushkov and Matuzov, *J. Gen. Chem.*, **14**, 120 (1944); *Chem. Abstr.*, **39**, 916 (1945).

[6] Dreisbach, U. S. Patent 2,159,370; *Chem. Abstr.*, **33**, 6875 (1939), describes the ethylation of chlorobenzene. He obtained about 80% of *m*-chloroethylbenzene contaminated with 20% of the *ortho* isomer. Some of our *m*-chloroethylbenzene was redistilled through a four-foot Vigreux column. The middle cut (88%) boiled at 65–68° (13 mm.), $n^{25}\mathrm{D}$ 1.5172. Oxidation of this fraction gave *m*-chlorobenzoic acid, m. p. 157–158° (cor.) after one crystallization from aqueous ethanol (Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1943, Vol. I, p. 439, gives m. p. 158°.)

[7] Emerson and Agnew, THIS JOURNAL, **67**, 518 (1945).

cc. of benzene and the combined distillate and washings were extracted three times with benzene. These combined extracts were washed free of acid with aqueous sodium bicarbonate and then distilled from a trace of sulfur and hydroquinone to give 183 g. (92.5%) of *m*-chlorostyrene, b. p. 76–81° at 17 mm. (62–63° at 6 mm.),[4] n^{25}_D 1.5616 (n^{20}_D 1.5619).[4]

Summary

The preparation of *m*-chlorostyrene from *m*-chloroethylbenzene by two routes has been described. The first involves oxidation to *m*-chloroacetophenone, hydrogenation to *m*-chlorophenylmethylcarbinol and dehydration in the vapor phase to *m*-chlorostyrene. The second involves chlorination to α,*m*-dichloroethylbenzene followed by dehydrochlorination in the vapor phase to *m*-chlorostyrene.

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The Synthesis and Reactions of Disazodicarboxylates[1]

BY NORMAN RABJOHN

The azo group in esters of azodicarboxylic acid is very reactive and will add to numerous compounds possessing active hydrogen atoms. Alder, Pascher and Schmitz[2] have shown that ethyl azodicarboxylate forms adducts with natural and synthetic rubbers.

The facility with which azo compounds of this type add to rubber and related polymers suggested that compounds containing two such active groups in the same molecule should be useful cross-linking agents. If current hypotheses concerning the nature of vulcanization are correct, then such compounds ought to be effective vulcanizing agents. They conceivably could be of value in quantitative vulcanization studies since they offer the possibility of introducing controlled numbers of cross-linkages between rubber molecules, or other similarly unsaturated polymers, by a comparatively simple addition reaction. Accordingly, the synthesis of disazodicarboxylates and the investigation of their properties was undertaken as described in the present paper.

A number of these azo esters have been obtained by the following series of reactions

$$\mathrm{HOROH} + 2\mathrm{COCl_2} \longrightarrow \mathrm{ClCO_2ROCOCl}\ (\mathrm{I}) + 2\mathrm{HCl}$$

$$\mathrm{H_2NNH_2} + (\mathrm{R'O})_2\mathrm{CO} \longrightarrow \mathrm{H_2NNHCO_2R'}(\mathrm{II}) + \mathrm{R'OH}$$

$$\mathrm{ClCO_2ROCOCl} + 2\mathrm{H_2NNHCO_2R'} \xrightarrow{\mathrm{R_3''N}} (\mathrm{R'OCONHNHCO_2})_2\mathrm{R}\text{—}\ (\mathrm{III}) + 2\mathrm{R_3''N{\cdot}HCl}$$

$$(\mathrm{R'OCONHNHCO_2})_2\mathrm{R}\text{—} \xrightarrow{[\mathrm{O}]} (\mathrm{R'OCON{=}NCO_2})_2\mathrm{R}\text{—}\ (\mathrm{IV}) + 2\mathrm{H_2O}$$

The nature of the R and R′ groups has been varied and their combinations are shown in Table II. The dichlorocarbonates (I) were prepared by two different procedures. Aromatic dichlorocarbonates were obtained by the method of Oesper, Broker and Cook[3]; aliphatic dichlorocarbonates were synthesized by merely adding a glycol to an excess of liquid phosgene. All of the aliphatic dichlorocarbonates are high-boiling liquids which can be distilled in some cases under reduced pressure without appreciable decomposition. Since they could not be obtained in an analytically pure condition, they were converted to the corresponding diurethans (Table I) for the purpose of identification.

The esters of hydrazine monocarboxylic acid were prepared according to the procedure of Diels.[4] The bis-hydrazodicarboxylates (III) (Table II) are all relatively high melting solids which were obtained in yields of 80–90%. They were oxidized to the corresponding disazodicarboxylates (IV) in good yields by means of nitric acid or hypochlorous acid. The dis-azo esters are in most instances viscous, orange-colored oils which are thermally unstable above 125° and cannot be distilled without decomposition; however, they appear to be stable at room temperature. The dis-azo esters prepared from aromatic dichlorocarbonates are solids. They decomposed within a few hours at room temperature or during attempts to purify them by crystallization. Only those disazodicarboxylates which are listed in Table III were obtained in a satisfactory state of purity. They absorbed the theoretical amount of hydrogen when shaken over platinum oxide catalyst, being regenerated to the bis-hydrazodicarboxylates.

All of the disazodicarboxylates reacted rapidly with natural and synthetic rubbers at relatively low temperatures; good vulcanizates were obtained without the aid of other ingredients. The vulcanization studies will be reported elsewhere.[5]

To gain an insight into the manner in which these dis-azo esters vulcanize rubber, a study was made of the reaction between ethyl azodicarboxylate (V) and 2-methyl-2-butene (VI). Although the former is monofunctional, its mode of addition should be analogous to that of a disazodicarboxylate. The 2-methyl-2-butene may be considered to be representative of an isoprene unit in natural

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(2) Alder, Pascher and Schmitz, *Ber.*, **76**, 27 (1943).

(3) Oesper, Broker and Cook, THIS JOURNAL, **47**, 2609 (1925).

(4) Diels, *Ber.*, **47**, 2183 (1914).

(5) Flory, Rabjohn and Shaffer, forthcoming publication.