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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(1) Presented in part at the September, 1946, Meeting of the American Chemical Society.

(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.

TABLE I

ALIPHATIC DIURETHANS ($H_2NCO_2ROCONH_2$)

R	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$—(CH_2)_2—$	165–166	$C_4H_8O_4N_2$	32.43	32.73	5.41	5.61
$—(CH_2)_3—$	168–169	$C_5H_{10}O_4N_2$	37.04	37.01	6.17	6.39
$—(CH_2)_4—$	198–199	$C_6H_{12}O_4N_2$	40.91	41.08	6.82	6.80
$—(CH_2)_6—$	187–188	$C_8H_{16}O_4N_2$	47.06	47.19	7.84	7.93
$—(CH_2)_{10}—$	171–172	$C_{12}H_{24}O_4N_2$	55.38	55.38	9.23	9.36
$—(CH_2CH_2)_2—O—$	150–151	$C_6H_{12}O_5N_2$	37.50	38.00	6.25	6.35

TABLE II

BIS-HYDRAZODICARBOXYLATES ($R'OCONHNHCO_2ROCONHNHCO_2R'$)

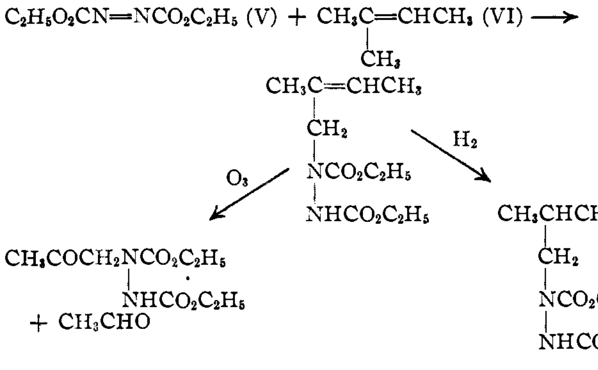
R'	R	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$—C_2H_5$	$—(CH_2)_2—$	104–105	$C_{10}H_{18}O_8N_4$	37.27	37.35	5.59	5.68
$—C_2H_5$	$—(CH_2)_4—$	178–179	$C_{12}H_{22}O_8N_4$	41.14	41.28	6.29	6.28
$—C_2H_5$	$—(CH_2)_6—$	154–155	$C_{14}H_{26}O_8N_4$	44.44	44.67	6.88	7.09
$—C_2H_5$	$—(CH_2)_{10}—$	87–88	$C_{18}H_{34}O_8N_4$	49.77	50.05	7.83	7.98
$—CH_2C_6H_5$	$—(CH_2)_{10}—$	79–80	$C_{28}H_{38}O_8N_4$	60.21	59.90	6.81	6.89
$—C_{10}H_{21}$	$—(CH_2)_{10}—$	91–92	$C_{34}H_{66}O_8N_4$	62.01	62.29	10.03	10.05
$—C_2H_5$	$—(CH_2CH_2)_2—O—$	129–130	$C_{12}H_{22}O_9N_4$	39.34	39.40	6.01	6.09
$—C_2H_5$	$—C_6H_4—$	191–192	$C_{14}H_{18}O_8N_4$	45.41	45.61	4.87	4.99
$—C_2H_5$	$—C_6H_4—C(CH_3)_2—C_6H_4—$	222–224	$C_{23}H_{28}O_8N_4$	56.56	56.26	5.74	5.94

TABLE III

DISAZODICARBOXYLATES ($R'OCON{=}NCO_2ROCON{=}NCO_2R'$)

R'	R	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$—C_2H_5$	$—(CH_2CH_2)_2—O—$	80–85 (10^{-4} mm.)	$C_{12}H_{18}O_9N_4$	39.78	40.04	4.97	5.13
$—CH_3$	$—(CH_2)_{10}—$	38–39	$C_{16}H_{26}O_8N_4$	47.76	47.83	6.47	6.52
$—C_{10}H_{21}$	$—(CH_2)_{10}—$	35–36	$C_{34}H_{62}O_8N_4$	62.39	62.75	9.48	9.60

rubber. The following reactions indicate that the azodicarboxylate system adds to the olefin by attacking a carbon atom *alpha* to a double bond.



It can be argued then that the disazodicarboxylates vulcanize rubber by the establishment of cross-links between polymer chains caused by the attachment of azodicarboxylate systems at *alpha* methylenic carbon atoms. This agrees with the findings of Farmer[6] that many reagents undergo reaction with rubber at this position.

Experimental

Preparation of Dichlorocarbonates.—The following procedure is representative of the method employed for the preparation of aliphatic dichlorocarbonates. Twenty grams (0.22 mole) of tetramethylene glycol was added dropwise to 150 g. (1.5 moles) of liquid phosgene which was cooled in an ice-bath. The addition of the glycol was regulated so that the temperature remained below 10°. The excess phosgene was allowed to evaporate and the residue was warmed at 40–50° (20 mm.) to remove traces of phosgene and hydrogen chloride. There was obtained 47.5 g. (99%) of tetramethylene dichlorocarbonate as an almost colorless, slightly viscous liquid. Due to a tendency to decompose at the high temperature required for distillation, it was impossible to obtain a sample pure enough for analysis. The dichlorocarbonate was identified by shaking a small sample with aqueous ammonia to obtain the corresponding diurethan (Table I).

All of the aliphatic dichlorocarbonates prepared by this procedure were obtained in essentially quantitative yields.

The aromatic dichlorocarbonates were synthesized by condensing the diphenols with phosgene in the presence of a tertiary amine according to the method of Oesper, Broker and Cook.[3]

Preparation of bis-Hydrazodicarboxylates.—The procedure employed for the preparation of decamethylene bis-methyl hydrazodicarboxylate is general for this class of compounds. To a solution of 12 g. (0.134 mole) of hydrazine monocarboxylic acid methyl ester in 200 cc. of dioxane were added dropwise 20 g. (0.067 mole) of decamethylene dichlorocarbonate and 13.5 g. (0.134 mole) of triethylamine. The dichlorocarbonate was kept in excess during the addition. The reaction mixture was allowed to stir until it had cooled and the precipitate of triethylamine hydrochloride was removed by filtration. The filtrate was concentrated under reduced pressure and the residue was dissolved in a mixture of ethyl acetate and

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(6) Farmer, *Trans. Faraday Soc.*, **38**, 340 (1942).

hexane. Upon standing for several hours a white solid precipitated; m. p. 109–111°; yield 23 g. (85%). After recrystallization from a mixture of ethyl acetate and hexane, the product melted at 112–113°.

Anal. Calcd. for $C_{16}H_{30}O_8N_4$: C, 47.29; H, 7.39. Found: C, 47.34; H, 7.59.

Preparation of Disazodicarboxylates.—The oxidation of decamethylene bis-methylhydrazodicarboxylate to the corresponding azo compound is typical. Sixteen grams of decamethylene bis-methylhydrazodicarboxylate was dissolved in 130 cc. of concentrated nitric acid. A slow oxidation took place and within about ten minutes an orange-colored oil formed as an upper layer. When this layer no longer appeared to increase, the reaction mixture was poured onto 500 g. of crushed ice. The azo compound was removed by extraction with benzene. The extract was washed with water, several times with 10% sodium bicarbonate solution and again with water. It was dried over anhydrous sodium sulfate and then concentrated under reduced pressure on a steam-bath. The residue was crystallized from a mixture of ethyl acetate and hexane. There was obtained 13 g. (82%) of decamethylene dis-methylazodicarboxylate as a bright, orange-colored solid; m. p. 38–39°.

Anal. Calcd. for $C_{16}H_{26}O_8N_4$: C, 47.76; H, 6.47. Found: C, 47.83; H, 6.52.

This compound was prepared also in satisfactory yield by passing chlorine into a well-stirred mixture of the bis-hydrazodicarboxylate and water.

Many of the disazodicarboxylates prepared by the nitric acid oxidation procedure did not form oil layers during the oxidation step. In such cases, the reaction became quite vigorous and was stopped by pouring onto ice.

Only those disazodicarboxylates which are solids (with the exception of diethylene dis-ethyl azodicarboxylate which was distilled at approximately 10^{-4} mm.) could be purified sufficiently for analysis. All of the disazodicarboxylates decomposed with the evolution of a gas when heated above 125°.

Preparation of Hydrazine Monocarboxylic Acid Esters.—The methyl and ethyl esters were obtained by the method of Diels.[4] The benzyl ester was prepared in a similar manner except that the condensation was carried out at steam-bath temperature and the ester was isolated as the hydrochloride salt; m. p. 186–187°. Neut. equiv. Calcd. for $C_8H_{11}O_2N_2Cl$: 202.5. Found: 205. Upon treating the hydrochloride with concentrated sodium hydroxide solution, the free ester resulted in 75% overall yield; m. p. 69–70°. It was purified by crystallization from a mixture of ethyl acetate and hexane. *Anal.* Calcd. for $C_8H_{10}O_2N_2$: C, 57.83; H, 6.02. Found: C, 57.83; H, 5.96. Hydrazine monocarboxylic acid *n*-decyl ester was obtained in 65% yield by heating di-*n*-decyl carbonate and 85% hydrazine hydrate at 115° for seventy-two hours. After crystallization from dilute alcohol, it melted at 58–59°. *Anal.* Calcd. for $C_{10}H_{24}O_2N_2$: C, 61.11; H, 11.11. Found: C, 61.35; H, 11.16.

Reduction of Decamethylene dis-Methyl Azodicarboxylate.—Two grams of the azo compound was dissolved in 100 cc. of dioxane and shaken with 0.1 g. of platinum oxide catalyst under hydrogen at a pressure of 50 lb./sq. in. The hydrogen uptake was rapid and within twenty minutes the solution was colorless. The drop in pressure corresponded to the theoretical amount of hydrogen required for reduction. The catalyst was removed by filtration and the filtrate was concentrated. The residue was dissolved in a mixture of ethyl acetate and hexane. There was obtained 1.9 g. of a white solid which melted at 112–113°. The melting point of a mixture of this substance and a known sample of decamethylene *bis*-methyl hydrazodicarboxylate was not depressed.

Condensation of Ethyl Azodicarboxylate with 2-Methyl-2-butene.—The ethyl azodicarboxylate was prepared according to the method of Ingold and Weaver.[7] 2-Methyl-2-butene was synthesized by dehydrating *t*-amyl alcohol after the procedure of Norris and Reuter.[8] The dehydration product (b. p. 36.5–38.5°) was purified[9] by careful fractionation with methyl alcohol through a 25 mm. × 72" Podbielniak column. The product was washed with water to remove the methyl alcohol, dried over anhydrous potassium carbonate and then refractionated though a 13 mm. × 72" Podbielniak column; $n^{20}\mathrm{D}$ 1.3874.

A mixture of 41.5 g. (0.24 mole) of ethyl azodicarboxylate and 50 g. (0.71 mole) of 2-methyl-2-butene was allowed to stand at room temperature for nine days. The excess 2-methyl-2-butene was removed and the residue was distilled *in vacuo*. There was obtained 54 g. (92%) of a viscous, colorless oil which boiled at 128–129° (3 mm.); $n^{20}\mathrm{D}$ 1.4613. *Anal.* Calcd. for $C_{11}H_{20}O_4N_2$: C, 54.10; H, 8.19. Found: C, 53.94; H, 8.22.

A 10-g. sample of this material was dissolved in 100 cc. of alcohol and reduced with hydrogen over Adams catalyst. The resulting product boiled at 115–116° (2 mm.); $n^{20}\mathrm{D}$ 1.4507. *Anal.* Calcd. for $C_{11}H_{22}O_4N_2$: C, 53.66; H, 8.94. Found: C, 53.63; H, 9.01.

Seven grams of the adduct of ethyl azodicarboxylate and 2-methyl-2-butene was dissolved in 100 cc. of chloroform. A stream of ozonized air, containing about 2% of ozone, was bubbled through the solution for six hours at 0°. The solvent was removed under reduced pressure and the residue was boiled with 50 cc. of water for three hours. The flask was equipped with a column to keep back the water and the gases were led below the surface of 50 cc. of alcohol. After decomposition of the ozonide had been completed, the alcohol solution was treated with 2,4-dinitrophenylhydrazine. A yellow colored solid was obtained which melted at 147–148°. The melting point of a mixture of this material and a known sample of acetaldehyde 2,4-dinitrophenylhydrazone showed no depression.

The residue was extracted with chloroform and the extract was washed with water, with sodium bicarbonate solution and again with water. It was dried over anhydrous sodium sulfate and the solvent removed. The residue amounted to about 6 g. It was distilled *in vacuo*; b. p. 150–151° (3 mm.); $n^{20}\mathrm{D}$ 1.4543.

Anal. Calcd. for $C_9H_{16}O_5N_2$: C, 46.55; H, 6.89. Found: C, 47.05; H, 7.14.

Summary

1. A method of synthesis of disazodicarboxylates has been described. These substances are capable of vulcanizing both natural and synthetic rubbers.

2. The condensation of ethyl azodicarboxylate with 2-methyl-2-butene has been studied. It has been shown that the azo ester system undergoes reaction at an α-methylenic carbon atom.

3. Accordingly, disazodicarboxylates must produce vulcanization by the establishment of cross-linkages between polymer chains.

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[7] Ingold and Weaver, *J. Chem. Soc.*, **127**, 378 (1925).

[8] Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927).

[9] The author wishes to thank Dr. J. R. Long for performing this purification.