TABLE I

DATA ON COPOLYMERIZATIONS BY DIFFERENT CATALYSTS OF 0.02 MOLE OF STYRENE AND 0.02 MOLE METHYL METHACRYLATE

Catalyst	Mole % catalyst	Temp., °C.	Time, hr.	Yield, % by wt. of monomers used	C, %	H, %	Mole % styrene in polymer
Na	[a]	Room	65	11	60.17 ± 0.04	8.16 ± 0.01	0.6 ± 0.1
$(C_6H_5)_3CNa$	1.0	Room	24.5	18.4	60.27 ± .24	8.12 ± .23	0.80 ± 0.65
$(C_6H_5)_3CNa$	0.5	Room	65	11.8	60.88	6.11	2.79
$(C_6H_5COO)_2$	0.1	60	7.7	12.3	76.18	7.99	50.19
$(p\text{-}ClC_4H_4COO)_2$	0.1	60	16	21.3	75.70	8.31	48.70
$(t\text{-}C_4H_9O)_2$	0.1	100	2.5	17.5	75.81 ± .58	8.15 ± .15	49.04 ± 1.80

[a] On shaking machine.

because its solubility in ether ensured separation from excess sodium) was prepared from triphenylmethyl chloride and sodium in ether solution.[8]

Procedure.—Techniques previously reported were used for the preparation[9] and purification[10] of the polymers. In the reaction with triphenylmethylsodium, an ether solution of the catalyst was added to the monomer mixture. The degassing process was carried out with a conventional high vacuum system and a pressure of 2.5 × 10^{-4} mm. was obtained at least three times before the sample was allowed to polymerize for the indicated time. Repetition of polymerizations previously reported[3] was undertaken to determine the accuracy in duplication of the previous work, and good agreement was obtained. The results are given in Table I.

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[8] *Org. Syntheses*, **19**, 83 (1939).

[9] F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944).

[10] F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

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1,3,5-Trichloro-2,4,6-tribromocyclohexane

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RECEIVED MAY 13, 1954

Benzene reacts with chlorine to form a mixture of isomers of benzene hexachloride and with bromine to yield a mixture of the hexabromides, but chlorine does not react with benzene hexabromide with the replacement of any bromine atoms. Under the conditions described below the reaction of benzene with a mixture of chlorine and bromine yields a product which is probably a mixture of isomers of 1,3,5-trichloro-2,4,6-tribromocyclohexane, eight of which are theoretically possible with a cyclohexane of planar configuration. On alkaline hydrolysis 3 moles of the alkali bromide and 1,3,5-trichlorobenzene were obtained. The formation of 1,3,5-trichloro-2,4,6-tribromocyclohexane is best explained if a chemical combination of chlorine and bromine is assumed; the existence of chlorine bromide has been suggested, but not conclusively demonstrated.

The insecticidal potency of the mixture against roaches and mites is about the same as that of crude benzene hexachloride.

Experimental

Under actinic irradiation and at temperatures below 10°, benzene reacted quantitatively with stoichiometric amounts of chlorine and bromine to yield a solid product which was recrystallized from hot glacial acetic acid as colorless plates of 1,3,5-trichloro-2,4,6-tribromocyclohexane, m.p. 171° with slight decomposition.[1]

Anal. Calcd. for $C_6H_6Cl_3Br_3$: C, 16.99; H, 1.43; Cl, 25.07; Br, 58.51; mol. wt., 424.24. Found: C, 16.3; H, 1.47; Cl, 22.38; Br, 56.42; mol. wt., 427.

The compound is soluble in most organic solvents with the exception of carbon tetrachloride. On alkaline hydrolysis it yielded 3 moles of alkali bromide and a water-insoluble oil, 1,3,5-trichlorobenzene; b.p. 208° (760 mm.), Cl 58%.

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[1] Tests were carried out by courtesy of Niagara Chemical Division of Food Machinery and Chemical Corporation, Middleport, N. Y.

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Pyrosynthesis of Aspartic Acid and Alanine from Citric Acid Cycle Intermediates[1]

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RECEIVED JUNE 21, 1954

Experiments directed toward synthesis of true protein, and elucidation of its primordial origin[2] and subsequent evolution[3] have been performed. In the course of these experiments, almost all chromatographic evaluations of pyropolymerization of various pairs of DL-amino acids revealed, following hydrolysis, a number of ninhydrin-reactive spots which exceeded the number of reactants. These results indicate that the conditions which produce polymers[2,4] from unsubstituted amino acids lead also to the formation of additional amino acids (and in part possibly to amines).

Attention was diverted to a possible thermal origin of aspartic acid from the citric acid cycle by the postulate that those features of current biochemistry which are biologically relatively ubiquitous were also part of a primordial biochemistry.[5] Over a century ago, aspartic acid had been prepared by heating ammonium fumarate or ammonium malate[6,7] although of course not with reference to the now recognized citric acid cycle.

In the present experiments, ammonium salts of two additional acids from the citric acid cycle were each heated for up to three hours at 200°, chromatographed, and also hydrolyzed and chromatographed. Faint ninhydrin spots were obtained from heated ammonium fumarate and ammonium malate, although there were none from ammonium citrate or ammonium succinate either before or

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[1] Journal paper No. J-2546 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 1111, supported by the Rockefeller Foundation.

[2] S. W. Fox and M. Middlebrook, *Federation Proc.*, **13**, 211 (1954).

[3] S. W. Fox, *Am. Naturalist*, **87**, 253 (1953).

[4] H. Schiff, *Ann.*, **307**, 231 (1899).

[5] Additional reasons for this particular study were the facts that aspartic acid is an *early* or the earliest amino acid in biosynthesis and that its metabolic origin is from the citric acid cycle (see E. Baldwin, "Dynamic Aspects of Biochemistry," the University Press, Cambridge, 1952).

[6] J. Wolff, *Ann.*, **75**, 294 (1850).

[7] Dessaignes, *Compt. rend.*, **30**, 324 (1850).