in the 278–291 mμ region. One pure isomer, assigned the 1,7-diyne structure IV or a stereoisomeric one for symmetry reasons, could be isolated in ca. 5% yield as very unstable dark-brown plates (red-brown in solution), m.p. 59–60° dec. (sample placed on block just before); $\lambda_{max}^{isooctane}$ 279 and 290 mμ (ϵ 49,500 and 51,000) with absorption beyond 600 mμ; acetylene band at 4.58 μ in the infrared (chloroform). The monocyclic nature of the substance was demonstrated by full hydrogenation to cyclohexadecane. In addition, the reaction of III with potassium t-butoxide produced at least 15% of 10-diphenylsuccindene (V)[5] [slightly yellow plates, m.p. 212–213°; $\lambda_{max}^{isooctane}$ 230, 236, 243, 303, 314, 323 and 330 mμ (ϵ 12,800, 14,700, 12,000, 24,500, 28,800, 20,800 and 17,800)], identified with an authentic sample kindly provided by Prof. Fieser. This transannular reaction product was formed in over 50% yield when III was treated with boiling ethanolic potassium hydroxide.

Coupling of the linear dimer II (1 part) with cupric acetate (5 parts) in pyridine (300 parts) and ether (300 parts)[6,7] at 55° for 3.5 hr. yielded (besides other substances) ca. 1.5% of another bisdehydro[16]annulene, as well as material with main ultraviolet maxima at 362 and 392 mμ which was also formed by treatment of II with potassium t-butoxide in t-butyl alcohol and presumably consists of conjugated hexadecahexaenediyne(s). The new bisdehydro[16]annulene formed dark-brown needles (red in solution), m.p. 79–80° dec. (sample placed on block just before); $C_{16}H_{12}$ (found: C, 94.13; H, 5.67); $\lambda_{max}^{isooctane}$ 273, 279 and 290 mμ (ϵ 61,500, 63,500 and 43,500) with absorption beyond 600 mμ; acetylene band at 4.60 μ in the infrared (chloroform); converted by full hydrogenation to cyclohexadecane. The substance was very unstable, e.g., it was almost completely decomposed after 15 minutes' standing in air and day-light, and detonated with a flash of fire on being rubbed with a spatula.

The last-described bisdehydro[16]annulene could not have been formed from II via III, since the latter was unaffected on being subjected to the reaction conditions which had given the conjugated substance. We believe the latter most probably to contain a 1,3-diyne grouping (VI or a stereoisomer), formed from II by rearrangement to hexadeca-3,5,7,9,11,13-hexaene-1,15-diyne(s) followed by oxidative ring-closure (or possibly by partial rearrangement of II, followed by ring-closure and further rearrangement). This type of pathway is supported by the formation of a considerable amount of conjugated hexadecahexaenediyne(s) in the reaction.

Partial hydrogenation of the last-mentioned bisdehydro[16]annulene in benzene over a "Lindlar" palladium catalyst yielded ca. 30% of a monodehydro[16]annulene (VII or a stereoisomer) as large brown plates (red-brown in solution), m.p.

(5) K. Brand and K. O. Müller, Ber., 55, 601 (1922); L. F. Fieser and M. M. Pechet, J. Am. Chem. Soc., 68, 2577 (1946).

(6) Inter al., see G. Eglinton and A. R. Galbraith, J. Chem. Soc., 889 (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, J. Am. Chem. Soc., 81, 4600 (1959).

(7) It is to be noted that the coupling of the monomer I with cupric acetate in pyridine yielded a variety of cyclic and linear products (to be reported in the full paper), but no cyclohexadecane derivatives.

86–87°; $C_{16}H_{14}$ (found: C, 93.06; H, 6.71); $\lambda_{max}^{isooctane}$ 283 and 296 mμ (ϵ 52,000 and 41,000) with absorption beyond 600 mμ; acetylene band at 4.65 μ in the infrared (KBr). The compound proved to be considerably more stable than its precursor, showing a normal m.p. and suffering only ca. 30% decomposition after being allowed to stand for 4 days in air and daylight. This hydrogenation in addition produced in low yield a less polar substance as an orange oil, to which we assign the [16]annulene structure (VIII or a stereoisomer) in view of the ultraviolet spectrum $\lambda_{max}^{isooctane}$ 282 and 353 mμ (ϵ 44,500 and 3,500)] and the infrared spectrum (absence of acetylene band in the 4.5–4.7 μ region). Apparently the same [16]annulene was formed by the partial hydrogenation of the monodehydro[16]annulene, as evidenced by the essentially identical ultraviolet spectra and chromatographic behavior. [16]-Annulene was unstable and soon decomposed on standing, either neat or in solution.

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THE PREPARATION OF trans 1,4-POLYBUTADIENE BY RHODIUM SALTS IN SOLUTION

Sir:

We wish to report the preparation of crystalline trans-1,4-polybutadiene by the catalytic action of solutions of Rh^{+++} salts on butadiene monomer. Water, ethanol, and dimethylformamide were used as typical solvents. Representative polymerization conditions are summarized in Table I. The polymer was gel free in hot xylene. Because of its high crystallinity, it was not soluble in cold benzene. Under the conditions listed, polymer was obtained which had intrinsic viscosities of 0.1 to 0.5 in tetralin at 135°. Intrinsic viscosities as high as 1.0 were obtained by running the polymerization in emulsion at low temperature, and at very low rhodium concentrations. Increasing the temperature or the rhodium concentration decreased the molecular weight of the polymer.

The fastest rates were observed when the reactions were carried out in water with a suitable emulsifier such as sodium lauryl sulfate or sodium dodecylbenzene sulfonate. There was no evidence of an induction period. The presence of hydroquinone or air did not reduce the rate.

All the Rh^{+++} salts listed in Table I were active catalysts, although some were effective under conditions in which others were ineffective. Thus, $RhCl_3$ produced no noticeable trans-polybutadiene after six hours at 80° in alcohol, whereas 1 g. of $Rh(NO_3)_3$ produced about 7 g. of polymer per hour under the same conditions. A solution of the nitrate in 95% ethanol saturated with butadiene gave crystalline polymer in an open flask in the atmosphere at room temperature. After one day, the polymer was removed by filtration, and was washed with more ethanol. The filtrate and combined washings were concentrated to about the original volume, and more butadiene was added. Polymerization occurred as before. The slightly slower rate could be attributed to loss of rhodium

TABLE I

POLYMERIZATION OF BUTADIENE BY RHODIUM SALTS

Conditions: 1 g. of rhodium salt, 100 g. of butadiene, 200 ml. of solvent in capped bottles

Rhodium salt	Solvent	Emuls.,[a] g.	Reaction temp., °C.	Yield, g./hr.	$[\eta]$ Tetralin 135°	% Cryst.[b]	Ratio[c] of trans	vinyl	cis
Rhodium chloride·3H₂O	Water	5	5	0.02	0.5	43	99	0.2	<1
Rhodium chloride·3H₂O	Water	5	50	2.4	0.4	37	99	0.3	<1
Rhodium chloride·3H₂O	Water	5	80	21	0.1	37	>98	0.2	1.2
Rhodium nitrate·2H₂O	Water	None	50	0.1	0.1	37	>96	<2	<2
Rhodium nitrate·2H₂O	Water	5	50	0.4	0.1	60	98	1	<1
Rodium nitrate·2H₂O	Ethanol	None	Room	0.1	0.1	41	98	0.5	<2
Rhodium nitrate·2H₂O	Ethanol	None	80	7.0	0.1	21	>90	<8	2.7
Rhodium nitrate·2H₂O	Dimethyl- formamide	None	Room	0.1	0.1	32	98	0.7	<2
Ammonium chlororhodate·1.5H₂O	Water	5	50	1.3	0.3	36	99	0.2	<1
Sodium chlororhodate·18H₂O	Water	5	50	1.5	0.3	49	>98	<1	<1

[a] Sodium dodecylbenzene sulfonate. [b] Estimated by X-ray diffraction.[1] [c] Determined by the infrared absorption in KBr discs by a method similar to that described by Hampton.[2] The ratios are normalized to 100% total unsaturation.

nitrate in the filtration step. This procedure of filtration and addition of butadiene to produce more *trans*-polybutadiene was repeated several times each week for several weeks. The catalyst was still active, although after repeated filtrations the concentration was so low that polymer was forming at a greatly reduced rate.

We believe that rhodium salt catalysis represents a novel method of vinyl polymerization, one which will give stereospecific polymer in water and other polar solvents, with or without emulsifier.

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(2) R. R. Hampton, *Anal. Chem.*, 21, 923 (1949).

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THE EFFECT OF UREA ON HYDROPHOBIC BONDS: THE CRITICAL MICELLE CONCENTRATION OF *n*-DODECYLTRIMETHYLAMMONIUM BROMIDE IN AQUEOUS SOLUTIONS OF UREA[1]

Sir:

In recent years the concept of denaturation has been profoundly modified. Oversimplified, but useful, arguments, suitable for discussion of the breakdown of a hydrogen-bonded structure in a vapor phase, have given way to more sophisticated treatment accounting for the existence of secondary structure through the manifold interactions possible in aqueous solutions.[2,3,4,5,6] Naturally,

(2) J. Sturtevant, S. A. Rice, and E. P. Geiduschek, *Disc. Far. Soc.*, 25, 138 (1958).

(3) W. Kauzmann, *Adv. in Protein Chem.*, 14, I (1959).

this re-examination of the thermodynamic effects responsible for stability has led to doubts concerning the effects responsible for instability, *i.e.*, the roles of specific denaturing agents in disrupting the secondary structure also have been re-examined. For example, the efficacy of urea as a denaturant always has been ascribed to the breaking of protein-protein hydrogen bonds and preferential formation of protein–urea hydrogen bonds. Recently, however, this has been called into question, and the hypothesis that urea breaks hydrophobic bonds, and owes at least some of its denaturing capacity to this property, has received some experimental support.[7,8,9] In this preliminary report, we describe experiments in which the effect of urea on hydrophobic bonds was tested by measuring (conductivity) critical micelle concentrations of a cationic detergent in aqueous solutions containing varying concentrations of urea. This work complements studies of the solubility of organic substances in aqueous urea.[7,8,10]

Preparation of *n*-Dodecyltrimethylammonium Bromide.—*n*-Dodecyl bromide was prepared from the corresponding alcohol.[11] The compound was distilled over the range 128–132.5° at 6.3 mm. pressure. The bromide was added slowly to a cold solution of excess trimethylamine in absolute ethanol and the mixture stirred at 0° for one hour. The solution was heated to reflux under a brine condenser, cooled, and the solvent evaporated in a Rinco apparatus. The salt was collected by vacuum filtration, dried, and recrystallized once from benzene–ether and once from acetone–ether. The product decomposed at 207° and contained 25.90% bromide (theoretical, 25.95%).

Conductivity Measurements.—Conductivities of solutions made up by weight were measured to four significant figures, using a Kohlrausch-type

(4) C. Tanford, *J. Am. Chem. Soc.*, 83, 1628 (1961).

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(10) D. Wetlaufer, personal communication.

(11) O. Kamm and C. Marvel, *J. Am. Chem. Soc.*, 42, 299 (1920).