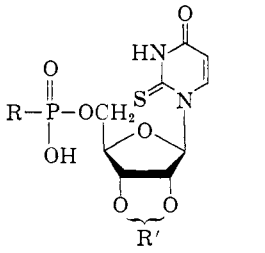

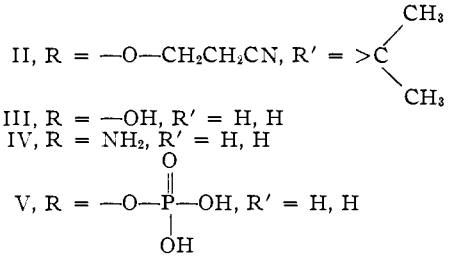

groups. 2-Thiouridine 5′-phosphate (III) was isolated in 56% yield based on I. Thiouridylic acid was converted to the N,N′-dicyclohexylguanidinium salt of 2-thiouridine 5′-phosphoramidate (IV) using the conditions described previously for uridine 5′-phosphoramidate,[6] but substituting dimethylformamide for formamide in the solvent mixture (83% yield). The amidate (IV, 0.45 mmole) was converted to 2-thiouridine 5′-diphosphate (V, TUDP) using dioxane diphosphoric acid[7] as described previously.[8] The product was isolated by ion exchange chromatography on Dowex-1-chloride (1.4 × 7 cm., 8% cross-linked): 0.003 *N* HCl + 0.04 *M* LiCl, 508 ml., TOD^{275} [9] = 595; 0.003 *N* HCl + 0.1 *M* LiCl, two peaks, 234 ml., TOD^{275} = 102; 590 ml., TOD^{275} = 3,780 (TUDP).

The isolated lithium salt[10] (100 mg., 42% yield based on IV) was slightly yellow. It gave a single ultraviolet absorbing spot upon electrophoresis (*p*H 3.5, citrate buffer) and it was recovered quantitatively from a single symmetrical peak after rechromatography by ion exchange.[11] Its ultraviolet absorption spectra at *p*H 2, 7 and 9 were similar to that of 2-thiouridine.[12]

Anal. S:labile P:total P: 1.06:1.00:2.00. Theoretical: 1.00:1.00:2.00.

In the presence of polynucleotide phosphorylase, TUDP showed an activity similar to UDP in the P^{32} exchange assay.[13] Polythiouridylic acid was synthesized by incubating TUDP (21 μmoles) with polynucleotide phosphorylase (4 units, gel fraction[13]) in 0.4 ml. of *p*H 8.0 Tris buffer (60 μmoles) containing Versene (0.4 μmole) and magnesium chloride (2 μmoles) at 30° for 4 hours.[14] The product was isolated as a white solid.[15] The polymeric nature of this material is indicated by gel formation during synthesis and its high sedimentation coefficient, S_{20} = 43 (cacodylate buffer *p*H 7, μ = 0.2), in the ultracentrifuge.

These results suggest that polynucleotide phosphorylase may be involved in the incorporation of 2-thiouracil into RNA *in vivo*. Further experiments on the preparation of mixed polynucleotides containing thiouridylic acid as well as the naturally occurring nucleotides are in progress.

Acknowledgment.—We are indebted to Drs. S. Mii and S. Ochoa for samples of polynucleotide phosphorylase and to Dr. R. C. Warner for the ultracentrifuge studies. This work was supported by a National Science Foundation Grant (NSF G-4867).

(6) R. W. Chambers and J. G. Moffatt, THIS JOURNAL, **80**, 3752 (1959).

(7) E. Baer, *ibid.*, **66**, 202 (1944).

(8) R. W. Chambers, *ibid.*, **81**, 2022 (1959); R. W. Chambers, P. Shapiro and V. Kurkov, *ibid.*, **82**, in press (1960).

(9) TOD^{275} = optical density (1 cm. light path) × volume (ml.) at 275 mμ and *p*H = 2.7.

(10) Isolation as described in ref. 8.

(11) UDP and TUDP are well separated by ion exchange. No contamination of the product with UDP could be detected.

(12) D. B. Strominger and M. Friedkin, *J. Biol. Chem.*, **208**, 663 (1954); G. Shaw, R. N. Warrener, M. M. Maguire and K. Phelps, *J. Chem. Soc.*, 2296 (1958).

(13) M. Grunberg-Manago, P. J. Ortiz and S. Ochoa, *Biochim. Biophys. Acta*, **20**, 269 (1956).

(14) Release of inorganic phosphate corresponded to 55% of the labile phosphate in TUDP.

(15) The isolation procedure was similar to that described previously for other polynucleotides; see ref. 13.

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RECEIVED DECEMBER 23, 1959

REDUCTIVE DEAMINATION OF ALIPHATIC AMINES

Sir:

A direct method for effecting reductive deamination of aliphatic primary amines ($RNH_2 \rightarrow RH$) has not been available.[1] We now have found that this conversion can be brought about if a sulfonamide derivative of the amine in alkaline medium is treated with hydroxylamine-O-sulfonic acid ($^+NH_3OSO_3^-$).[2] This general procedure was used: the sulfonamide (1 g.) was dissolved in a hot alkaline solution (*ca.* 100 ml.) made up from sodium hydroxide (10–12 g.), water (70–90 ml.) and ethanol[3] (10–30 ml.). Solid $^+NH_3OSO_3^-$ (15–25 equivalents[4]) was added in small batches (*ca.* 0.5 g. every minute).[5] The mixture was distilled (*ca.* 1 hr.) and the product (hydrocarbon) was extracted from the aqueous distillate with CCl_4 and assayed by infrared spectroscopy. Unconverted sulfonamide was recovered from the original mixture by acidification, then extraction.

The generality of the reaction is indicated by our results (Table I) with a variety of aliphatic amines (and even with an aromatic amine). The yields vary widely but are generally excellent when corrected for recovered starting material. Clearly, optimum conditions for conversion have not been defined, and many modifications (even in the nature of the reagent itself) suggest themselves.

A reasonable pathway for the reaction is shown. The formation of the N–N bond is of added attraction because it might involve an electron deficient

(1) In contrast, this transformation is accomplished easily in the aromatic series (N. Kornblum, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. II, 1944, p. 262).

(2) F. Sommer, O. Schulz and M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

(3) Sometimes ethanol could be omitted, but usually it was needed to help keep the sulfonamide dissolved.

(4) The reagent decomposes in aqueous alkali[2] and in ethanol (R. Nast, K. Nyul and E. Grziwok, *ibid.*, **267**, 304 (1952)).

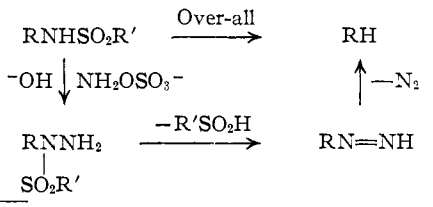
(5) This allowed sufficient time for boiling and gas evolution to subside between additions.

nitrogen species (NH).[6] The intermediates at the end stages of the reaction are also of more general interest because of their similarity to those in Wolff–Kishner reductions,[7] and also because of current interest in the mechanisms of electrophilic substitutions on carbon.[8]

TABLE I

	Amine	Sulfonamide derivative[a]	Yield of hydrocarbon, % Actual	Corrected
1	Benzylamine	Bs	63	>95
2(i)	α-Phenylethylamine	Ms[b]	60	81
(ii)	α-Phenylethylamine	Ms[b]	81[c]	86
3(i)	2-Phenyl-2-butylamine	Bs	10	>95
(ii)	2-Phenyl-2-butylamine	Bs	33[d]	>95
4	*n*-Hexylamine	Ts	41	>95
5	2-Octylamine	Ts	17	93
6	2,4,4-Trimethyl-2-pentylamine	Ts	12	>95
7	Cyclohexylamine	Bs	23	72
8	9-Amino-9,10-ethano-9,10-dihydroanthracene	Ms	6	81
9	β-Naphthylamine	Ts[b]	19	[e]

[a] Bs = benzenesulfonamide; Ts = toluenesulfonamide; Ms = methanesulfonamide. [b] Ethanol omitted from alkaline solution. [c] 45 equivalents of reagent used; product removed by five successive distillations, each conducted after 20% of the reagent had been added. [d] 50 equivalents of reagent, with a distillation conducted midway as well as at the end. [e] Not determined.



(6) A. Meuwsen and R. Gösl, *Angew. Chem.*, **69**, 754 (1957).

(7) D. Todd, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. IV, 1948, p. 378; R. B. Turner, R. Anliker, R. Helbling, J. Meier and H. Heusser. *Helv. Chim. Acta*, **38**, 411 (1955); N. J. Leonard and S. Gelfand, THIS JOURNAL, **77**, 3272 (1955); G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **32**, 1817 (1949).

(8) D. J. Cram, *et al.*, THIS JOURNAL, **81**, 5740–5785 (1959).

(9) This work was supported by a Frederick Gardner Cottrell grant from Research Corporation, and by the Alfred P. Sloan Foundation.

(10) Alfred P. Sloan Foundation Fellow.

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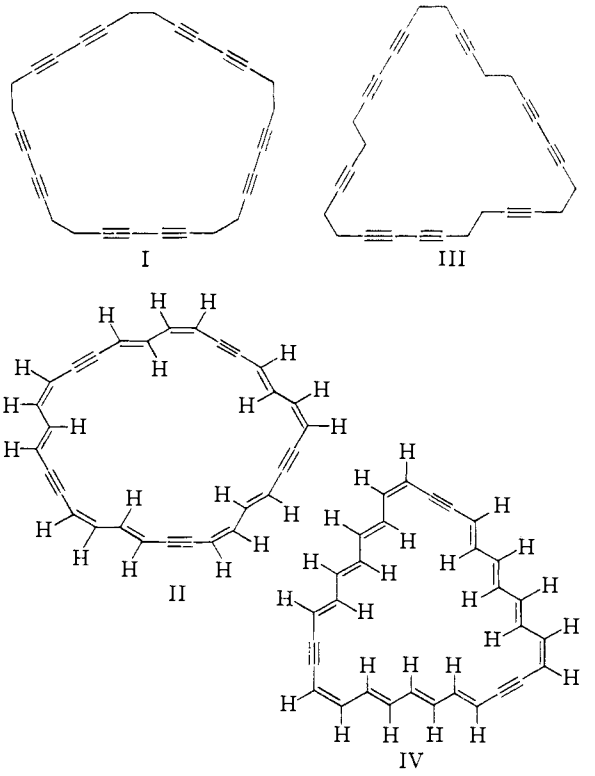
UNSATURATED MACROCYCLIC COMPOUNDS. XII.[1] SYNTHESIS OF TWO COMPLETELY CONJUGATED THIRTY-MEMBERED RING CYCLIC SYSTEMS

Sir:

We have prepared cyclotriaconta-1,3,7,9,13,15,-19,21,25,27 - decaene - 5,11,17,23,29 - pentayne (II or a stereoisomer) and cyclotriaconta-1,3,5,7,-11,13,15,17,21,23,25,27 - dodecaene - 9,19,29 - triyne (IV or a stereoisomer), completely conjugated thirty-membered ring cyclic polyene-ynes containing five and three acetylenic bonds, respectively. These represent the first monocyclic conjugated 30 π-electron systems and they comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π-electrons].

The first substance was obtained in *ca.* 20% yield from cyclotriaconta-1,3,7,9,13,15,19,21,25,27-decayne (I) (the cyclic "pentamer" of 1,5-hexadiyne)[2] by treatment with potassium *t*-butoxide in *t*-butyl alcohol–benzene at 90° for 30 minutes. The resulting isomer (found: C, 94.18; H, 5.42) formed orange-red crystals from ether (red in solution), which decomposed when heated; $\lambda_{max}^{dioxane}$ (principal bands) 307, 318, 378 and 396 mμ (ε = 42,000, 39,500, 105,000 and 126,000); $\lambda_{max}^{benzene}$ (principal bands) 310, 320, 383 and 400 mμ (ε = 38,000, 35,500, 101,000 and 122,000). The infrared spectrum (KBr) showed bands at 3.31 μ (—CH=), 4.64 μ (—C≡C—), 7.11 μ (*cis*-double bond), 7.77 and 10.34 μ (*trans*-double bond). Full hydrogenation (platinum, dioxane) gave cyclotriacontane,



m.p. and mixed m.p. 55–57°. The rearrangement doubtless took place analogously to that of the cyclic "trimer"[3] and "tetramer"[1] of 1,5-hexadiyne to give a fully conjugated decaene-pentayne, and the product is most probably the symmetrical 1,7,13,19,25-pentayne (II or a stereoisomer).

The second conjugated substance was prepared in this way. Reaction of *trans*-1,4-dibromo-2-butene with allylmagnesium bromide at 5° gave *ca.* 50% of *trans*-1,5,9-decatriene [b.p. 69–70° (18 mm.), $n^{28}D$ 1.4432; found: C, 87.82; H, 11.63], which on conversion to the hexabromide (mixture of isomers) and subsequent dehydrobromination with sodamide in liquid ammonia[4] yielded *ca.* 25% of 1,5,9-decatriyne [m.p. 46°, b.p. 61–63° (2 mm.); found: C, 91.82; H, 7.66]. Oxidation with cupric acetate in pyridine[2,5] at

(1) Part XI, see F. Sondheimer and R. Wolovsky, THIS JOURNAL, **81**, 4755 (1959).

(2) F. Sondheimer, Y. Amiel and R. Wolovsky, *ibid.*, **79**, 4247 (1957).

(3) F. Sondheimer and R. Wolovsky, *ibid.*, **81**, 1771 (1959).

(4) See R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 120 (1950).

(5) See G. Eglinton and A. R. Galbraith, *Chemistry & Industry*, 737 (1956); *J. Chem. Soc.*, 889 (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, THIS JOURNAL, **81**, 4600 (1959).