evidence for the formation of a reduction product in the anolyte, and the magnesium appeared to enter solution in its normal dipositive state. However, investigation of the catholyte upon completion of electrolysis revealed the presence of a polymer.

The catholyte, following an electrolysis at a current density of approximately 0.004 amp. per sq. cm., was treated with ice water, neutralized with 6 *M* hydrochloric acid, and the resulting white precipitate was collected by filtration and dried. The solid was dissolved in benzene, the solution filtered and the filtrate evaporated, leaving a glassy, brittle residue. *Anal.* calcd. for $(C_8H_8)x$: C, 92.27; H, 7.73. Found: C, 92.31; H, 7.78. The molecular weight was determined to be about 1800 by the viscosity method.[7] The solid material obtained from the catholyte after an electrolysis carried out at a current density of 0.0007 amp. per sq. cm. (*Anal.* Found: C, 92.07; H, 7.88) had a molecular weight of approximately 2800.[8] Control experiments revealed that styrene subjected to the conditions cited above, except for the electrolysis, could be recovered unchanged.

Conclusive proof that the polymerization was initiated by electrons supplied by the cathode and not by sodium metal plated out during electrolysis has been obtained. In one experiment, electrolysis was carried out in the usual manner but in the absence of styrene. The latter substance was then added, the mixture permitted to stand for 46 hr., and the polymer which formed (buff in color) was isolated as described above. *Anal.* Found: C, 90.94; H, 7.89; N, 0.94; mol. wt., 1600. In a second experiment, metallic sodium was added to a solution of styrene and sodium iodide in pyridine and the mixture was allowed to stand for 43 hr. at 30°. The polymer which was produced was also buff colored. *Anal.* Found: C, 90.06; H, 7.75; N, 1.07; mol. wt., 1500. Calculation of molecular weights from nitrogen analyses gave results in substantial agreement with those from viscosity measurements. The presence of nitrogen in the polymers formed in the reactions with sodium strongly suggests that the effective initiating agent in these cases is an anion formed by transfer of an electron from sodium to pyridine. Initiation of polymerization of styrene by anions has been observed previously.[9] The absence of nitrogen in the polymers obtained from electrolyses would appear to eliminate definitely from further consideration the possibility of an anion-catalyzed polymerization.

The only other report of initiation of polymerization at a cathode is that of Parravano,[10] who found that the efficiency of polymerization of methyl methacrylate in aqueous solution depended on the hydrogen overvoltage as well as on the current density. However, the evidence indicated that polymerization was initiated by atomic hydrogen deposited at the cathode rather than by electrons.

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[7] A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

[8] Neither polymer contained any nitrogen, as shown by direct determination.

[9] (a) P. Hermann and D. Vorlander, *Abhandlunger Naturforschenden Gesellschaft zu Halle*, **21**, 251 (1899); (b) R. G. Beeman, THIS JOURNAL, **70**, 3115 (1948); (c) J. J. Sanderson and C. R. Hauser, *ibid.*, 1595 (1949); (d) M. G. E. Evans, W. C. E. Higginson and N. S. Wooding, *Rec. trav. chim.*, **68**, 1069 (1949); (e) W. C. E. Higginson and N. S. Wooding, *J. Chem. Soc.*, **760** (1952); (f) N. S. Wooding and W. C. E. Higginson, *ibid.*, 774 (1952).

[10] G. Parravano, THIS JOURNAL, **73**, 628 (1951).

BIOSYNTHESIS OF CERAMIDE BY RAT BRAIN HOMOGENATES[1]

Sirs:

The formation of sphingosine *in vivo* has been investigated in this laboratory[2] and elsewhere.[3] Recently, Brady and co-workers have reported the incorporation of labeled serine by a dialyzed supernatant solution of rat brain into a sphingosine fraction obtained by acid hydrolysis of a lipid extract.[4] The conversion of radioactive serine to ceramide (N-acylsphingosine) by rat brain homogenates has now been demonstrated. When 3-C^{14} DL-serine was added to a sucrose homogenate obtained from the brain of 15–20 day old rats and the mixture was incubated with triphosphopyridine nucleotide, adenosine triphosphate, nicotinamide, magnesium, pyridoxal phosphate, tris buffer, and palmityl coenzyme A (Table I), labeled ceramide was formed.

Ceramide was isolated by stopping the reaction with trichloracetic acid and extracting the residue with 2:1 chloroform–methanol. The lipid mixture was passed through a column containing Florisil, Dowex 2 and Dowex 50 in order to remove ionic lipids.[5] The solvent was removed and the neutral lipids were taken up in chloroform and added to a column of silicic acid which was developed with increasing concentrations of methanol in chloro-

TABLE I

FORMATION OF CERAMIDE

Each tube contained 100 μM. Tris buffer, *p*H 7.5, 30 μM. $MgSO_4$, 40 μM. nicotinamide, 5 μM. ATP, 1 μM. TPN, 1 λM. Palmityl CoA, 5 μM. 3-C^{14} DL-serine 500,000 c./min./μM., and 1 ml. of enzyme obtained after centrifuging a 20% homogenate in 0.25 *M* sucrose and 0.001 *M* Versene for 10 minutes at 600 g. ATP was omitted in Expt. 2. 1 μM. DPN, 1 μM. CoA, 5 μM. DL-O-P-serine, 2 μM. sphingosine, and 5μM. n-palmiylserine were added as indicated. Each tube in Expt. 4 contained 1 mg. of Tween 20. The final volume was 2 ml. and incubations were carried out at 37° for 1 hr.

Expt.	Additions	Total counts/min.
1	Complete	490
	Complete, zero time	15
	No TPN	385
	DPN, no TPN	460
	P-Serine instead of serine	165
2	Complete	665
	CoA, no Palmityl-CoA	295
3	Complete	1100
	+ N-Palmitylserine	850
4	Complete	1055
	+ Sphingosine	590

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[1] Supported by a grant from the U. S. Public Health Service.

[2] (a) I. Zabin and J. F. Mead, *J. Biol. Chem.*, **205**, 271 (1953); (b) **211**, 87 (1954).

[3] D. B. Sprinson and A. Coulon, *ibid.*, **207**, 585 (1954).

[4] R. O. Brady and G. J. Koval, THIS JOURNAL, **79**, 2648 (1957).

[5] N. S. Radin, F. B. Lavin and J. R. Brown, *J. Biol. Chem.*, **217**, 789 (1955).

form. Only one radioactive peak was observed, which corresponded in position to authentic ceramide. When this radioactive material was hydrolyzed, and the hydrolysate was partitioned between water and chloroform, more than 90 per cent. of the radioactivity was found to be in the organic phase. Chromatography of the hydrolyzed chloroform-soluble material on silicic acid showed that the radioactive compound was eluted from the column in the same area as sphingosine.

Radioactivity in the ceramide decreased to less than half when coenzyme A instead of palmityl coenzyme A was added to the incubation mixture. In the absence of pyridine nucleotides the amount of tracer in the product also decreased. In several experiments, which are not shown here, addition of ATP caused a variable effect. Substitution of labeled phosphoserine for C^{14} serine caused a decrease to about one-third in the radioactivity of the ceramide fraction, indicating that phosphoserine is not an intermediate. Addition of non-labeled N-palmitylserine did not significantly change the amount of radioactivity in ceramide, but when sphingosine was added, the incorporation of tracer was reduced to about one-half. Whether this indicates that sphingosine is an inhibitor or an intermediate in ceramide formation cannot yet be decided.

Burton and co-workers have shown that uridine diphosphogalactose is involved in cerebroside formation,[6] and Sribney and Kennedy have found that cytidine diphosphocholine reacts with N-acyl sphingosine to form sphingomyelin.[7] These results and those reported here suggest that ceramides are common intermediates in sphingolipid formation, as suggested earlier by Thannhauser and Reichel.[8]

(6) R. M. Burton, M. A. Sodd and R. O. Brady, *Federation Proc.*, **16**, 161 (1957).

(7) M. Sribney and E. P. Kennedy, *ibid.*, **16**, 253 (1957).

(8) S. J. Thannhauser and M. Reichel, *J. Biol. Chem.*, **113**, 311 (1936).

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BOOK REVIEWS

Neuere Anschauungen der Organischen Chemie. Organische Chemie für Fortgeschrittene. Zweite Gänzlich Umgearbeitete Auflage. By EUGEN MÜLLER, O. Professor und Direktor des Instituts für Angewandte Chemie der Universität Tübingen. Springer-Verlag, Berlin W 35, Reichpietschufer 20 (West-Berlin), Germany. 1957. xii + 550 pp. 25 × 18 cm. Ganzleinen DM 59.60.

"Newer Views of Organic Chemistry" is an advanced textbook, the first edition of which was published in 1940 and was made available in this country through the Alien Property Custodian. The new edition is thoroughly revised and brought up-to-date, but in it is kept what is perhaps its most attractive feature, the organization of the material according to types of bonds. The three main subdivisions deal with single, double and triple bonds. For instance, the first main section starts with a qualitative discussion of valence, treating both the valence bond and molecular orbital approximations. This is followed by the carbon–hydrogen bond, where hybridization of bond orbitals is introduced, and a chapter on carbon–carbon single bonds. This chapter deals with paraffins and contains an excellent review of ring compounds, including conformational considerations, and optical activity. A discussion of carbon–halogen bonds follows, which allows the inclusion of substitution and displacement reactions and Walden inversion. The next chapter deals briefly with carbon–oxygen and carbon–sulfur bonds, and with oxonium salts, and sections on the carbon–nitrogen single bond, ammonium and sulfonium compounds, and the semi-polar link, including ylids, concludes the first large section. An analogous division is followed for double bonds (carbon–carbon and carbon–oxygen double bonds, conjugated and cumulative systems, tautomerism, aromatic chemistry) and for triple bonds (acetylenes, nitriles, cyanates), except that also nitrogen–nitrogen double bonds (azoxy and azo compounds) and triple bonds (aliphatic and aromatic diazonium compounds, azides) are included. A short chapter on bivalent carbon (carbon monoxide and derivatives, methylene) concludes the book. Each chapter is usually preceded by a short quantum-mechanical description of the nature of the bond to be discussed, often with illustrations taken from Coulson's book. Although the conventional chapter on physical properties is omitted, use is made of such data, particularly dipole moments and bond distances and angles, in discussing the character of the various bonds. Ionic and radical reactions are treated side by side at the appropriate places.

The organization of the book has the advantage of being systematic, and the disadvantage, not too serious, that not everything in organic chemistry fits neatly into such a system. Thus, quantum-mechanical resonance is introduced only about one-third of the way through the book, in the discussion of olefins, hyperconjugation toward the end, and the Wagner–Meerwein and similar rearrangements are taken up in the section on aromatic substitution, in connection with the Friedel–Crafts reaction.

In contemporary organic chemistry various topics and ideas have received different treatment and particularly different emphasis in different countries, and the reader on this side of the Atlantic should not expect a literal translation of English–American developments into German. There are some topics and treatments which recur particularly in the German literature and also are given space here: the alternating effect, the development of mesomerism taking pyrylium salts as the starting point, the structure of the solid sodium salts of tautomeric substances, the great interest in diazomethane. Some topics, such as displacement or eliminations reactions, acid-base catalysis, the relation between structure and reactivity, are not treated as thoroughly as is customary in similar books, others, particularly reactions of acetylenic or nitrogen containing substances, or the oxo reaction, more thoroughly. A chapter found in the previous edition on stable free radicals, containing much of the author's own important contributions, has been omitted, but some of his earlier work on biradicals, and his more recent work on the tri-*t*-butylphenoxy radical, is mentioned. The reader will be surprised to see how many modern concepts are discussed under their English names, or are introduced under those names, *i.e. orbitals, covalent radius, total bond order, staggered and eclipsed forms, transition state, bridged ions, sandwich structures.*