TABLE I

Acid[a]	Double bonds	Length of dimeric acid, Å.	Shortening,[b] Å.	Length of c-axis of urea host, Å.
Stearic	None	50.11 ± 0.20		11.03 ± 0.02
Oleic	1 *cis* $\Delta^{9,10}$	48.15 ± 0.20	0.88 ± 0.10	11.00 ± 0.02
Linoleic	2 *cis* $\Delta^{9,10,12,13}$	46.65 ± 0.20	0.87 ± 0.05	11.00 ± 0.02
Elaidic	1 *trans* $\Delta^{9,10}$	49.75 ± 0.20	0.18 ± 0.10	11.02 ± 0.02
Linolelaidic	2 *trans* $\Delta^{9,10,12,13}$	49.30 ± 0.20	0.20 ± 0.05	11.03 ± 0.02

[a] Acids of high purity were kindly provided by the Research Division of Armour & Co., General Mills, Inc., and the Hormel Institute. [b] Shortening = stearic acid dimer length − unsaturated fatty acid dimer length/2 × number of double bonds in the molecule.

These data clearly show that an isolated *trans* double bond shortens a molecule 0.19 Å., whereas an isolated *cis* double bond shortens it 0.88 Å.

Squalene has a total of six double bonds. The four middle ones can have the main chain substituents either *cis* or *trans* with respect to each other. Assuming that in the thiourea adducts, squalene and fully hydrogenated squalene stretch out their maximum normal length in the thiourea framework as the fatty acids do in urea adducts, and assuming that the same shortening effect for isolated *cis* or *trans* double bonds applies, a comparison of the lengths of these two molecules should indicate the number of *cis* or *trans* double bonds present (Table II).

TABLE II

	$n^{25}D$	Length, Å.	c-Axis, Å.
Hydrogenated squalene	1.4509	31.33 ± 0.15	12.54 ± 0.02
Squalene	1.4941	30.60 ± 0.15	12.56 ± 0.02

The shortening for six *trans* double bonds would be 1.1 ± 0.3 Å., whereas the shortening for one *cis* and five *trans* double bonds would be 1.8 ± 0.3 Å. Since the measured shortening was only 0.73 ± 0.30, natural squalene must be the all-*trans* isomer.

Without further stereochemical change, all-*trans* squalene could cyclize[6] to form the required all-*trans* fused rings A to B to C to D of cholesterol.[6]

The difference between the length, measured by X-rays, of an isoprene unit in rubber (one *cis* double bond), and that of β-gutta-percha (one *trans* double bond) is 0.67 Å.[7] This is identical to the difference in length found by us between a *cis* and a *trans* double bond in the chain of an adducted molecule (0.88 − 0.19 = 0.69 Å.).

Although the method was used here to differentiate *cis* and *trans* isomers, it could be applied to any structural problem where the length of an adducted molecule is discriminating. The method is being further investigated. Details and further applications will be reported later.

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(5) R. B. Woodward and K. Bloch, THIS JOURNAL, **75**, 2023 (1953); see also R. G. Langdon and K. Bloch, *J. Biol. Chem.*, **200**, 135 (1953); W. G. Dauben and K. H. Takemura, THIS JOURNAL, **75**, 6302 (1953).

(6) R. B. Turner in "Natural Products Related to Phenanthrene," L. F. Fieser and Mary Fieser, 3rd ed. Reinhold Publ. Corp., New York, N. Y., p. 620.

(7) c-Axis (rubber) minus 2 c-axis (β-gutta-percha)/2; C. W. Bunn, *Proc. Roy. Soc.* (*London*), **180**, 40 (1942).

SALT EFFECTS AND ION-PAIRS IN SOLVOLYSIS[1]

Sir:

We have observed some striking salt effects on rates of acetolysis of a number of benzenesulfonates which yield carbonium ions with bridged structures. The addition of, *e.g.*, lithium perchlorate in low concentrations in acetolysis of, *e.g.*, 2,4-dimethoxyphenylethyl or 3-anisyl-2-butyl *p*-bromobenzenesulfonate (ROBs) gives a two-stage effect: (i) an initial very steep rise in the first-order titrimetric rate constant, k_t, from the value in the absence of salt, k_t°; (ii) a subsequent small increase in k_t, nearly perfectly linear in salt concentration, [$LiClO_4$]. A short extrapolation of the linear part of the plot of k_t *vs.* [$LiClO_4$] to zero [$LiClO_4$] yields the intercept $k^\circ_{ext.}$. The linear part of the plot may be expressed by: $k_t = k^\circ_{ext.}(1 + b[LiClO_4])$. The behavior of any system may be characterized by the ratio $k^\circ_{ext.}/k^\circ_t$, the slope b and the [$LiClO_4$] where k_t is midway between k_t° and $k^\circ_{ext.}$, namely $[LiClO_4]_{1/2}$. Sample data are illustrated:

Compound	°C.	$k^\circ_{ext.}/k^\circ_t$	$[LiClO_4]_{1/2}$	b
(*p*-$CH_3OC_6H_4$)(CH_3)$_2$-CCH_2OTs	25	1.00		16
threo-$CH_3CH(C_6H_5)$-$CH(OTs)CH_3$	50	1.00		37
exo-NorbornylOBs	25	1.00		37
threo-$CH_3CH(C_6H_4$-OCH_3-*p*)$CH(OBs)$-CH_3	25	2.59	2.3×10^{-3}	22
erythro-$CH_3CH(C_6H_4$-OCH_3-*p*)$CH(OBs)$-CH_3	25	3.08	3.8×10^{-3}	19
$CH_3CH(C_6H_4OCH_3$-*p*)-CH_2OTs	50	2.5	3.2×10^{-3}	24
Cholesteryl OTs	50	2.3	4×10^{-5}	28
2,4-$(MeO)_2C_6H_3CH_2$-CH_2OBs	50	2.2	6×10^{-5}	13

The lithium perchlorate is evidently involved in altering ion-pair return.[2] For example, only the shallow linear salt effect is observed with *p*-methoxyneophyl OTs, a system where the observed k_t is equal to the total ionization rate, k_1. However, the presence of ion-pair return is not a sufficient condition for the appearance of the steep salt effect, for it is absent with the norbornyl and 3-phenyl-2-butyl systems.[2b]

With the *threo*-3-anisyl-2-butyl and 2-anisyl-1-propyl systems, k_1 has been obtained by polarimetric[2b] or other kinetic methods[2c] and these follow

(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) *E.g.*, S. Winstein, *et al.*, THIS JOURNAL, (a) **73**, 1958 (1951); (b) **74**, 2165 (1952); (c) **74**, 2171 (1952).

the equation $k_1 = k_1^\circ (1 + b[LiClO_4])$, with b equal to 16 and 11, respectively. In these cases, k° exceeds $k^\circ_{ext.}$ substantially, k_1/k_t being 4.1 and 3.9, respectively, with no added salt, decreasing sharply during the early salt additions and subsequently only slowly. Where lithium perchlorate displays the unusually large salt effect it is evidently eliminating a definite substantial portion of, but not all, ion-pair return.

Our interpretation is that two varieties of ion-pair coexist in these cases of acetolysis: (i) the previously[2] discussed "intimate" or "internal" type consisting of a pair of ions in contact, with no interposed solvent molecules; and (ii) the "external" or "solvent-separated" type, the usual conception of a pair of solvated ions held together by coulombic attraction in a solvent of low dielectric constant. In acetolysis some systems return essentially only from the first of these ion-pair stages (internal return[2]). Others return also from the second of these stages and here, lithium perchlorate can be specifically effective in preventing such return.

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BOOK REVIEWS

Biochemie. Naturforschung und Medizin in Deutschland 1939–1946. Edited by RICHARD KUHN, Kaiser-Wilhelm-Institut für Medizineische Forschung, Heidelberg. Verlag Chemie, G.m.b.H., Weinheim/Bergstr., Germany. 1953. Vol. II, 241 pp. Vol. III, 201 pp. Vol. IV, 318 pp. 15 × 22 cm. Price, DM 15, -, DM 13, -, and DM 17, -, respectively.

These volumes encompass practically every aspect of German biochemical endeavor from 1939–1946. Most of the references may be found in American literature such as "Advances in. . . ." series, "Vitamins and Hormones," etc. However, "Biochemie" presents a complete and succinct aggregate of the German investigations, some of which are from journals not appearing in American libraries or reviews.

Particularly noteworthy in volume II are the chapters on "Pflanzliche Giftstoffe" and "Tierische Gifte" by B. Witkop and H. Behringer, respectively. Although "Biochemie der Tumoren" by H. Lettre, "Blastokoline" by F. Moewus, "Immunchemie" by H. Schmidt and O. Westphal and "Serologie" by H. Schmidt are comprehensive, the contents have since been thoroughly covered by American articles. Other chapters on "Radioactive Tracers" by K. Starke and "Electron Microscopy" by G. Bergold seem primitive in the light of present knowledge.

The contents of volume III are unusually well written and informative. "Aminosäuren, Peptide und Proteine" by Th. Wieland, "Polysaccharide" and "Lignin" by K. Freudenberg, and "Sterine und verwandte Naturstoffe" by H. Lettre present thorough coverage of these multifaceted subjects. "Gärungsfermente" by O. Warburg and "Fermente der biologischen Oxydation" by F. Lynen are not only reviews but carefully woven stories of progress in those fields. "Süssmandel—Emulsion und verwandte Carbohydrasen" by B. Helferich is an autobibliography.

In volume IV, U. Westphal's presentation of "Hormone" is scholarly, but studies on pituitary hormones and adrenocortical steroids have advanced so rapidly since 1946 that much of the information is either passé or strictly of historical value. Although "Vitamine" by G. Wendt falls within the latter category, some of the references, especially to enzyme-vitamin interrelationships, are still refreshing enough to be of interest. The same is true of "Wuchsstoffe" by E. F. Möller and F. Weygand. K. Scharrer's treatment of "Agrikulturchemie" read much like an abstract of "Bodenkunde u. Pflanzenernähr."

In general, the photomicrographs, charts and chemical formulas are clearly reproduced and lucid. Certainly these volumes represent excellent reference compilations for both the novice and experienced investigator.

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Les Proteines: Rapports et Discussions. Neuvieme Conseil de Chimie tenu a l'Universite de Bruxelles du 6 au 14 Avril 1953. By Institut International de Chimie Solvay. R. STOOPS, Editeur, 76–78 Rue Coudenberg, Brussels, Belgium. 1953. 350 pp. 17.5 × 24.5 cm. Price, 700 Belgian Francs.

The Proceedings of the Ninth Solvay Conference, held at Brussels in April, 1953, have now been recorded in this valuable book on proteins. The inherent interest of the book is enhanced by its prompt publication, only a few months after the conference. It deserves close attention from all who are seriously concerned with modern protein chemistry. The emphasis throughout is on proteins as chemical substances and—in the last two papers—on systems involving enzyme proteins; there is no attempt to discuss the intermediary metabolism of proteins or their role in nutrition.

K. O. Pedersen opens with a paper on the molecular weights of proteins, with special emphasis on recent developments in ultracentrifuge studies, and a critical examination of the sources of some discrepancies in published measurements. An extensive table of recent molecular weight values derived from sedimentation and diffusion is included. Linus Pauling discusses the configuration of polypeptide chains in proteins. This is in many ways the best exposition yet published by Pauling of the structure of the α-helix, the pleated sheets and other related configurations of polypeptide chains. The great importance of these configurations for the understanding of protein structure now appears indubitable. Sir Lawrence Bragg follows with a brief but valuable discussion of recent developments, and current thinking, in the work of the group concerned with X-ray study of proteins at Cambridge. It is perhaps appropriate to remark here that major developments have occurred in the Cambridge laboratories during the last six months—unfortunately too late to be recorded here. J. D. Watson and F. H. C. Crick provide a short note on the stereochemical structure of deoxyribose nucleic acid—one of the most important of recent developments in biochemistry, which has been expounded at greater length elsewhere. A. C. Chibnall gives a critical discussion of the chemical constitution of the proteins, with special emphasis on the development of new approaches to the problem of determining the sequence of amino acid residues in peptide chains. R. L. M. Synge discusses electrophoresis, chromatography and related physical methods in relation to protein chemistry, in a highly suggestive paper which deserves close attention from all who are interested in this field. V. Desreux and E. Fredericq discuss fractionation and purification of proteins. The discussion is relatively brief, considering the vastness of the field, and quite properly lays major emphasis on some of the newest developments in techniques of fractionation. M. L. Anson gives a provocative discussion of