

most certainly not the methyl derivative of *p*-methoxydibenzoylmethane.

#### Experimental

A mixture of 2 g. of *p*-methoxydibenzoylmethane (m. p. 132°, prepared from the dibromide of benzal-*p*-methoxyacetophenone by the action of alcoholic potassium hydroxide followed by acidification), 2 g. of dry silver oxide, 50 cc. of dry ether and 8 g. of methyl iodide was refluxed for six hours, filtered, evaporated to a small volume and low-boiling petroleum ether added to faint turbidity. The yield was 1.7 g. (80%), m. p. 72°. The residual reddish oil has so far not crystallized.

An identical product and percentage yield was obtained by the same procedure, starting with a mixture of 15 g. of *p*-methoxydibenzoylmethane, 15 g. of silver oxide, 100 cc. of ordinary acetone and 30 g. of methyl iodide. The filtered solution was evaporated, the oily residue dissolved in ether, the suspended silver iodide removed and the product finally isolated as above.

In either case the product tends to separate as an oil unless the solution is seeded just after the petroleum ether is added and if the growth of the crystals is hurried.

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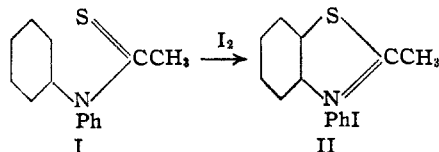
### A Direct Synthesis of 2-Methylbenzothiazolium Salts<sup>1</sup>

BY L. G. S. BROOKER AND H. W. J. CRESSMAN

One of the simplest methods of preparing bases of the benzothiazole and naphthothiazole series is that devised by Jacobson,<sup>2</sup> which consists in the oxidation of the thioacetyl derivatives of primary aromatic amines in cold alkaline solution. Alkyl quaternary salts of these bases may be prepared by direct addition of alkyl iodides, *p*-toluenesulfonates, or the like.

It is not possible to attach simple aryl or certain other groups to the nitrogen atoms of benzothiazole bases in this way, however, and 2-methyl-3-phenylbenzothiazolium iodide (II) has been prepared by another route<sup>3</sup> which utilizes 3-phenyl-2(3)-benzothiazolone<sup>4</sup> as the starting material but which involves several steps.

Jacobson's alkaline oxidative method cannot be applied to the thioacetyl derivatives of secondary amines such as I, since such compounds are insoluble in alkali, but oxidation of I with iodine in aqueous acetic acid solution brought about the desired ring closure, and II was obtained in small



yield as the triiodide, which gave the iodide on treatment with sulfur dioxide.<sup>5</sup>

(1) Communication No. 1009 from the Kodak Research Laboratories.

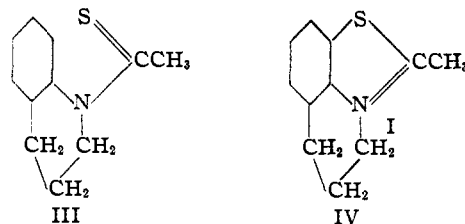
(2) Jacobson, *Ber.*, **19**, 1067 (1886).

(3) (a) Brooker and Williams, U. S. Patent 2,330,203; (b) Brooker, Keyes and Williams, *THIS JOURNAL*, **64**, 200 (1942).

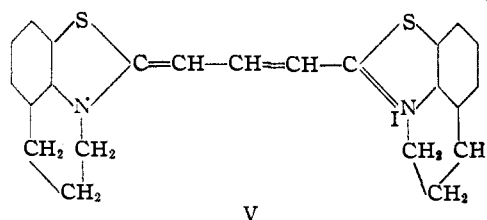
(4) Passing, *J. prakt. Chem.*, **153**, 1 (1939).

(5) Brooker and Cressman, U. S. Patent 2,317,357.

Starting with thioacetyl-1,2,3,4-tetrahydroquinoline (III), on the other hand, it was possible by this method to prepare the hitherto unknown 2-methyl-3,4-trimethylenebenzothiazolium iodide (IV) in moderately good yield. The 2-methyl



group in this salt is very reactive, and the carbocyanine dye V, for example, was obtained quite



smoothly using ethyl orthoformate. This dye is the higher vinylenes homolog of a simple thiancyanine containing 3,4-trimethylene rings prepared by König, Kleist and Götze<sup>6</sup> from 3,4-trimethylene-2(3)-benzothiazolone. A number of other dyes have been prepared using IV.<sup>5</sup>

#### Experimental

**1-Thioacetyl-1,2,3,4-tetrahydroquinoline** was prepared by heating 17.5 g. (1 mol) of 1-acetyl-1,2,3,4-tetrahydroquinoline with 11.1 g. (0.5 mol) of phosphorus pentasulfide in 30 cc. of dry pyridine to the refluxing point of the solvent for one half-hour with stirring. After allowing to cool, water precipitated an oily product that became crystalline on stirring with fresh portions of water. It separated from methyl alcohol in lustrous, almost colorless crystals with m. p. 68-70°; yield 70-74%.

*Anal.* Calcd. for C<sub>11</sub>H<sub>13</sub>NS: S, 16.77. Found: S, 16.62.

**2-Methyl-3,4-trimethylenebenzothiazolium Iodide (IV)**—In a typical experiment, 5.7 g. (1 mol) of 1-thioacetyl-1,2,3,4-tetrahydroquinoline was mixed with 15.2 g. (2 mols) of iodine, 2.5 g. (1 mol) of anhydrous sodium acetate, 4.5 g. (1 mol) of sodium iodide and 300 cc. of 50% acetic acid and the mixture boiled under reflux for one hour; triiodide (4.5 g., 26% yield) separated on cooling. This could be recrystallized from acetic acid in yellowish crystals with m. p. 121-123° dec.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>I<sub>2</sub>NS: I, 66.67. Found: I, 64.85.

The salt was reduced by bubbling sulfur dioxide through the hot suspension in absolute ethyl alcohol. The insoluble salt gradually dissolved, and the iodide separated on cooling; yield was almost quantitative. After a further crystallization from methyl alcohol, the almost colorless crystals had m. p. 254-256°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>INS: I, 40.03. Found: I, 40.24.

**3,4,3',4'-Di-(trimethylene)-thiacarbocyanine Iodide (V)**.—One and one-tenth grams of IV (2 mols), 1 g. of ethyl orthoformate (1 mol plus 300% excess), and 30 cc. anhydrous pyridine were heated under reflux for forty-five

(6) König, Kleist and Götze, *Ber.*, **64**, 1664 (1931).

minutes. The dye (0.75 g., 85% yield) separated on chilling and crystallized from methyl alcohol (700 cc. per g.) in a brownish felt of crystals with m. p. 308-309° dec.

*Anal.* Calcd. for  $C_{23}H_{21}IN_2S_2$ : I, 24.58. Found: I, 24.85.

The bluish-red methyl alcoholic solution had  $\lambda_{max}$ . of 5555 Å.

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RESEARCH LABORATORIES  
EASTMAN KODAK COMPANY  
ROCHESTER 4, N. Y.

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## The Elastic Element of Skeletal Muscle

BY HENRY B. BULL

Within recent years there has been great interest shown in rubber-like elasticity and the statistical theory of such elasticity has been formulated. It is the purpose of this note to show the close analogy between the contraction of rubber-like materials and that of muscle.

An immediate difficulty is encountered when a comparison between rubber and muscle is attempted. The resting state of a muscle is its extended state, while the resting state of rubber is its contracted state. When a muscle is allowed to contract isometrically, the tension exerted becomes progressively less as the length of the muscle is made smaller relative to that of the length of the resting muscle. The plot of the isometric tensions as a function of the length of the contracted fiber is clearly a stress-strain curve of muscle. The problem is then to extrapolate this stress-strain curve to zero stress from which the length of the completely contracted fiber can be estimated. The experiments of Ramsey and Street<sup>1</sup> allow such an extrapolation to be made. These workers have measured the isometric tensions exerted by single muscle fibers from the semi-tondonosus muscles of frogs (*Rana pipiesus*).

Out of the several experiments selected by Ramsey<sup>2</sup> as representing in his opinion the most perfect of his measurements that identified as 12-20-38 allows the best extrapolation into the region of low tensions. For this fiber, the tension values extrapolate to zero at about 30% of the resting length. This length is assumed to represent the length of the completely contracted fiber and is analogous to rubber in its unstretched state. Assigning the value of unity to the length of this completely contracted fiber, the lengths of the fiber at tensions greater than zero have been expressed relative to this completely contracted length. The tensions have been expressed in terms of dynes per sq. cm. of cross section of the completely contracted fiber. These tensions are plotted against the relative length of the fiber and the results are shown in Fig. 1.

(1) Ramsey and Street, *J. Cellular Comp. Physiol.*, **15**, 11 (1940).

(2) Ramsey, private communication.

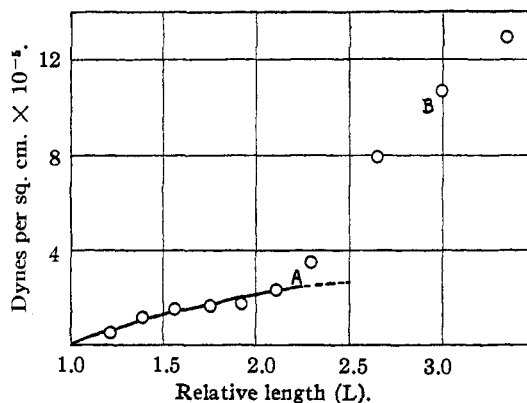


Fig. 1.—Isometric tensions plotted against the relative extension of the completely contracted fiber. The points represent the recalculated data of Ramsey and Street. The solid line is a plot of equation 1.

Comparison of Fig. 1 with the stress-strain curves for vulcanized rubber shows<sup>3</sup> a striking similarity between the stress-strain character of rubber and that of muscle. According to statistical theory, the region from the origin to A represents the straightening of randomly kinked molecular chains of the polymer while the region from A to B represents for the most part a crystallization of the polymer.

The statistical equation<sup>4</sup> which expresses the force exerted by a fiber in the region from the origin to point A has the form

$$F = \alpha \left( L - \frac{1}{L^2} \right) \quad (1)$$

where  $F$  is the force exerted by the elastic fiber at constant temperature,  $\alpha$  is a constant and  $L$  is the length of the fiber relative to that of the completely contracted length. Equation 1 has been fitted to the data plotted in Fig. 1 and the best curve drawn in. The numerical value of  $\alpha$  is about  $1.2 \times 10^5$  dynes per sq. cm. The modulus of elasticity of the fiber at zero extension is evidently  $3\alpha$  or is  $3.6 \times 10^5$  dynes per sq. cm.

The interpretation of the stress-strain curve for muscle is complicated by the fact that skeletal muscle is made up of alternate birefringent and isotropic disks. These disks are known as A- and I-disks, respectively. When a muscle contracts, the A-disks contract but the I-disks extend. Naturally, the A-disks contract more than the I-disks stretch, so that the net effect is that the muscle shortens.<sup>5</sup> It would be impossible with our present information to correct for the contribution to the length of the fiber made by the I-disk. Such a correction would be particularly difficult to apply in the case of the greatly contracted state and the effect of the I-disks on the stress-strain curve of muscle has been neg-

(3) Anthony, Caston and Guth, *J. Phys. Chem.*, **46**, 826 (1942).

(4) Guth and James, *Ind. Eng. Chem.*, **33**, 624 (1941).

(5) Buchthol, Knappels, and Lindhard, *Skad. Arch. of Physiol.*, **73**, 163 (1936).