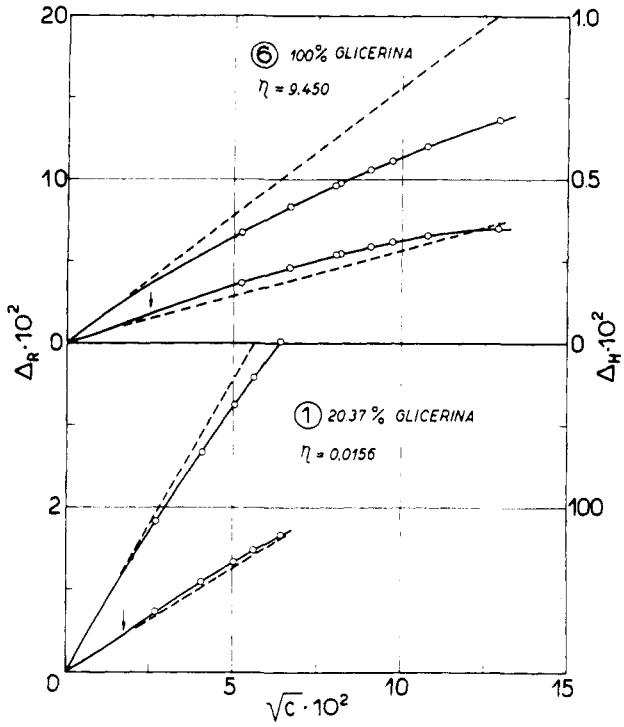

Fig. 1.—Relaxation and hydrodynamic terms in conductance for glycerol (top) and water-glycerol (bottom). Arrows show theoretical inflection points of Δ_R curves.

decrease due to purely hydrodynamic effects. The dotted lines correspond to the Onsager limits $\alpha c^{1/2}$ and $\beta c^{1/2}$. The solid curves are calculated using macroscopic dielectric constants and viscosities (and $\mathring{a} = 3.8$), while the points represent observations. The absolute values of the Δ's differ enormously for the systems shown, due to the thousand-fold change in viscosity, but qualitatively the two sets of curves are identical (except for the larger relative deviations from the limiting law in glycerol due to its lower dielectric constant). The validity of the continuum model is thus verified. Experimental details will be published shortly.

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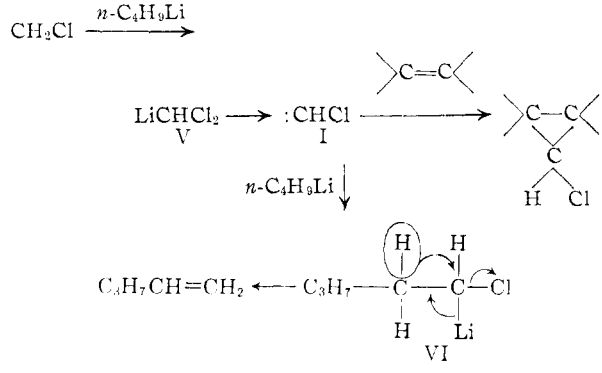
RECEIVED AUGUST 3, 1959

SYNTHESES OF CHLOROCYCLOPROPANES FROM METHYLENE CHLORIDE AND OLEFINS

Sir:

The formation of dihalocarbenes in reactions of haloforms with bases has been well substantiated.[1] We now wish to report two novel reactions which strongly suggest the existence of chlorocarbene (I) as a reaction intermediate. When *n*-butyllithium is added to methylene chloride in the presence of olefins at −25°, chlorocyclopropanes are formed in fair to good yields depending on the structure of the olefin. Thus 2,3-dimethylbutene-2 gave 67% of 1-chloro-2,2,3,3-tetramethylcyclopropane (II) (b.p. 72° (105 mm.), n^{20}D 1.4458; found: C, 63.22; H, 9.86; Cl, 26.50), *trans*-butene-2 40% of 1-chloro-2,3-*trans*-dimethylcyclopropane (III) (b.p. 91° (755 mm.), n^{20}D 1.4286; found: C, 57.13; H, 8.87; Cl, 33.84), and cyclohexene 31% of 7-chlorobicyclo[4.1.0]heptane (IV) (b.p. 94–97° (70 mm.); found: C, 64.28; H, 8.39; Cl, 26.94). The cyclopropane structures assigned to II and III were consistent with their infrared and n.m.r. spectra which provided no evidence of unsaturation. The *trans* configuration of the methyl groups in III was evident from its n.m.r. spectrum, which showed two partially overlapping doublets between 210 and 220 c.p.s. (relative to external benzene, measured at 40 mc.) to prove the non-equivalence of the methyl groups. II and III were free of isomers within the limit of detection (~1%) by vapor phase chromatography. V.p.c. analysis of IV, however, revealed the presence of two isomers in a 1:2,2 ratio.[2] Reduction of the mixture IV using sodium in liquid ammonia to yield 85% of pure bicyclo[4.1.0]heptane demonstrated that the isomers in which the chlorine occupies either an *exo* or *endo* position were both formed.

The observed exclusive *cis* addition and increase in yield with increasing nucleophilicity of the olefin[3] is consistent with the postulation of chlorocarbene as an intermediate in this reaction. The probable precursor to I, dichloromethyllithium (V), appears to be of low stability since no dichloroacetic acid could be detected after carbonation of the reaction mixture of *n*-butyllithium and methylene chloride at −70°.



Chlorocarbene as a strong electrophilic reagent can be expected to react readily with butyllithium. In line with this expectation, pentene-1, identified as its dibromide, was formed in 82% yield when methylene chloride was added to *n*-butyllithium in ether at −25°. This novel olefin synthesis may be explained by the addition of I to butyllithium yielding 1-chloro-*n*-amyllithium (VI), which undergoes α-elimination and forms the olefin via a hydride shift. An alternative mechanism proceeding through the formation of *n*-amyl chloride, then by β-elimination can be ruled out on the basis that β-elimination from primary halides on reaction with alkyllithium compounds does not proceed readily.[4]

(1) (a) J. Hine, THIS JOURNAL, **72**, 2438 (1950); (b) W. von E. Doering and A. K. Hoffman, *ibid.*, **76**, 6162 (1954).

(2) The predominant isomer had the longer retention time.

(3) (a) P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956); (b) W. von E. Doering and Wm. A. Henderson, *ibid.*, **80**, 5274 (1958).

(4) K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

Further studies of the reactivity of chlorocarbene and the different behavior of methylene bromide toward butyllithium will be the subject of a detailed publication.

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RECEIVED JULY 9, 1959

CHROMATOGRAPHY OF MYOSIN

Sir:

The general method of Peterson and Sober[1] has been applied to the muscle protein, myosin or "myosin A." Myosin A[2,3,4] freed of myosin B by dialysis against 0.2 *M* KCl, 0.01 *M* tris *p*H 7.4 in the presence of adenosine triphosphate and by 1 hour of centrifugation at 55,000 × *g* was passed through a diethylaminoethyl cellulose column equilibrated with a solvent 0.2 *M* KCl, 0.01 *M* tris *p*H 7.4. An ascending gradient to 1.0 *M* KCl was applied (Fig. 1), and protein concentration was measured[5] in the effluent. Protein recovery was better than 80%.

TABLE I

Prepn.		α	β
19	$\bar{M}_w \times 10^{-5}$	4.52	6.10
	$\bar{r}_g$	437	474
	V_m (2 d.)	4.7	9.5
22	$\bar{M}_w \times 10^{-5}$	4.55	5.00
	$\bar{r}_g$	434	560
	V_m (12 d.)	0.4	3.8
28	$\bar{M}_w \times 10^{-5}$	4.02	5.60
	$\bar{r}_g$	475	634
	V_m (3 d.)	5.0	17
33	$\bar{M}_w \times 10^{-5}$	4.21	6.36
	$\bar{r}_g$	430	500
	V_m (0 d.)	8.0	8.7
	V_m (11 d.)	1.0	8.0
21	$\bar{M}_w \times 10^{-5}$	4.00	..
	$\bar{r}_g$	434	..

Myosin is resolved into at least two components, α and β (Fig. 1). Neither component shows a turbidity drop on adenosine triphosphate addition, confirming the elimination of myosin B. The α-component probably is highly purified myosin. The data[6] of Table I yield an average $\bar{M}_w$ of 4.3 × 10^5 g. and an average $\bar{r}_g$ of 442 Å. $\bar{M}_w$ from ultracentrifuge work[7] is 4.2 × 10^5 g. This shows that the two methods can agree; moreover the straightness of the Zimm light-scattering plot (Fig. 1) does not encourage speculation about myosin nonuniform substructure.[8] In this work the "full" Zimm plot (*i.e.*, intensities at various concentrations as well as at various angles) was not attempted because it has been shown[8] that in 0.6 *M* KCl the second virial coefficient is essentially zero. The β-component is heavier (average $\bar{M}_w$, 5.77 × 10^5 g.) and more extended (average $\bar{r}_g$ 542 Å.); also its specific ATPase activity,[9] V_m, (Table I) is greater and more thermostable than that of the α-component. Scattered observations suggest that β may be transformable into α, either by warming briefly from 4 to 25°, or by aging.

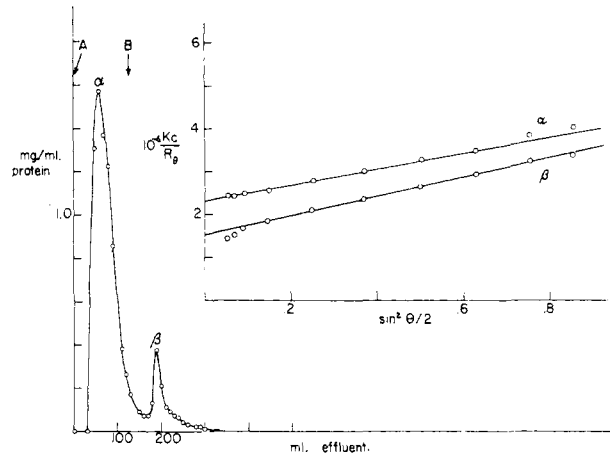

Fig. 1.—Chromatography on a 13 × 2.5 cm. column of diethylaminoethyl cellulose (1 meq./g.); eluting solutions: A—0.2 *M* KCl, 0.01 *M* tris *p*H 7.4; B—gradient elution to 1.0 *M* KCl; flow rate 60 ml./hr.; 10 ml. fractions were collected. The gradient used was composed of two cone-cylindrical vessels filled with 250 ml. of 1.0 *M* KCl, 0.01 *M* tris *p*H 7.4 and 125 ml. of 0.2 *M* KCl, 0.01 *M* tris *p*H 7.4. Insert shows: Zimm plot of α and β fractions in 0.5 *M* KCl, 0.01 *M* tris *p*H 7.4.

The author is indebted to Dr. M. Gellert for guidance in light-scattering measurements, to Dr. M. F. Morales for general counsel, and to Dr. W. Niemierko for valuable criticisms. This work was supported by a Rockefeller Fellowship and by Training Grant 2G-174 of the U.S.P.H.S.

(1) E. Peterson and H. A. Sober, THIS JOURNAL, **78**, 751 (1956).

(2) A. Szent-Györgyi, "Muscular Contraction," Academic Press, Inc., New York, N. Y., 1947.

(3) Dr. J. Botts, private communication.

(4) H. H. Weber and H. Portzehl, *Advances in Protein Chemistry*, **7**, 161 (1952).

(5) O. H. Lowry, N. J. Rosebrough, A. L. Farr and R. J. Randall, *J. Biol. Chem.*, **193**, 265 (1951).

(6) For specific refractive index increment the value of 0.209 ml./g. was used.

(7) P. H. von Hippel, H. K. Schachman, P. Appel and M. F. Morales, *Biochim. Biophys. Acta*, **28**, 504 (1958).

(8) A. Holtzer and S. Lowey, THIS JOURNAL, **81**, 1370 (1959).

(9) μ mole P·sec.$^{-1}$ g. protein^{-1} in 0.5 *M* KCl, 0.1 *M* tris, 10^{-3} $CaCl_2$, *p*H 8.0, 25°. The age of myosin preparation (in days) is indicated in parentheses.

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RECEIVED JULY 6, 1959

OPTICAL ROTATORY DISPERSION STUDIES. XXX.[1] DEMONSTRATION OF BOAT FORM IN A 3-KETO STEROID[2]

Sir:

Kinetically controlled bromination of 2α-methylcholestan-3-one[3] (or of its enol acetate) leads to 2-bromo-2-methylcholestan-3-one (m.p. 136–138°), whose spectral properties ($\lambda_{max}^{CHCl_3}$ 5.84 μ; $\lambda_{max}^{cyclohex}$ 313 mμ) require[4] an axial bromine atom. By

(1) Paper XXIX, P. Crabbé, C. Djerassi, E. J. Eisenbraun and S. Liu, *Proc. Chem. Soc.*, in press.

(2) Supported by grant No. CY-2919 from the National Cancer Institute.

(3) Y. Mazur and F. Sondheimer, THIS JOURNAL, **80**, 5220 (1958).

(4) (a) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *ibid.*, **74**, 2828 (1952); (b) R. C. Cookson, *J. Chem. Soc.*, 282 (1954).