

6-aminopiperonal with dimethyl acetylenedicarboxylate (52% yield); analyses and infrared spectrum are consistent with this formulation. In this case a crystalline uncyclized aldehyde intermediate could be isolated.

Extension of the synthesis to a variety of other heterocycles, many either not known or accessible only with difficulty at present, is in progress.

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### REDUCTION OF DIAZONIUM BOROFLUORIDES BY SODIUM BOROHYDRIDES

Sir:

The vast literature on the aromatic diazonium salts<sup>1</sup> provides numerous reagents for decomposing these reactive entities but with few exceptions these familiar reactions are all carried out in the aqueous medium in which the salts are made. This condition, of course, precludes the use of reagents which require non-aqueous or non-hydroxylic media and so unnecessarily limits the scope of reactions of which diazonium salts are probably capable.

It is well known that the borofluoride salts, however, are quite stable and can be made easily and dried for use in non-aqueous media.<sup>2</sup> In a course of studies aimed at illuminating further the non-aqueous reactions of diazonium borofluorides the reaction of sodium borohydride was examined in several solvents. The simplest and usually best procedure was to add the solid borohydride in small portions to a chilled methanolic solution, or suspension, of the diazonium borofluoride. On pouring the resultant solution carefully onto ice and hydrochloric acid, the crude product usually is precipitated crystalline. Alternatively, a chilled solution of NaBH<sub>4</sub> in dimethylformamide is added to a chilled solution of the diazonium salt in the same solvent (in which in our experience they are always soluble) and worked up as above. The cases examined are tabulated. In no instance did the use of LiAlH<sub>4</sub> solutions instead improve the yield.

TABLE I

R =	Product	Solvent	Yield, %	Crude m.p., °C.
<i>o</i> -Phenyl	Biphenyl	DMF	75	67-69
2,5-Dimethoxy	Hydroquinone Dimethyl ether	MeOH	61	54-55 <sup>a</sup>
<i>p</i> -Carboxy	Benzoic acid	MeOH	68	115-120
<i>o</i> -Carboxy	Benzoic acid	MeOH	77	115-118
<i>p</i> -Carbethoxy	Benzoic acid <sup>b</sup>	MeOH	54 <sup>b</sup>	117-119
2,4-Dinitro	<i>m</i> -Dinitrobenzene	MeOH	48	90

<sup>a</sup> After sublimation. <sup>b</sup> After saponification of total ester.

(1) K. H. Saunders, "The Aromatic Diazo-compounds," Edward Arnold, London, 1949.

(2) A. Roe, "Organic Reactions," John Wiley and Sons, New York, N. Y., 1949, Vol. 5, p. 193.

Previous methods for reducing diazonium salts having been so uncertain,<sup>1</sup> the present method bids fair to provide a reliable means of achieving the replacement of diazonium groups by hydrogen and hence of removing from aromatic rings such groups as amino, nitro and carboxyl, which are readily convertible to the diazonium salt.

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### TOTAL SYNTHESIS OF *d,l*-LONGIFOLENE

Sir:

Among the most noteworthy of recent developments in the terpene field has been the clarification of the structure of the tricyclic sesquiterpene longifolene, C<sub>15</sub>H<sub>24</sub>. An X-ray crystallographic study of the known hydrochloride (C<sub>15</sub>H<sub>25</sub>Cl), accomplished without recourse to chemical information, led to the formulation of this derivative as I,<sup>1</sup> and from the combination of this result with independent chemical studies<sup>2</sup> expression II was derived for longifolene itself (absolute configuration as indicated<sup>3</sup>). This novel proposal, which conflicted with some of the degradative work previously published,<sup>4</sup> has since been supported by the revision of earlier data and by new evidence.<sup>5,6</sup> Nonethe-



less, the problem of degradation is such that even at present the chemical facts alone do not constitute a proof of structure. An account is given of the total synthesis of *d,l*-longifolene by operations which generate structure II unambiguously.

The path of synthesis proceeds from resorcinol *via* 1,6-dioxo-8 $\alpha$ -methyl-1,2,3,4,6,7,8,8 $\alpha$ -octahydronaphthalene (III)<sup>7</sup> in seventeen steps. Selective ketalization of III with ethylene glycol-benzene-*p*-toluenesulfonic acid mixture at reflux gave the monoketal IV (66%) m.p. 62-64<sup>o</sup>,<sup>8</sup> infrared max. 6.0  $\mu$ , ultraviolet max. EtOH 241 m $\mu$  (log  $\epsilon$ , 4.0) (C, 70.33; H, 8.09) which afforded by treatment with ethylidene triphenylphosphine<sup>9</sup> (from triphenyl-ethylphosphonium bromide and *n*-butyllithium) the diene V (90% yield as an oily *cis-trans* mixture), b.p. *ca.* 110<sup>o</sup>, (0.1 mm.), ultraviolet max. EtOH 235, 243 m $\mu$  (log  $\epsilon$ , 4.34, 4.38) (C, 76.99; H, 9.33).

(1) R. H. Moffett and D. Rogers, *Chem. and Ind.*, 916 (1953).

(2) (a) P. Naffa and G. Ourisson, *ibid.*, 917 (1953); (b) G. Ourisson, G. Dupont, R. Dulou and P. Naffa, *Bull. Soc. chim., France*, 5, 21, 1075, 1115, 1410, 1415 (1954).

(3) G. Ourisson, *Chem. and Ind.*, 918 (1953).

(4) See J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, 2nd ed., Cambridge University Press, New York, N. Y., 1952, p. 92.

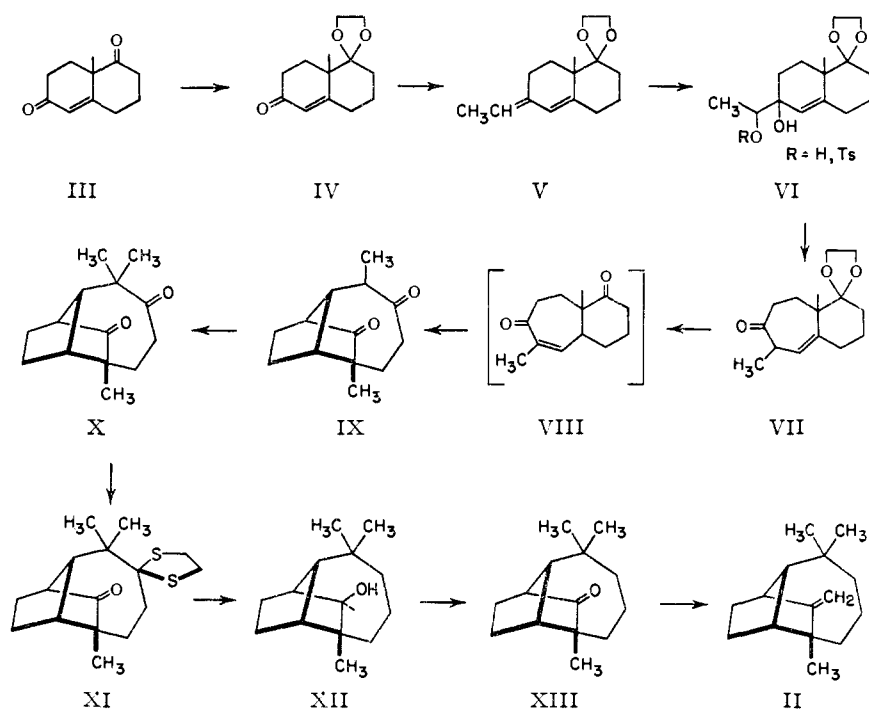
(5) T. Kubota and I. Ogura, *Chem. and Ind.*, 951 (1958).

(6) R. Mayer and K. Starosta, *J. prakt. Chem.*, 4, 11, 165 (1960).

(7) P. Wieland and K. Miescher, *Helv. Chim. Acta*, 33, 2215 (1950); S. Swaminathan and M. S. Newman, *Tetrahedron*, 2, 88 (1958); M. S. Newman and A. B. Mekler, *J. Am. Chem. Soc.*, 82, 4039 (1960).

(8) Previously reported as a liquid. J. Kalvoda and H. Loeffel, *Helv. Chim. Acta*, 40, 2340 (1957).

(9) U. Schöllkopf, *Angew. Chem.*, 71, 260 (1959).



Selective hydroxylation with osmium tetroxide (one equivalent in ether-pyridine at 0°)<sup>10</sup> converted V to a solid mixture of stereoisomeric diols VI (R = H), m.p. ca. 106–109° (C, 66.94; H, 8.97), which could be transformed into the corresponding secondary monotosuenesulfonate VI(R = Ts) by treatment with *p*-toluenesulfonyl chloride in methylene chloride-pyridine and thence by pinacol rearrangement in tetrahydrofuran-lithium perchlorate<sup>11</sup>-calcium carbonate into the unconjugated cycloheptenone VII (41–48% over-all yield from V), b.p. ca. 135° (0.05 mm.), (C, 71.98; H, 8.87) infrared max. 5.85  $\mu$ , no conjugated ketone absorption in the ultraviolet, yellow color with tetranitromethane. Mild acid-catalyzed hydrolysis of the ketal-ketone VII (25°, 2 *N* hydrochloric acid for 6 hours) produced the corresponding unconjugated diketone, infrared max. 5.85  $\mu$ ; more drastic conditions (100°, 2 *N* hydrochloric acid for 24 hours) led to the conjugated diketone VIII, infrared max. 5.85, 5.99  $\mu$ , ultraviolet max. EtOH 236  $m\mu$  ( $\log \epsilon$ , 3.95).<sup>12</sup>

The tricyclic ring system of longicamphenylone was constructed from the conjugated diketone VIII by joining the methylenic carbon alpha to the carbonyl of the six-membered ring in VIII to the trigonal carbon beta to the carbonyl of the seven-membered ring using an intramolecular version of the Michael reaction. The bridging reaction has been effected from either VIII or the non-conjugated isomer (preferably the latter) in ethylene glycol containing triethylamine at 225° for 24 hours in 10–20% yield.

(10) For isolation procedure see J. S. Baran, *J. Org. Chem.*, **25**, 257 (1960).

(11) S. Winstein, S. Smith and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959).

(12) The route reported here for the conversion IV  $\rightarrow$  VII represents a new method of ring expansion which to our knowledge is superior to any of the existing procedures as applied to conjugated cyclenones. In fact, exhaustive studies of such procedures for the specific case of IV were uniformly unsuccessful.

The crystalline product, m.p. 109–110°, has been identified as IX by analysis (C, 75.58; H, 8.73) and spectral data; infrared max. 5.75, 5.85  $\mu$  (both intense, no hydroxyl or C=C) no high intensity ultraviolet absorption, proton magnetic resonance (in CDCl<sub>3</sub>) at 8.89  $\tau$  (3 protons, sharp)

( $-\overset{\text{H}}{\text{C}}-\text{CH}_3$ ) and 8.97, 8.85  $\tau$  (1.5 protons each, sharp)

( $-\overset{\text{H}}{\text{C}}-\text{CH}_3$ ) with no olefinic protons, no color with tetranitromethane.<sup>13</sup>

Monomethylation of IX using the trityl sodium-methyl iodide procedure<sup>14</sup> afforded the crystalline C<sub>14</sub> diketone X (60% yield), m.p. 119°, infrared max. 5.75, 5.87  $\mu$ , sharp proton

resonance (in CDCl<sub>3</sub>) at 8.68  $\tau$  (3 protons) ( $-\overset{\text{H}}{\text{C}}-\text{CH}_3$ ) and 8.85  $\tau$  (6 protons) ( $\text{CH}_3\overset{\text{H}}{\text{C}}-\text{CH}_3$ ) (C, 76.68; H,

9.06) which was converted into the monoethylene-thioketal XI (72%), m.p. 167–168°, infrared max. 5.74  $\mu$ , three methyl resonance peaks in the n.m.r. spectrum (CDCl<sub>3</sub>) at 8.60, 8.68 and 9.0  $\tau$ . Reduction of the keto thioketal XI with lithium aluminum hydride yielded the corresponding alcohol, transformed by direct hydrazine reduction<sup>15</sup> to *d,l*-longicamphenylol (XII), spectroscopically and vapor chromatographically identical with an authentic sample prepared by hydride reduction of *d*-longicamphenylone.<sup>2</sup> Oxidation of XII with chromic acid afforded *d,l*-longicamphenylone (XIII) (C, 81.72; H, 10.71), m.p. 17–18°, identical with authentic *d*-longicamphenylone, m.p. 50–51°, spectroscopically (infrared n.m.r.) and vapor chromatographically.

The *d,l*-ketone XIII was methylated by reaction with methyl lithium to the corresponding tertiary alcohol which was dehydrated by thionyl chloride-pyridine to *d,l*-longicamphenylone (II), a colorless liquid, (C, 88.18; H, 11.72), spectroscopically and vapor chromatographically identical with natural *d*-longicamphenylone (70% over-all yield from XI).

It is a pleasure to acknowledge financial support from the National Science Foundation (G-9999) and the Higgins Fund of Harvard University and experimental help at various stages of the problem from J. C. Fratantoni, R. T. LaLonde and J.

(13) A related intramolecular Michael reaction is involved in the transformation of sautonin to santonic acid: S. Cannizzaro and F. Sestini, *Gazz. chim. ital.*, **2**, 241 (1873); R. B. Woodward, F. J. Brutschy and H. Baer, *J. Am. Chem. Soc.*, **70**, 4216 (1948).

(14) E. J. Corey and E. W. Cantrall, *ibid.*, **80**, 499 (1958); **81**, 1745 (1959).

(15) V. Georgian, R. Harrison and N. Gubitsch, *ibid.*, **81**, 5835 (1959).

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THE ABSOLUTE RATE CONSTANT OF PROPAGATION OF ANIONIC POLYMERIZATION OF STYRENE<sup>1</sup>

Sir:

Anionic polymerization of styrene and of some other monomers, if carried out in a suitable solvent such as tetrahydrofuran, leads to formation of "living" polymers, *i.e.*, polymeric species which are not terminated and which retain their ability to grow.<sup>2,3</sup> The lack of termination in anionic polymerization enables one to determine the absolute value of the respective rate constant of propagation by applying the technique to be described. A solution of low molecular weight "living" polystyrene (mol. wt. 1000-2000) and a solution of monomeric styrene, both prepared in tetrahydrofuran, are introduced through capillaries into a T-shaped 3-way stopcock. A rapid mixing takes place in the barrel of the stopcock, and thereafter the reacting mixture flows through a third capillary into a beaker holding a solution of water or of methyl iodide dissolved in tetrahydrofuran. The polymerization which ensues on mixing the respective reagents is terminated instantly by their contact with the solution contained in the beaker, and the time of polymerization, determined by the capillary volume and the rate of flow, may be made as short as 0.1 sec.

TABLE I

RATE CONSTANT OF PROPAGATION OF "LIVING" POLYSTYRENE IN TETRAHYDROFURAN AT 25°; Na<sup>+</sup> IS COUNTER ION

Run	Initial concn. of "living" polymers in the capillary, moles/l.	Initial concn. of styrene in the capillary, moles/l.	<i>t</i> , sec.	% conversion	Rate constants moles <sup>-1</sup> sec. <sup>-1</sup>
1-1	0.486 × 10 <sup>-2</sup>	0.223	0.792	87.3	523
1-2	.486 × 10 <sup>-2</sup>	.222	.455	65.8	
1-3	.485 × 10 <sup>-2</sup>	.224	.305	53.9	
2-1	.340 × 10 <sup>-2</sup>	.097	.743	78.4	554
2-2	.337 × 10 <sup>-2</sup>	.098	.574	69.4	
2-3	.339 × 10 <sup>-2</sup>	.097	.447	56.9	
2-4	.337 × 10 <sup>-2</sup>	.098	.331	45.9	
3-1	.374 × 10 <sup>-2</sup>	.131	.750	78.2	545
3-2	.370 × 10 <sup>-2</sup>	.128	.551	67.6	
3-3	.370 × 10 <sup>-2</sup>	.127	.414	53.5	
3-4	.367 × 10 <sup>-2</sup>	.128	.310	45.2	
4-1	.379 × 10 <sup>-2</sup>	.130	.706	81.7	570
4-2	.373 × 10 <sup>-2</sup>	.132	.561	69.0	
4-3	.371 × 10 <sup>-2</sup>	.133	.400	57.9	
4-4	.368 × 10 <sup>-2</sup>	.134	.297	47.4	

(1) This work was supported by a grant from the National Science Foundation, G-14393, and by the Quartermaster Corp., Grant No. DA-19-129-QM-1297.

(2) M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

(3) M. Szwarc, *Nature*, **178**, 1168 (1956).

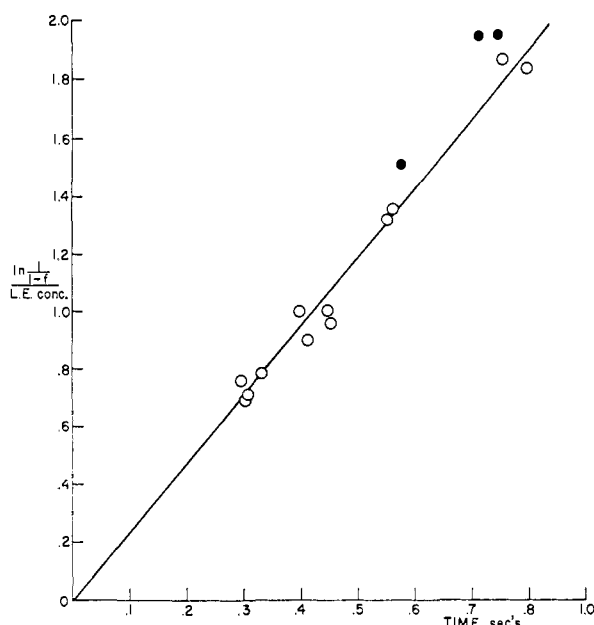


Fig. 1.—The black points were not taken into account in calculating the "least" square line.

The concentrations of the "living" ends and of the monomer are determined carefully at the beginning and at the end of each series of experiments. The rate of flow of each solution is measured directly and maintained constant in each run. Changing the pressure of pure nitrogen above each liquid permits one to vary the time of polymerization of an individual experiment. Both solutions are thermostated and the heat capacity of the reacting mixture is chosen in such a way that

TABLE II

DEPENDENCE OF  $k_p$  ON THE CONCENTRATION OF "LIVING" ENDS

System polystyrene in THF solution, counter-ion Na<sup>+</sup>, T is 25°

Concn. in moles/l. × 10 <sup>2</sup>	$k_p$ l. moles <sup>-1</sup> sec. <sup>-1</sup>
0.145	575
0.170	560
0.34	554
0.37	545
0.37	570
0.49	523
0.76	425
1.00	290
1.15	285

the adiabatic polymerization does not raise the temperature by more than 1°. The conversion of the monomer into polymer is determined directly, and the results obtained in four series of experiments are given in Table I and in Fig. 1. Since the concentration of "living" ends remains constant in each experiment, the plot shown in Fig. 1 produces a straight line and its slope gives the respective rate constant of propagation. This slope, calculated by the least square method, leads to a value of 550 l. moles<sup>-1</sup> sec.<sup>-1</sup>, and on assumption that the line must go through the origin, a least square value of 548 is obtained. The agreement between both values shows that the time of