

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.

DEPARTMENT OF CHEMISTRY JAMES B. HENDRICKSON
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES 24, CALIFORNIA RICHARD REES

RECEIVED JANUARY 10, 1961

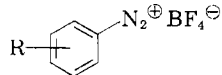
REDUCTION OF DIAZONIUM BOROFLUORIDES BY SODIUM BOROHYDRIDES

Sir:

The vast literature on the aromatic diazonium salts¹ 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.² 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 NaBH₄ 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 LiAlH₄ solutions instead improve the yield.

TABLE I

REDUCTION OF				
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 ^a
<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 ^b	MeOH	54 ^b	117-119
2,4-Dinitro	<i>m</i> -Dinitrobenzene	MeOH	48	90

^a After sublimation. ^b 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,¹ 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.

DEPARTMENT OF CHEMISTRY JAMES B. HENDRICKSON
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA

RECEIVED JANUARY 23, 1961

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, C₁₅H₂₄. An X-ray crystallographic study of the known hydrochloride (C₁₅H₂₅Cl), accomplished without recourse to chemical information, led to the formulation of this derivative as I,¹ and from the combination of this result with independent chemical studies² expression II was derived for longifolene itself (absolute configuration as indicated³). This novel proposal, which conflicted with some of the degradative work previously published,⁴ has since been supported by the revision of earlier data and by new evidence.^{5,6} 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 α -methyl-1,2,3,4,6,7,8,8 α -octahydronaphthalene (III)⁷ 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^o,⁸ infrared max. 6.0 μ , ultraviolet max. EtOH 241 μ (log ϵ , 4.0) (C, 70.33; H, 8.09) which afforded by treatment with ethylidene triphenylphosphine⁹ (from triphenyl-ethylphosphonium bromide and *n*-butyllithium) the diene V (90% yield as an oily *cis-trans* mixture), b.p. *ca.* 110^o, (0.1 mm.), ultraviolet max. EtOH 235, 243 μ (log ϵ , 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. Nafa and G. Ourisson, *ibid.*, 917 (1953); (b) G. Ourisson, G. Dupont, R. Duiou and P. Nafa, *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).