

propyl ether. After refluxing for 24 hours a clear, yellow solution containing metallic tin resulted. The ether was distilled and the product sublimed. Infrared analysis indicated approximately 50% reduction.

Reduction of benzoquinone was vigorous and exothermic, leading initially to the precipitation of quinhydrone, which redissolved as it in turn was reduced completely within 2 hours. The product hydroquinone was converted to quinhydrone by addition of more benzoquinone for isolation.

The *meso*-hydrobenzoin from reduction of benzil was isolated after the di-*n*-butyltin had been converted to the oxide by the addition of 30% hydrogen peroxide.

Isomeric alcohol mixtures obtained from *d*-carvone and *l*-methanol had specific rotations (*c* 2, chloroform) of +34.0° and -21.31°, respectively, from which the compositions reported in Table II were estimated.

Reductions with Phenyltin Trihydride.—To 2.94 g. (30.0 mmoles) of cyclohexanone was added 50 ml. of ether containing 25.5 mmoles of phenyltin trihydride. The reaction flask was cooled in an ice-bath. A pale yellow solid began to form in the orange solution and precipitation continued for several hours. The mixture was then allowed to stand at room temperature for 4 days. An infrared spectrum indicated about one-third reduction of the ketone and the presence of considerable hydride. Upon warming, decomposition of the hydride occurred, but further reduc-

tion of ketone did not seem to take place. The cyclohexanol was not isolated. Similar results were observed with 4-*t*-butylcyclohexanone and *l*-menthone.

Reductions with Butyltin Trihydride. 4-*t*-Butylcyclohexanone.—To 1.54 g. (10.0 mmoles) of 4-*t*-butylcyclohexanone in a long test-tube was added 4.6 g. (25.0 mmoles) of butyltin trihydride. The mixture was allowed to stand at room temperature for a day. Since the reaction was incomplete, the mixture was heated at 40-50° for 4 hours whence the reduction was complete. Heating at 75° for 2 hours destroyed the remaining hydride, leaving a solid red mass in the bottom of the tube. Heating on the steam-bath caused the alcohol to sublime and deposit near the top of the tube where 91% was collected. The procedure for reduction of 4-methylcyclohexanone was essentially the same.

Characterization of the Tin-containing Product from Butyltin Trihydride Reductions.—The product remaining in the test-tube after the above experiments was pyrophoric. In order to obtain the product in an analytically pure state reductions were carried out with acetone with extreme precautions taken to exclude air. From one such reduction a deep red amorphous solid was isolated.

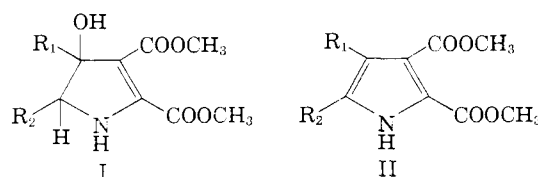
Anal. Calcd. for C₈H₉Sn: C, 27.31; H, 5.16; Sn, 67.52. Found: C, 27.23; H, 5.21, Sn, 66.57.

COMMUNICATIONS TO THE EDITOR

A NEW HETEROCYCLE SYNTHESIS: PYRROLES AND QUINOLINES

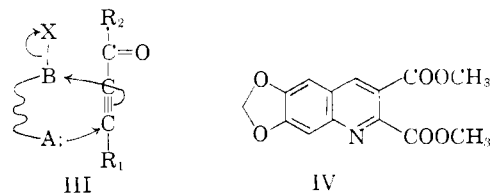
Sir:

Impelled by an interest in providing a better synthesis of pyrroles, we were led to consider Michael addition of amines to acetylenic ketones as a means of affording the enamine moiety of these heterocycles. In particular the appropriate amines should be α -amino-ketones so that the enamine, once formed, could be cyclized and dehydrated to complete the synthesis of the pyrrole ring. α -Amino-ketones, however, dimerize readily to dihydropyrazines and are stable only as their salts.¹ It was deemed reasonable, however, that in the presence of a relatively weak base the salts would generate a concentration of free base low enough to hamper the bimolecular dimerization but suitable for Michael addition to the acetylenic carbonyl compound. Accordingly, when equimolar quantities of α -aminopropiophenone hydrochloride, sodium acetate, and dimethyl acetylenedicarboxylate were boiled in methanol, NaCl deposited over several minutes and after ten minutes, filtration and evaporation afforded an 80% yield of I ($R_1 = C_6H_5$; $R_2 = CH_3$), m.p. 108°, which was converted readily to II ($R_1 = C_6H_5$; $R_2 = CH_3$), m.p. 182-183°, on boiling half an hour with a little HCl/CH₃OH and recrystallizing. The infrared spectra and analyses confirmed these formulations (infrared I, 2.85, 2.95, 5.80, 5.92, 6.21 μ ; II, 2.85, 5.80, 5.92 μ). Isolation of the intermediate I was of course not necessary and these pyrroles were prepared in the indicated yields without isolation of intermediates: II ($R_1 = R_2 = C_6H_5$), m.p. 192°, 44%; II ($R_1 = C_6H_5$, $R_2 = CH_3$),



m.p. 182-183°, 81%; II ($R_1 = R_2 = CH_3$), m.p. 142-143°, 20%. In each case the analyses were consistent with these formulations. Of these only the diethyl ester of II ($R_1 = R_2 = CH_3$) previously has been prepared, by Fischer² by the Knorr synthesis, m.p. 110°; prepared in the present procedure using diethyl acetylenedicarboxylate, the same diethyl ester had m.p. 112-113°.

The great ease and relatively high yields of this synthesis prompted us to a consideration of the extension of the approach to other heterocycles. The synthetic conception may be generalized as in III to indicate its broad potential for the production of heterocyclic nuclei; it should be noted that the acetylenic carbonyl reactant provides asymmetric directionality so that only a single isomer will



form and also affords one unit of unsaturation toward the ultimate heteroaromatic system. We have demonstrated this expanded scope in the production of the quinoline IV, m.p. 178-179°, from

(1) A. H. Corwin, "Heterocyclic Compounds," Vol. 1, p. 287, ed. R. C. Elderfield, John Wiley and Sons, New York, N. Y., 1950.

(2) H. Fischer and W. Kutscher, *Ann.*, **481**, 199 (1930).

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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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

| 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> -Carbomethoxy | 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.

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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, 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.^{2a,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, 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. 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).