mation. However, we felt that it would be most interesting to examine at least one example involving diazofluorene. We felt that this would be particularly interesting since Horner and Lingnau[12] have found that of the many addends that they investigated, in no case were they able to isolate the pyrazoline. Under the conditions of a base-washed flask in the presence of triethylamine, methyl acrylate gave a 75% yield of the corresponding recrystallized 2-pyrazoline.

It, therefore, appears that the conditions discussed above might be fairly general for the synthesis of 2-pyrazolines with two phenyl rings attached to the number five carbon.

Experimental[15]

Diphenyldiazomethane.—Diphenyldiazomethane was prepared by the method of Miller[16] with one modification. The oxidation was conducted in an open flask at room temperature with vigorous stirring.

Diazofluorene.—Diazofluorene was prepared according to the method of Schonberg, Awad, and Liatif,[17] m.p. 93–94.5°, lit. m.p. 94–95°.

General Procedure for the Reaction of Diphenyldiazomethane with Methyl Acrylate.—Reactions were run in stock, three-neck 100-ml. flasks. The flask was equipped with a pressure-equalizing addition funnel, a ball joint Herschberg stirrer, and an outlet to a gas buret. The flask was immersed in a 30-gal. tank equipped with a thermostatically controlled refrigerating unit and a continuous duty recirculating pump. This apparatus was capable of maintaining a preset temperature of ±0.5°. In a typical run, 0.55 g. (6.4 mmoles) of freshly distilled methyl acrylate and 25 ml. of the reaction solvent (usually pentane or hexane) were placed in the previously prepared reaction flask. In the runs using base, 0.571 g. (6.43 mmoles) of freshly distilled triethylamine was introduced into the reaction flask at this point. Diphenyldiazomethane (1.13 g., 5.83 mmoles) was dissolved in 25 ml. of the solvent and placed in the addition funnel. When the closed system had come to equilibrium, the solution of diazoalkane was added rapidly to the reaction mixture. The mixture was then stirred until either the color had disappeared or until gas evolution ceased. In general, at 20° in the presence of triethylamine, the reaction required approximately 16 hr. to reach completion.

The reaction mixture was worked up only if the amount of nitrogen evolved was negligible or nearly quantitative.

5,5-Diphenyl-3-carbomethoxy-2-pyrazoline.—The pyrazoline ester was obtained by removing the solvent on a Roto-Vac at room temperature from the above mixture (from which no gas evolution had been observed) and crystallizing the residue from methanol-water. In this manner, as high as 70% of the calculated amount of pure pyrazoline was obtained, m.p. 138–140° dec. Instability of the ester (apparently due to small quantities of oxygen) precluded sending the material off for analysis. However, nitrogen analysis was effected in these laboratories.

Anal. Calcd. $C_{17}H_{16}N_2O_2$: N, 10.01. Found: N, 10.09. The 2-pyrazoline was further characterized by its infrared and ultraviolet spectra. In the infrared, the compound showed strong absorptions at 3.00 (N–H), 6.00 (conjugated C=O), 6.42 μ (C=N). In the ultraviolet, the product showed one absorption at 298 mμ (log ϵ 4.02), in methanol.

5,5-Diphenyl-2-pyrazoline-3-carboxylic Acid.—A reaction mixture obtained by the above synthetic method using diphenyldiazomethane in the presence of triethylamine was worked up by first removing the solvent on a Roto-Vac, being careful to keep the temperature at 0°. The residue was then treated with cold methanol containing a slight excess of the calculated amount of potassium hydroxide. This mixture was then placed in the refrigerator overnight. The alcohol was removed from the reaction mixture and the residue taken up in water. Following acidification, the pyrazoline acid crystallized on the side of the flask on gentle warming. The crystalline acid was collected and recrystallized from methanol-water to give 70% (average of several runs) of acid, m.p. 187–189° dec. Several recrystallizations from methanol–water gave an analytical sample, m.p. 188–189° dec. Infrared absorptions appeared at 3.00 (N–H), 3.8 (broad absorption, O–H), 6.00 (conjugated carbonyl), 6.40 μ, (C=N). The acid showed a maximum in the ultraviolet at 292 mμ, (log ϵ 3.89), in methanol. Due to the sensitivity of the pyrazoline to oxygen, the recrystallized samples were stored under dry argon.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.28; H, 5.40; N, 10.51.

2,2-Diphenylcyclopropanecarboxylic Acid.—This known acid[3,10] was isolated in high yield (average of several runs, 86%) from crude reaction mixtures from which nearly quantitative nitrogen evolution had been observed. Isolation was effected by evaporating the reaction mixture *in vacuo* to near dryness. The residue was dissolved in methanol containing a slight excess of the calculated amount of potassium hydroxide and allowed to remain at room temperature overnight. The alcohol was removed from the reaction mixture and the residue taken up in water. The acid precipitated upon acidification of the aqueous solution, m.p. 161–163°, lit.[10,3] m.p. 163–164.5°, 170–171°. Recrystallization from acetone–water gave a product, m.p. 167–169°.

Reaction of Diazofluorene with Methyl Acrylate.—The reaction between diazofluorene and methyl acrylate was carried out in the manner as described for the reaction with diphenyldiazomethane with a few minor changes. Enough benzene was used in the reaction mixture to bring all of the diazofluorene into solution. It was also found that 20–24 hr. were generally required to complete the reaction. The pyrazoline ester was isolated by filtering a reaction mixture (run in a base-washed flask in the presence of triethylamine) in which no nitrogen evolution had been observed (75% yield, m.p. 187–189° dec.). Recrystallization from methanol–water gave colorless crystals, m.p. 188–189° dec. Significant infrared absorptions appeared at 2.99, 6.01 and 6.51 μ.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.10; H, 5.41; N, 10.03. Found: C, 73.17; H, 5.15; N, 10.10.

The acid was isolated in exactly the same manner as described above. The recrystallized acid (75% calcd., m.p. 169–171° dec.) decomposes so rapidly that analysis was not possible. However, its infrared spectrum was typical of a 2-pyrazoline acid showing a sharp N–H absorption at 3.00, a broad O–H band centering about 3.9, a conjugated carbonyl at 6.09 and a C=N peak at 6.49 μ. Further evidence for the structure was obtained by converting the acid back to the analyzed and characterized ester by adding the acid to a solution of diazomethane in ether and evaporating to dryness.

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[15] Melting points are uncorrected.

[16] J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

[17] A. Schonberg, W. Awad, and N. J. Liatif, *J. Chem. Soc.*, 1368 (1951).

Organoboron Compounds. XV. Equilibrium in the Thermal Isomerization of Secondary and Tertiary to Primary Alkyl Groups in Trialkylboranes[1,2]

P. A. McCusker, Frances M. Rossi, John H. Bright, and G. F. Hennion

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

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In connection with a detailed study of the kinetics of the thermal isomerization[3] of secondary and tertiary alkyl to primary alkyl groups in trialkylboranes, it was necessary to establish if equilibrium existed among

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[1] Previous paper, P. A. McCusker, P. L. Pennartz, and R. C. Pilger, Jr., *J. Am. Chem. Soc.*, **84**, 4362 (1962).

[2] Contribution from the Radiation Laboratory operated by the University of Notre Dame under contract with the Atomic Energy Commission.

[3] Reviewed by H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chap. 9, pp. 136–149.

the groups of isomers involved in the reactions chosen for this work.

When triisopropylborane (I) was heated in the 135–146° range under dry nitrogen, these isomerizations

$$\underset{\text{I}}{(i\text{-Pr})_3\text{B}} \rightleftharpoons \underset{\text{II}}{(i\text{-Pr})_2\text{B}(n\text{-Pr})} \rightleftharpoons \underset{\text{III}}{(i\text{-Pr})\text{B}(n\text{-Pr})_2} \rightleftharpoons \underset{\text{IV}}{(n\text{-Pr})_3\text{B}}$$

proceeded slowly to equilibrium mixtures. These mixtures were distillable *in vacuo* below 100° without disproportionation or isomerization, and were analyzed readily by gas–liquid chromatography (g.l.c.) over "Silicone 550" at 97°. Fortunately, this analytical procedure revealed the exact distribution of isopropyl and *n*-propyl groups among the four isomers. The equilibrium mixtures contained chiefly, IV, some III, very little II, and no I. The equilibrium composition at 146° was determined in two ways: (a) heating of IV for 47 hr. gave a mixture containing 0.5% II, 14% III, and 85.5% IV; (b) a mixture originally containing 1% II, 23% III, and 76% IV heated for 37 hr. gave a product containing 0.5% II, 16% III, and 83.5% IV. The equilibrium composition at 135° was similarly determined: (a) IV heated for 72 hr. gave a product having no I, <0.1% II, 10% III, and 90% IV; (b) heating a mixture originally containing 15.8% III and 84.2% IV for 147 hr. gave a product containing no I, < 0.3% II, 14.4% III, and 85.6% IV.

Similar results were obtained by heating tri-*sec*-butylborane (V) and tri-*n*-butylborane (VIII). In these instances, however, direct analysis by g.l.c. failed and the equilibrium mixtures could be analyzed only by determination of the relative amounts of *sec*-butyl and *n*-butyl alcohols produced by hydrogen peroxide oxidation. Analysis of ethereal solutions of these alcohols was accomplished very well by g.l.c. over "Ucon Polar" at 115°. Heating of either V at 191° for 26 hr. or VIII at 190° for 7 hr. or 14 hr. gave, after oxidation, 6% *sec*-butyl alcohol and 94% *n*-butyl alcohol. These data indicate, by analogy with the *n*-propyl *vs.* isopropyl case, the equilibrium composition of butylboranes to be as follows: no V, trace of di-*sec*-butyl-*n*-butylborane (VI), 18% di-*n*-butyl-*sec*-butylborane (VII), and 82% VIII at 190–191°.

Thermal isomerization of diisobutyl-*t*-butylborane[4] (IX) gave a significantly different result in that the formation of triisobutylborane (X) was essentially irreversible. Thus, heating of X for 20 hr. in one experiment and for 35 hr. in another, both at 135°, followed by peroxide oxidation and g.l.c. gave isobutyl and *t*-butyl alcohols in a ratio greater than 99.7:0.3. When X was heated for 7 hr. at 186° similar analysis gave the alcohols in the ratio 99.3:0.7. A mixture originally containing 7.2% IX and 92.8% X, heated for 23 hr. at 188° gave, after oxidation, isobutyl and *t*-butyl alcohols in a 99.5:0.5 ratio. Furthermore, the kinetics of the isomerization of IX to X at five temperatures between 125 and 150° indicate a clean, irreversible unimolecular process.

The data presented above permit the following conclusions: (a) for the equilibrium III $\rightleftharpoons$ IV at 146°, $K \simeq 5.7$ and $\Delta F = -1.4 \pm 0.06$ kcal./mole; at 135°, $K \simeq 7.5$ and $\Delta F = -1.6 \pm 0.1$ kcal./mole; (b) for VII $\rightleftharpoons$ VIII at 190°, $K \simeq 4.5$ and $\Delta F \simeq -1.4$ kcal./mole; (c) for IX $\rightleftharpoons$ X at 135°, $K > 99$ and $\Delta F > -3.7$ kcal./mole; at 186°, $K \simeq 54$ with $\Delta F \simeq -3.5$ kcal./mole. These findings supplement those of Brown[3] and establish that the stability of alkyl groups attached to boron is primary > secondary ≫ tertiary. It should be noted also that the equilibrium mixtures of trialkylboranes contain the unsymmetrical isomers (*e.g.*, II and III) which survive without disproportionation.

The kinetics and the mechanisms of these isomerizations will be discussed in a later communication.

Experimental

Trialkylboranes.—Triisopropyl- (I), tri-*n*-propyl- (IV), tri-*sec*-butyl- (V), tri-*n*-butyl- (VIII), and triisobutylborane (X) were prepared by the alkylation of boron trifluoride (as the etherate) with the appropriate Grignard reagent in anhydrous ether.[5] Products were fractionally distilled *in vacuo;* a high degree of isomer purity was established in each case by oxidation to the corresponding alcohol,[6] easily recognized by g.l.c. Compounds I and IV were also checked directly by g.l.c. and were observed to give single, distinct, and reproducible peaks. Diisobutyl-*t*-butylborane (IX) was prepared from *t*-butyl chloride, boron trifluoride, and magnesium in anhydrous ether as previously described.[4]

Product Analysis.—Gas–liquid chromatography was accomplished with the "Kromo-Tog I" and 2-m. columns supplied by Hypren Co., Pittsburgh, Pa. Alcohols, singly or in mixtures, were recognized by comparison with authentic samples using "Ucon Polar" columns at *ca.* 115°. The propylboranes were resolvable with "Silicone 550" columns at 97°. Higher trialkylboranes were decomposed during g.l.c. over all columns used; in these cases analysis could be made only *via* the alcohols produced by oxidation.

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[4] G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **80**, 617 (1958).

[5] E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

[6] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956).

The Preparation of Some Benzyl-*o*-nitrophenylglyoxals and Cyclization of Their Quinoxalines

R. Percy Barnes, Joseph H. Graham,[1] and
M. A. Salim Qureshi[2]

*Department of Chemistry, Howard University, Washington,
District of Columbia*

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C. W. Muth, *et al.*,[3,4] have reported examples in the biphenyl series of the condensation of a nitro group in the 2-position with an activated methylene group in the 2′-position with the production of cyclic amine oxides.

With the idea that benzyl-*o*-nitrophenylglyoxals might similarly lead to substituted quinoline N-oxides, we prepared the following glyoxals.

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[1] Taken from Ph.D. thesis, Howard University, 1959.

[2] In partial fulfillment of the requirements for the M. S. degree.

[3] C. W. Muth, J. C. Ellers, and O. F. Folmer, *J. Am. Chem. Soc.*, **79**, 6500 (1957).

[4] C. W. Muth, N. Abraham, L. Linfield, R. B. Wotring, and E. A. Pacofsky, *J. Org. Chem.*, **25**, 736 (1960).