from benzyl chloride and sodium iodide[10] and purified by recrystallization from ethanol. Nickel carbonyl was prepared by the procedure of Chiusoli and Mondelli.[11] Anhydrous nickel bromide was prepared as described in the literature.[12] Ethanol was dried by magnesium and iodine and then distilled. Tetrahydrofuran was refluxed with sodium and benzophenone until the solution turned blue and was then distilled. Cyclohexane, benzene, and toluene were dried over sodium wire and then distilled. N,N-Dimethylformamide and dimethyl sulfoxide, reagent grade materials, were fractionated and dried over a molecular sieve. Acetonitrile and nitromethane were distilled over phosphorus pentoxide. All solvents were saturated with argon before use. The analysis of nickel and bromide in aqueous solution was performed as described in the text.[13]

General Procedure.—A mixture of 7.5 g (0.05 mole) of nickel carbonyl and 0.05 mole of benzyl halide in 50 ml of solvent was stirred at 50–60° for 50 hr under an atmosphere of argon. The solvent was then removed by an aspirator and the residue was extracted with ether (or the reaction mixture was partitioned between ether and water when N,N-dimethylformamide or dimethyl sulfoxide was used as solvent). The extract was washed with water and dried over anhydrous magnesium sulfate. After the ether was removed the residue was distilled at reduced pressure. The distillate was analyzed and identified by gas–liquid partition chromatography and infrared and nmr spectra with authentic samples. Yields were calculated by gas–liquid partition chromatography and nmr spectra from the relative areas of singlet methylene peaks of benzyl groups.

4-Iodo-*n*-butyl Phenylacetate.—A mixture of 7.5 g (0.05 mole) of nickel carbonyl and 10.9 g (0.05 mole) of benzyl iodide in 50 ml of tetrahydrofuran was treated as described above. Distillation at reduced pressure gave two fractions: fraction 1, 0.9 g, bp 120–140° (0.5 mm); and fraction 2, 10.3 g, bp 145–160° (0.5 mm). Each fraction was analyzed by gas–liquid partition chromatography and infrared and nmr spectra. Fraction 1 was shown to be a mixture of 0.2 g of bibenzyl and 0.6 g of dibenzyl ketone. Fraction 2 was shown to consist of 0.2 g of dibenzyl ketone and 9.8 g of 4-iodo-*n*-butyl phenylacetate. The analytical sample of the ester was obtained by repeated distillation, bp 157–158° (0.5 mm).

Anal. Calcd for $C_{12}H_{15}O_2I$: C, 45.31; H, 4.74; I, 39.89; mol wt, 318. Found: C, 45.45; H, 4.76; I, 40.12; mol wt, 316.

Its nmr spectrum in CCl_4 exhibited a singlet (five protons) at τ 2.82, a triplet (two protons) at 5.99 (J = 6 cps), a singlet (two protons) at 6.51, a triplet (two protons) at 7.06 (J = 6 cps), and a multiplet (four protons) at τ 8.29, consistent with the structure $C_6H_5CH_2COOCH_2CH_2CH_2CH_2I$.

Benzylation of Benzene.—A solution of 7.5 g (0.05 mole) of nickel carbonyl and 6.4 g (0.05 mole) of benzyl chloride in 50 ml of benzene was stirred at 50–60° for 50 hr under argon. The reaction mixture was filtered to remove nickel chloride deposited during the reaction. The filtrate was washed with water and dried over anhydrous magnesium sulfate. Removal of benzene and distillation under vacuum gave the following fractions: fraction 1, 3.3 g, bp 74–75° (0.5 mm); fraction 2, 0.7 g, bp 150–160° (0.5 mm); and 1.3 g of polymeric residue. On standing fraction 1 crystallized. Recrystallization from ethanol provided white needles, mp 26–27°, and no depression resulted on admixture with diphenylmethane (mp 27°). Fraction 2 was shown to be a mixture of dibenzylbenzenes, but the relative amounts of the three isomers were not determined. Three crystallization from ethanol gave white needles: mp 78–80° (melting points of 1,2-, 1,3-, and 1,4-dibenzylbenzene are 78, 59, and 86°, respectively[14]).

Anal. Calcd for $C_{20}H_{18}$: C, 93.02; H, 6.98; mol wt, 258. Found: C, 93.08; H, 7.00; mol wt, 261.

Its nmr spectrum in CCl_4 exhibited a singlet (ten protons) at τ 3.01, a singlet (four protons) at 3.12, and a singlet (four protons) at 6.18.

Benzylation of Toluene.—A mixture of 7.5 g (0.05 mole) of nickel carbonyl and 8.6 g (0.05 mole) of benzyl bromide in 50 ml of toluene was treated in the similar manner described for the benzylation of benzene. The 5.3-g fraction, bp 85–90° (0.7 mm), was shown to be monobenzylation products of toluene by gas–liquid partition chromatography with authentic samples. The authentic samples of *o*-, *m*-, and *p*-benzyltoluene were prepared by coupling reactions between the Grignard reagent of *o*-, *m*-, or *p*-bromotoluene and benzyl chloride. Analysis of the monobenzylation products by gas–liquid partition chromatography using a Z 45 capillary column at 190° showed that only *ortho* (46.6 min) and *para* (48.9 min) isomers were obtained and the relative peak area of *ortho* to *para* was 74:100, which was consistent with the observation from the infrared spectrum.

Registry No.—Nickel carbonyl, 13463-39-3; bibenzyl, 103-29-7; dibenzyl ketone, 102-04-5; 4-iodo-*n*-butyl phenylacetate, 15135-08-7; 1,2-dibenzylbenzene, 792-68-7; 1,3-dibenzylbenzene, 15180-20-8; 1,4-dibenzylbenzene, 793-23-7.

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(11) G. P. Chiusoli and G. Mondelli, *Chem. Ind.* (Milan), **43**, 259 (1961).

(12) R. B. King, *Organometal. Syn.*, **1**, 71 (1965).

(13) T. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. 2, 9th ed, William T. Hall, 1942, pp 93, 297.

(14) J. A. Smythe, *J. Chem. Soc.*, **121**, 1277 (1922); G. Stradnikow and L. Kaschtanow, *Ber.*, **61**, 1389 (1928).

Synthesis of Benzaldehyde-d_1 *via* an Ylide Intermediate[1]

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Aldehydes labeled with deuterium at C-1 have become increasingly valuable in studies of chemical and biochemical reaction mechanisms[2] and methods affording their facile preparation are therefore of wide interest.

Although it has been reported[3] that decarboxylation of aromatic α-keto acids required 13-hr refluxing in the presence of both benzoic anhydride and pyridine, in our hands phenylglyoxylic acid was readily transformed into benzaldehyde (70–74% yield) after 1 hr at 125° in the sole presence of 1.1 molar equiv of a tertiary base in which the nitrogen has the sp^3 configuration. Thus N,N-dimethyl-*p*-toluidine, N-ethylmorpholine, or N,N-dimethylbenzylamine all functioned equally well, whereas when the sp^2-hybridized pyridine was used the yield of aldehyde fell to 30–34%.

These results are consistent with the steric requirements for an intramolecularly hydrogen-bonded intermediate II, formed by nucleophilic attack of the base on the keto carbonyl carbon of the acid I. The intermediate II, or its tautomer IIa, readily loses carbon dioxide to afford the resonance-stabilized ylide III, transformed by loss of base to the aldehyde. Similar ammonium ylides have been reported in the literature.[4]

This mechanism is supported by the following observations. (1) When 2,6-lutidine was used as the base, the yield of aldehyde fell to 1% and more than 90% of phenylglyoxylic acid was recovered. This result is attributable to the additional steric interference between the methyl group of the sp^2-hybridized base and the substrate.[5] (2) Using mesitylglyoxylic acid, under the same conditions under which phenylglyoxylic acid gave benzaldehyde, no decarboxylation took place and

(1) Supported by the National Institutes of Health, U. S. Public Health Service (Research Grant HE-5881).

(2) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Am. Chem. Soc.*, **88**, 3595 (1966), and references cited therein.

(3) T. Cohen and I. H. Song, *ibid.*, **87**, 3780 (1965).

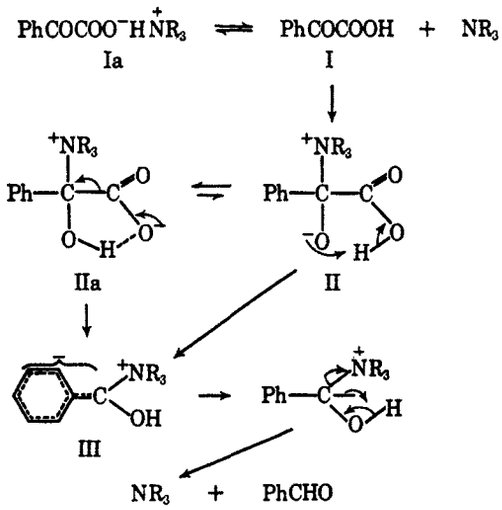
(4) (a) J. Watson and P. Haake, *J. Org. Chem.*, **30**, 1122 (1965); (b) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929); (c) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 253–260.

(5) H. C. Brown, D. Gintis, and H. Podall, *J. Am. Chem. Soc.*, **78**, 5375 (1956).

more than 95% of the acid was recovered. Steric hindrance to the formation of the intermediate II may thus equally originate on the keto acid. (3) The high yields of aldehydes obtained from polycyclic arylglyoxylic acids[6] are in agreement with the increasing resonance stabilization conferred upon the ylide III by the larger aromatic systems. (4) Heating the acid alone under the above conditions of time and temperature did not effect decarboxylation. When only 0.1 molar equiv of a tertiary base was used, the decarboxylation proceeded, although at a slower rate. This indicates that a proportion of the acid I initially exists as the salt Ia. (5) In aliphatic α-keto acids the resonance stabilization of the ylide III is lacking, and the need for more vigorous conditions is therefore to be expected. Thus 2-ketodecanoic acid required 9-hr heating to 150–160° in presence of N,N-dimethyl-*p*-toluidine to give 55–59% of *n*-nonanal. After 5 hr, the yield was 30–32%, and no reaction was observed after 1 hr.[7]

Phenylglyoxylic acid-d_1, containing 90% deuterium in the carboxyl group (based on nmr integration), on decarboxylation in the presence of N-ethylmorpholine similarly gave benzaldehyde-d_1 shown to contain 90% deuterium at C-1. If the decarboxylation was carried out in the presence of N,N-dimethyl-*p*-toluidine, the resulting benzaldehyde contained only 10% deuterium in the aldehyde moiety, and this result is clearly due to the facile proton exchange in the aromatic ring which anilines are known[8] to undergo in the presence of acids.

The ready decarboxylation of arylglyoxylic acids described above is particularly useful in view of their accessibility[6] from the corresponding aryl methyl ketones, and the method provides a simple synthesis of aldehydes either in the protium or in the deuterium form.



Experimental Section

Decarboxylation of Phenylglyoxylic Acid. General Procedure.—A mixture of 1.0 g of phenylglyoxylic acid and 1.1 molar equiv of a tertiary amine was heated under a nitrogen atmosphere at 125–130° (oil bath) for 1 hr. The flask was then cooled; the contents were taken up in 30 ml of ether. The ether solution (washed successively with 4% HCl solution, saturated sodium carbonate solution, and water) was treated with 15 ml of 95% ethanol and then with dinitrophenylhydrazine solution, warmed to 60° to remove ether, and allowed to stand at room temperature for 2–3 hr. The dinitrophenylhydrazones had mp 237–239°, undepressed on admixture with authentic benzaldehyde dinitrophenylhydrazone.

Benzaldehyde-d_1.—A solution of 2.0 g of phenylglyoxylic acid in 25 ml of benzene was treated successively with three 2-ml portions of deuterium oxide (99.9%) and the water removed by azeotropic distillation. Distillation to dryness under reduced pressure gave the deuterated acid as needles, mp 65–66°, containing 90% deuterium in the carboxyl group by nmr integration.

Decarboxylation of this acid by the general procedure described above, using N-ethylmorpholine as the base, and evaporation of the ether solution gave benzaldehyde-d_1 (single peak by glpc, retention time identical with that of an authentic sample) showing 90% deuterium on the aldehyde carbon by nmr integration.

When the base used was N,N-dimethyl-*p*-toluidine, the aldehyde contained only 10% deuterium at C-1.

Decarboxylation of 2-Ketodecanoic Acid.—A mixture of 0.2 g (0.0011 mole) of 2-ketodecanoic acid and 0.2 g (0.0015 mole) of N,N-dimethyl-*p*-toluidine was heated under a nitrogen atmosphere at 150–160° (oil bath) for 9 hr. The product was worked up as described in the general procedure to afford the dinitrophenylhydrazone, mp 101–102° (undepressed upon admixture with authentic *n*-nonanal dinitrophenylhydrazone). In a duplicate determination the ether solution, after washing with 4% HCl and carbonate solution, was dried over $MgSO_4$ and filtered; the ether was removed under reduced pressure. The infrared spectrum and glpc retention time (single peak) of the residue were identical with those of authentic *n*-nonanal.

Registry No.—Benzaldehyde-d_1, 3592-47-0.

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(7) The reported failure of the decarboxylation with pyridine alone, the reported[8] need for the long reaction period in the case of phenylglyoxylic acid, and the low yield of impure aldehyde in the aliphatic example cited[8] may thus be accounted for by the use of too low a reaction temperature.

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Nucleophilic Displacement in a Propargyl *p*-Toluenesulfonate[1-3]

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Ethynylation of *O*-substituted *aldehydo* sugars, to give 1-substituted propargyl alcohol derivatives (reaction 1), offers a useful method for extending the

$$\text{RCHO} \longrightarrow \text{RCHC}{\equiv}\text{CH} \quad (1)$$
(OH)

carbon chain of sugars and provides potential routes to a wide range of modified sugars of biological interest.[5-7] The reaction leads to a pair of diastereoisomers, which can be separated by gas–liquid partition chromatography[2,5] or by fractional crystalliza-

(1) Part V in the series "Extension of Sugar Chains Through Acetylenic Intermediates."

(2) Previous paper in this series: D. Horton, J. B. Hughes, and J. K. Thomson, *J. Org. Chem.*, **33**, 728 (1968).

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(4) To whom inquiries should be addressed.

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(7) J. L. Godman and D. Horton, *ibid.*, **4**, 392 (1967).