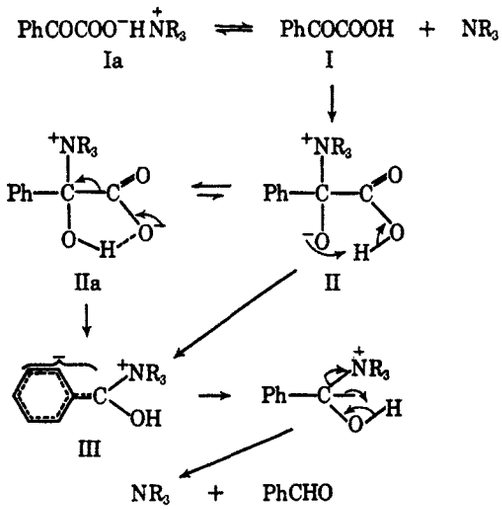
more than 95% of the acid was recovered. Steric hindrance to the formation of the intermediate II may thus equally originate on the keto acid. (3) The high yields of aldehydes obtained from polycyclic arylglyoxylic acids[6] are in agreement with the increasing resonance stabilization conferred upon the 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.

(6) J. C. Craig, J. W. Loder, and B. Moore, *Australian J. Chem.*, **9**, 222 (1956).

(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.

(8) (a) C. K. Ingold, C. G. Raisin, and C. L. Wilson, *J. Chem. Soc.*, 915 1636 (1936); (b) A. P. Best and C. L. Wilson, *ibid.*, 28 (1938); (c) N. Okazaki and M. Koidzume, *Bull. Chem. Soc. Japan*, **16**, 371 (1941); (d) V. Gold, R. W. Lambert, and D. P. N. Satchell, *J. Chem. Soc.*, 2461 (1960).

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).

(3) Supported by the National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare, Bethesda, Md.; Grant No. GM-11976-03 (The Ohio State University Research Foundation Project 1820). Funds for the nmr spectrometer were provided by the National Science Foundation, Washington, D. C.

(4) To whom inquiries should be addressed.

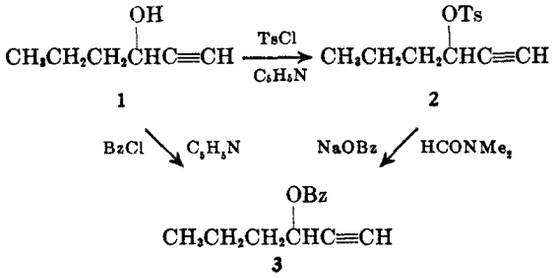
(5) D. Horton, J. B. Hughes, and J. M. J. Tronchet, *Chem. Commun.* (London), 481 (1965).

(6) D. Horton and J. M. J. Tronchet, *Carbohydrate Res.*, **2**, 315 (1966).

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

tion of suitable *O*-substituted derivatives.[6,7] Racemization at the newly formed asymmetric center has been shown not to occur under mild acidic or basic conditions.[7] For synthetic purposes, replacement of the hydroxyl group by an external nucleophile would offer a method for stereochemical interconversion and for introduction of a nitrogen, sulfur, or other atom, at the position adjacent to the ethynyl group. However, the possibility exists that the propargyl alcohol derivative, suitably substituted to give the oxygen atom good leaving-group character, might not suffer direct nucleophilic attack at the saturated carbon atom, but might react by some other pathway. Attack at the alkyne terminus by an SN2′ type of process could give a terminally substituted allene derivative, or an elimination reaction could give a vinylacetylene. This report describes the reaction of the *p*-toluenesulfonic ester of a simple model compound, 1-hexyn-3-ol (**1**), with benzoate ion in *N*,*N*-dimethylformamide, and demonstrates that replacement of the *p*-tolylsulfonyloxy group by a benzoyloxy group can be effected without rearrangement in this system.

p-Toluenesulfonation of 1-hexyn-3-ol (**1**) in pyridine requires critical control of reaction conditions, probably because quaternization of pyridine by the product is facile.[8] Preparation of the ester by a published procedure[8] gave a product that contained a number of by-products, as revealed by thin layer chromatography. 3-*p*-Tolysulfonyloxy-1-hexyne (**2**) prepared by a modified procedure was chromatographically homogeneous and was characterized by ir and nmr spectroscopy (see Experimental Section). When the *p*-toluenesulfonate **2** was heated with an excess of sodium benzoate in *N*,*N*-dimethylformamide for 5 hr at 120–130° the starting material underwent complete conversion, and a chromatographically homogeneous product was isolated in 56% yield. It was identified as 3-benzoyloxy-1-hexyne (**3**) by ir and nmr spectroscopy, and by direct comparison with an authentic sample of **3** prepared by benzoylation of **1**.



The result indicates that the major course of the reaction involves direct replacement at C-3 of the *p*-tolysulfonyloxy group by a benzoyloxy group. The nmr spectrum of the product did not reveal a detectable proportion of 1-benzoyloxyhexa-1,2-diene. The possibility cannot be excluded that, in addition to mechanical losses leading to diminution in yield, some of **2** may have undergone elimination; the resultant hex-3-en-1-yne would have been lost when the solvent was evaporated. The present data do not permit conclusions to be drawn on the stereochemistry or molecularity of the reaction.

(8) G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

Nmr spectroscopy is an extremely effective tool for studying the structure and reactions of terminal acetylenes, because the proton of the C≡CH group gives a characteristic signal near τ 7.5 that is split into a narrow doublet by long-range coupling if a methine group is adjacent to the ethynyl group.[2,5-7] In the case of the *p*-toluenesulfonate **2**, however, the signal of the acetylenic proton is obscured by the signal of the aryl methyl group, when the spectrum is measured in chloroform-*d*. This undesirable feature could be circumvented by use of a specific solvent shift. When the spectrum of **2** was measured in carbon tetrachloride, the chemical shifts of all protons were essentially the same as in chloroform-*d*, except for the signal of the acetylenic proton (H-1), which was shifted upfield by 0.15 ppm, so that the H-1 signal was clearly observable as a discrete, narrow doublet. The acetate of **1** was prepared and it was likewise found that the acetylenic proton experienced specific shielding, causing an upfield shift of 0.11 ppm, when the solvent was changed from chloroform-*d* to carbon tetrachloride.

Experimental Section[9]

DL-3-*p*-Tolysulfonyloxy-1-hexyne (2).—To a solution of DL-1-hexyn-3-ol[10,11] (**1**, 20 g) in dry pyridine (100 ml) at 0° was added a solution of *p*-toluenesulfonyl chloride (21 g) in dry pyridine (100 ml) at 0°, and the mixture was kept for 11 hr at room temperature. The solution was cooled, a few milliliters of water was added, and after 30 min the solution was poured into ice and water (800 ml). The product was extracted with three 100-ml portions of chloroform, the extract was washed three times with 100-ml portions of water, and the dried (magnesium sulfate) extract was evaporated. Pyridine was removed from the resultant oil by coevaporation with toluene, and the product was purified by passing a solution of the oil, in benzene, through a short column packed with silica gel.[12] Evaporation of the solvent gave 12.3 g (25%) of **2** as a chromatographically homogeneous, yellow oil: R_f 0.8 (19:1 benzene–methanol); λ_{max}^{film} 3.00 (C≡CH), 4.73 (C≡C), 6.25, 6.76 (aryl), 8.46 μm (sulfonate); nmr (chloroform-*d*), τ 2.12, 2.28, 2.58, 2.72 (four-proton A_2B_2 system, aryl protons), 4.93 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6.2 Hz, $J_{1,3}$ = 2 Hz, H-3), 7.55 (four-proton broad singlet, H-1 and CH_3 of Ts), 8.02–8.82 (four-proton multiplet, H-4, -5 methylene protons), 9.09 (three-proton perturbed triplet, H-6 methyl protons). The nmr spectrum in carbon tetrachloride was closely similar, except that the H-1 signal was shifted upfield to τ 7.70, where it was observed as a sharp doublet, separated from the aryl methyl group signal at τ 7.55.

Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.89; H, 6.32.

The following, alternative procedure was also employed. To a suspension of *p*-toluenesulfonyl chloride (20 g) in dry pyridine (11 ml) at 15° was added DL-1-hexyn-3-ol (10 g) dropwise, with the temperature being maintained at 10–20° for 30 min. The mixture was kept for a further 40 min at 20° and then for 18 hr at 4°. The product was then isolated by the procedure used in the preceding preparation, to give 22.2 g (86%) of **2** as a dark yellow oil. Tlc indicated the presence of three minor components in addition to **2**. The nmr spectra of the two products were closely similar.

By a somewhat different procedure, Eglington and Whiting[8] reported a crude yield of 70%.

(9) Evaporations were performed under diminished pressure. Infrared spectra were measured with a Perkin-Elmer Model 137 infrared spectrophotometer. Nuclear magnetic resonance spectra were measured at ~35° with a Varian A-60 nmr spectrometer, with tetramethylsilane (τ 10.00) as the internal standard. Thin layer chromatography was performed with silica gel G, activated for 2 hr at 110°, as the adsorbent and indication was effected with sulfuric acid or iodine vapor.

(10) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(11) Supplied by Aldrich Chemical Co., Inc., Milwaukee, Wis.

(12) Silica Gel Davison, grade 950, 60–200 mesh, Davison Division of the W. R. Grace Co., Inc., Baltimore, Md.

DL-3-Benzoyloxy-1-hexyne[12] (3). A. From DL-3-Tolysulfonyloxy-1-hexyne (2).—A stirred mixture of DL-3-*p*-tolysulfonyloxy-1-hexyne (2, 2.00 g) and sodium benzoate (7.5 g) in dry *N,N*-dimethylformamide (300 ml) was heated for 5 hr at 120–130°. The solution was poured into ice and water (800 ml) and the mixture was extracted with three 100-ml portions of chloroform. The extract was washed with three 100-ml portions of water and dried (magnesium sulfate) and the solvent was evaporated at 60° (3–4 torr) to yield a yellow chromatographically homogeneous, mobile oil. Distillation gave 894 mg (56%) of pure **3**: bp 96–98° (0.7 torr); R_f 0.9; λ_{max}^{film} 3.12 (C≡CH), 4.77 (C≡C), 5.80 μm (C=O); nmr (chloroform-*d*), τ 1.89, 2.53 (multiplets, five protons, aryl), 4.32 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6.5 Hz, H-3), 7.52 (one-proton doublet $J_{1,3}$ = 2 Hz, H-1), 8.32, 9.02 (multiplets, seven protons, propyl).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.23; H, 6.95.

B. From DL-1-Hexyn-3-ol (1).—To a solution of 1 (2 g) in dry pyridine (20 ml) at 0° was added benzoyl chloride (2.7 ml, ~1.1 mole equiv) dropwise with shaking. The solution was kept for 1 hr at 0° and a further 3 hr at room temperature. A few drops of water were then added and after 10 min the mixture was poured into aqueous sodium hydrogen carbonate (400 ml). The product was extracted with three 50-ml portions of chloroform, and the extract was washed with two 50-ml portions of water, dried (magnesium sulfate), and concentrated. Pyridine was removed by coevaporation with toluene, and the product was distilled to give 2.2 g (53%) of **3**, bp 80–82° (0.1 torr), identical with the product prepared by method A, by tlc and by comparative ir and nmr spectra.

Nmr Data for DL-1-Hexyn-3-ol (1) and Its Acetate.—Substance 1 (R_f 0.5 in 9:1 benzene–ether) gave the following data (carbon tetrachloride): τ 5.69 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6 Hz, $J_{1,3}$ = 2 Hz, H-3), 6.65 (one-proton singlet, OH), 7.65 (one-proton doublet, H-1), 8.40, 9.05 (multiplets, seven protons, propyl).

Acetylation of 1 with acetic anhydride and pyridine gave chromatographically homogeneous DL-3-acetoxy-1-hexyne: bp 155–165° (760 torr) (lit.[10] bp 74° (30 torr)); R_f 0.9 (9:1 benzene–ether); λ_{max}^{film} 3.05 (C≡CH), 4.73 (C≡C), 5.75 μm (OAc), OH absent; nmr (carbon tetrachloride), τ 4.69 (one-proton triplet of narrow doublets, $J_{3,4}$ = 6 Hz, $J_{1,3}$ = 2 Hz, H-3), 7.65 (one-proton doublet, H-1), 7.99 (three-proton triplet, OAc), 8.39, 9.03 (multiplets, seven protons, propyl). In chloroform-*d* the spectrum was closely similar, except that the H-1 signal was observed at τ 7.54 and the acetoxy group signal was observed at 7.93.

Registry—1, 15352-98-4; 1 acetate, 15352-99-5; 2, 15353-00-1; 3, 15353-01-2.

(13) M. Koulkes and I. Marszak, *Bull. Soc. Chim. France*, 556 (1952).

Reaction of Bromine with α-Phenylcinnamic Acid

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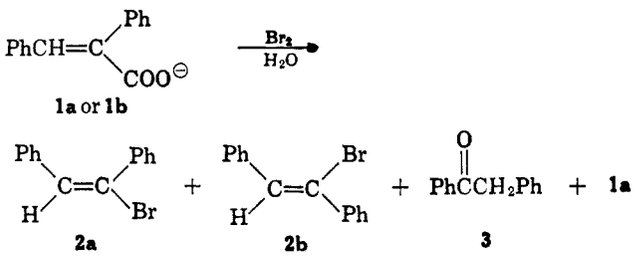
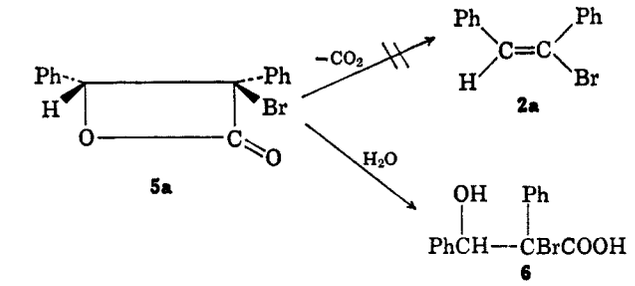
In connection with other studies we wished to obtain samples of *cis*- and *trans*-bromostilbene. An attractive synthesis appeared to be that reported by Berman and Price[2] in which the sodium salts of α-phenylcinnamic acids gave these bromostilbenes upon treatment with bromine in water. The reaction was reported as going in a stereospecific manner with retention; *i.e.*, sodium *cis*-α-phenylcinnamate (**1a**) gave *cis*-bromostilbene (**2a**) and sodium *trans*-α-phenylcinnamate (**1b**) gave *trans*-bromostilbene (**2b**).[3] In our hands, under similar conditions, these sodium salts of α-phenylcinnamic acid gave α-bromostilbenes with little stereoselectivity. In addition to the α-bromostilbenes obtained, deoxybenzoin (**3**) was also a major product and, in fact, in the reaction of bromine with **1b**, **3** proved to be the major product.

Adding 1 equiv of Br_2 to a solution of **1a** in slightly basic aqueous solution at 55° gave **2a**, **2b**, and **3** (in the ratio of 21:16:11, respectively) along with recovered **1a**. This same reaction with **1b** gave **2a**, **2b**, **3** (in the ratio of 8:5:61), and **1a** with no observable amount of **1b** recovered.



Varying the temperature from 40 to 70° had little effect on the course of the reaction. Increasing the base concentration gave lower yields, presumably owing to the consumption of bromine by hydroxide ion, but did not significantly affect the relative amounts of reaction product.

The stereoselectivity of these reactions of **1a** and **1b** with bromine as observed by Berman and Price[2] was explained by invoking a bromonium ion intermediate (**4**) which lost carbon dioxide before equilibration could take place through an open carbonium ion. They ruled out the formation of the lactone **5** since this should not lose carbon dioxide to give bromostilbene[4] but should undergo hydrolysis in protic solvent to give β-hydroxy acid (**6**).[5,6] In contrast, Tarbell and Bartlett[7] observed the formation of lactones in the bromination of α,β-unsaturated carboxylic acids. These lactones opened to the corresponding β-hydroxy acids upon hydrolysis.



The fact that we observe little or no stereoselectivity in this reaction strongly suggests that the intermediate bromonium ion goes to or equilibrates with an open-chain carbonium ion (**7**) thus inducing loss of stereochemistry. Such a species as **4** or **7** can lose carbon dioxide and give bromostilbene, or ring close to give

(1) To whom inquiries should be sent: Department of Chemistry, University of Maryland, College Park, Md.

(2) J. D. Berman and C. C. Price, *J. Am. Chem. Soc.*, **79**, 5474 (1957).

(3) Berman and Price[2] report isolating a 20% yield of diphenylacetylene from this latter reaction. We observe at the most only trace amounts of diphenylacetylene.

(4) A. Basler, *Ber.*, **16**, 3001 (1883).

(5) H. Staudinger, *ibid.*, **41**, 1355 (1908).

(6) H. Solkowski, *J. Prakt. Chem.*, **106**, 253 (1923).

(7) D. S. Tarbell and P. D. Bartlett, *J. Am. Chem. Soc.*, **59**, 407 (1937).