dienals.[3] Also, it was observed that the 2,4-dinitrophenylhydrazones of hexa-2,4-dienal and hepta-2,4-dienal, synthesized by an alternate route,[6,8] proved to be identical to corresponding derivatives obtained in the present study.

In contrast to existing methods[6,11] used for preparation of some 2,4-dienals, the method described here offers the following advantages: starting materials are commercially available, all steps may be carried out in one flask without isolation of intermediates, the product is easy to purify, yields are good, and the general applicability is firmly established.

EXPERIMENTAL

Aldehydes. The saturated normal aliphatic aldehydes required were obtained from commercial sources. All, except formaldehyde, were dried over anhydrous sodium sulfate and distilled through a 90-cm. fractionating column packed with glass helices.

1-Methoxybut-1-en-3-yne. The commercially available material,[12] freshly redistilled, was used.

Ethyl bromide. Commercially available material was dried over calcium chloride and redistilled.

Tetrahydrofuran. Commercially available tetrahydrofuran was freshly distilled from lithium aluminum hydride before each preparation. Tetrahydrofuran was permitted to stand in contact with lithium aluminum hydride for at least 16 hr. before distillation. Occasionally a batch of tetrahydrofuran required two treatments before it was suitable.

Melting point determinations. Melting points were determined on an electrically heated stage and are corrected. A procedure was adopted in which the sample was placed on the stage only after the latter had been preheated to within about 5° of the expected melting point. This procedure avoids decomposition and in some instances resulted in both a sharper and higher melting point.

Deca-2,4-dienal. (VI, R = C_5H_{11}). Since all preparations, except for pentadienal, were carried out in the same way, only one example will be given for the preparation of the C_6 to C_{12} members of the series.

1-Methoxybut-1-en-3-yne, 26.2 g. (0.32 mole), dissolved in 175 ml. of tetrahydrofuran was added dropwise with stirring to a Grignard reagent prepared from 7.3 g. of magnesium and 32.8 g. of ethyl bromide in 200 ml. of tetrahydrofuran while the mixture was maintained at about 40°. After an additional hour of stirring at room temperature, the reaction flask was cooled and there was added over a 20-min. period a solution of 25 g. (0.25 mole) of hexanal dissolved in 50 ml. of tetrahydrofuran. After 2 hr. of stirring at room temperature, the mixture was cooled and treated with 11.5 g. (0.25 mole) of absolute ethanol. Twenty minutes later, solid lithium aluminum hydride, 9.5 g. (0.25 mole) was added in small portions over a 20- to 30-min. interval. The mixture was stirred for 2 hr. at room temperature and permitted to stand overnight. It was then treated successively with ethyl acetate (12 ml.), water (56 ml.), and 4*N* sulfuric acid (280 ml.). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the ether extracts were combined, washed once with 10% sodium carbonate solution, three times with water, and dried over sodium sulfate. Most of the solvent was distilled off through a Vigreaux column at atmospheric pressure, but reduced pressure was employed to distill off final amounts of solvent. The residue was then fractionally distilled *in vacuo* through a column 90 cm. long by 10 mm. outside diameter packed with glass helices. After a small forerun, deca-2,4-dienal (20.4 g., 54% yield) boiling at 114–116° (10 mm.) was obtained.

Pentadienal. (VI, R = H). For preparation of this member of the series, formaldehyde was sublimed from dry paraformaldehyde by heating the latter in an oil bath at 200° and was swept into the reaction mixture with a stream of nitrogen as described by Gilman and Catlin.[13] When 0.25 mole of paraformaldehyde was used, 8.1 g. of material boiling at 49.5–56.5° (52 mm.), $n_{\rm D}^{25}$ 1.4894, were obtained. This material, although obviously impure, doubtless consisted mostly of pentadienal, for it gave a red 2,4-dinitrophenylhydrazone, m.p. 178–180°, and the fraction showed maxima at 285 and 325 mμ in the ultraviolet spectrum. A purer product, b.p. 52–52.4°, $n_{\rm D}^{25}$ 1.5110 was obtained by using only 0.25 mole of 1-methoxybut-1-en-3-yne and 0.4 mole of paraformaldehyde. This procedure apparently consumes all of the enzyne compound; hence it cannot contaminate the product. Details of the properties of this particular preparation of pentadienal and the 2,4-dinitrophenylhydrazone are shown in Tables I and II.

A sample of pentadienal which the authors prepared according to Woods and Sanders,[4] was observed to have the following properties: b.p. 53–54° (46 mm.); $n_{\rm D}^{24}$ 1.5114; $\lambda_{\rm max}$ at 258.5 and 325 mμ; 2,4-dinitrophenylhydrazone, red, m.p. 179–181°, $\lambda_{\rm max}$ 384 mμ.

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Metalation Reactions of Triphenylgermyllithium

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Reactions of triphenylgermyllithium already reported[1] have pointed out the versatility of this re-

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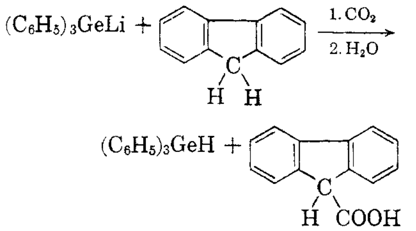
agent for the preparation of organogermanium compounds. We have found, in addition, that triphenylgermyllithium metalates fluorene to give high yields of fluorene-9-carboxylic acid on carbonation.



(1)

In addition to the acid, there are obtained small amounts of hexaphenyldigermane, hexaphenyldigermoxane, and unreacted fluorene. The hexaphenyldigermane may have been unreacted starting material used for the preparation of the triphenylgermyllithium; however, from a large number of reactions involving this reagent, we have found that the cleavage of hexaphenyldigermane is complete. Also, hexaphenyldigermane has often been obtained from reactions involving triphenylgermyllithium when the starting material for its preparation was tetraphenylgermane. It is believed that the hexaphenyldigermane formed in this reaction may have resulted from the reaction of the triphenylgermyllithium with triphenylgermane formed in the metalation.[2]

$$(2)\ (C_6H_5)_3GeLi + (C_6H_5)_3GeH \longrightarrow (C_6H_5)_3GeGe(C_6H_5)_3 + LiH$$

The hexaphenyldigermoxane obtained in the metalation reaction probably resulted from the hydrolysis of the triphenylgermane under the conditions used in working up the products.

The formation of 9-fluorenyllithium might possibly be explained as occurring from the metalation of fluorene by phenyllithium. The latter compound would be present if the triphenylgermyllithium dissociated into diphenylgermanium and phenyllithium in a manner proposed by D'Ans, *et al.*[3] for triphenyltinlithium.

$$(3)\ (C_6H_5)_3GeLi \longrightarrow (C_6H_5)_2Ge{:} + C_6H_5Li$$

That such is not the case for triphenylgermyllithium has been demonstrated by many reactions. First, if such a dissociation were to take place, then carbonation should yield benzoic acid, and no such acid has been found in several carbonation reactions of triphenylgermyllithium in this laboratory. Second, bromination of the dissociated triphenylgermyllithium would give dibromodiphenylgermane; however, when triphenylgermyllithium was brominated there was obtained hexaphenyldigermane in high yield, along with bromotriphenylgermane. No dibromodiphenylgermane or its hydrolysis product was isolated. The yield of fluorene-9-carboxylic acid was about 60% indicating that the dissociation, if present, would be displaced far to the right. Thus, phenyllithium and diphenylgermanium would be present in excess and the carbonation and bromination reactions should probably give high yields of the benzoic acid and dibromodiphenylgermane, respectively.

Although phenyllithium gives a high yield of fluorene-9-carboxylic acid on carbonation when reacted with fluorene in diethyl ether,[4] it was believed that such might not be the case in ethylene glycol dimethyl ether, the solvent in which triphenylgermyllithium is prepared and used. In the first place, the phenyllithium might cleave the solvent and therefore reduce the concentration of the organolithium reagent, and secondly the solvent has been found to play an important role in the rates of metalation reactions.[4] For this reason phenyllithium was prepared in ethylene glycol dimethyl ether and the metalation of fluorene carried out to give only 25% of fluorene-9-carboxylic acid. Therefore, the high yield of fluorene-9-carboxylic acid from the reaction of fluorene with triphenylgermyllithium probably could not have been due to any phenyllithium present.

The attempted metalation of dibenzofuran with triphenylgermyllithium gave only hexaphenyldigermane, triphenylgermanecarboxylic acid, recovered dibenzofuran, and triphenylgermyl triphenylgermanecarboxylate. The latter compound has been isolated previously[1b] from the thermal decomposition of triphenylgermanecarboxylic acid, and also from the carbonation of triphenylgermyllithium.[5]

EXPERIMENTAL[6]

Reaction of triphenylgermyllithium with fluorene. To an ethylene glycol dimethyl ether (GDME) solution of triphenylgermyllithium prepared from 6.0 g. (0.01 mole) of hexaphenyldigermane[1c] was added 3.3 g. (0.02 mole) of fluorene dissolved in 30 ml. of GDME. No heat was evolved, however the color changed to the distinctive orange color of 9-fluorenyllithium. After stirring 19.5 hr. the mixture was carbonated by pouring it into a slurry of Dry Ice and diethyl ether. After warming to room temperature, 130 ml. of 3*N* hydrochloric acid was added. The ether layer was separated and washed with two 100-ml. portions of 5% sodium hydroxide solution. This alkaline solution was acidified by the addition of concentrated hydrochloric acid precipitating 2.9 g. (69%) of fluorene-9-carboxylic acid melting at 224°. Washing with petroleum ether gave 2.3 g. of acid melting at 225°. A mixed melting point with authentic fluorene-9-carboxylic acid showed no depression.

The ether layer obtained above was filtered to give 0.4 g. of hexaphenyldigermane melting at 345–347°; then it was dried over anhydrous sodium sulfate and the solvents dis-

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[6] All melting points are uncorrected. Reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. All petroleum ether mentioned in this manuscript boiled over the range 60–70°.

tilled to leave a liquid from which separated an additional 0.1 g. of hexaphenyldigermane melting over the range 338–344° (total yield 0.5 g., 8.3%). The mother liquor was dissolved in petroleum ether; then by volume reduction and cooling there was obtained 2.1 g. of crystals melting over the range 90–180°. This was recrystallized from the same solvent to give 1.3 g. (21%) of hexaphenyldigermoxane, m.p. 185–186°, and 0.2 g. (6%) of recovered fluorene melting over the range 115–119°.

A second run using the same quantities of materials gave almost exactly the same results.

Reaction of triphenylgermyllithium with dibenzofuran. Using the same procedure as above, the triphenylgermyllithium from 6.0 g. of hexaphenyldigermane was allowed to react with 3.4 g. (0.02 mole) of dibenzofuran. Work-up of the reaction mixture in the same manner as above yielded 1.6 g. (25%) of triphenylgermanecarboxylic acid, m.p. 184–186°, 0.4 g. (6.7%) of hexaphenyldigermane, m.p. 344–345°, 0.9 g. (14%) of triphenylgermyl triphenylgermanecarboxylate, m.p. 165–166°, and 0.7 g. (20.6%) of recovered dibenzofuran, m.p. 86–87°. No dibenzofuran-4-carboxylic acid was isolated.

Reaction of phenyllithium with fluorene in GDME. Phenyllithium was prepared in GDME by the reaction of bromobenzene (15.7 g., 0.1 mole) with lithium wire (1.47 g., 0.21 g.-atom) to give a deep green solution. Acid titration indicated a yield of 0.0283 mole or 28.3%.

To this stirred lithium reagent was added an excess of fluorene (12.2 g., 0.074 mole) dissolved in GDME. After the first addition an orange color appeared, however upon further stirring it was replaced by the blue-green color. When the addition of fluorene was complete the color remained orange. After stirring 22 hr. the mixture was carbonated and allowed to warm to room temperature. Work-up as previously mentioned gave 2.0 g. of light brown acid melting over the range 205–215°. Recrystallization from acetic acid gave 1.0 g. (25% based on phenyllithium) of fluorene-9-carboxylic acid, melting over the range 218–222°.

The ether layer was dried and the solvents distilled to leave a residue which was recrystallized from ethanol to give 8.0 g. (67%) of recovered fluorene, m.p. 116–118°.

Reaction of triphenylgermyllithium with bromine. A solution of triphenylgermyllithium from 6.0 g. of hexaphenyldigermane was cooled to −25°, then 2.4 g. (0.015 mole) of bromine dissolved in GDME was added dropwise while the temperature was maintained between −20° and −25°. When the addition was complete the mixture was stirred and allowed to warm to room temperature overnight. This mixture was filtered and the precipitate washed with ether, 10% hydrochloric acid, and hot petroleum ether to give 4.6 g. (78%) of hexaphenyldigermane, melting over the range 339–343°. The ether layer was dried and the solvents distilled to leave a residue which was recrystallized from ethanol to give 0.2 g. (2.6%) of bromotriphenylgermane, m.p. 138–140°.

The hexaphenyldigermane obtained from this reaction could not have been unreacted starting material because the solubility is such that very little dissolved in the solvent and any amount would be visible before the bromine was added, especially at the low temperatures used in the reaction.

A second run using exactly the same conditions and amounts of starting materials yielded 4.7 g. (78%) of hexaphenyldigermane and 0.9 g. (11.8%) of bromotriphenylgermane.

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Some Organolithium Compounds of Quinoline and 2-Phenylquinoline

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In a recent publication from this laboratory,[1] the first preparation of 1-isoquinolyl- and 2-quinolyllithium was reported. These organolithium reagents were prepared from 1-bromoisoquinoline and 2-bromoquinoline, respectively, by means of the halogen-metal interconversion reaction with *n*-butyllithium between −50 and −60°. When 1-isoquinolyl- and 2-quinolyllithium were carbonated, the predominant products were 1,1′-diisoquinolyl- and 2,2′-diquinolyl ketone, respectively, rather than the expected acids.

The preparation of 4-quinolyllithium was effected in the same manner as was the 2-isomer. 4-Bromoquinoline was treated with *n*-butyllithium between −50 and −60° for 20 min. The approximate yield of 4-quinolyllithium (80%) was determined by a reaction with benzophenone to give the tertiary carbinol, α,α-diphenyl-4-quinolinemethanol.

The similarity in the reactivity of the 2- and 4-position in quinoline led the authors to consider the possibility that the carbonation of 4-quinolyllithium might yield 4,4′-diquinolyl ketone as the 2-isomer had yielded 2,2′-diquinolyl ketone. The only product that could be detected, however, from the carbonation of 4-quinolyllithium was 4-quinolinecarboxylic acid which was isolated in a yield of 39%. Two possible explanations for the failure of 4-quinolyllithium to form the ketone, in appreciable quantities, on carbonation are as follows: the lesser degree of reactivity of 4-quinolyllithium as compared to the 2-isomer, or the 4-quinolyllithium's effective reactivity was reduced due to its insolubility in diethyl ether at −50°.

The preparation of 2-(*p*-lithiophenyl)- and 2-(*m*-lithiophenyl)quinoline was achieved also by the use of the halogen-metal interconversion reaction. 2-(*p*-Bromophenyl)- and 2-(*m*-bromophenyl)quinoline were treated with *n*-butyllithium at −20° for 20 min. The yields of 2-(*p*-lithiophenyl)- and 2-(*m*-lithiophenyl)quinoline, based on the crude acids obtained on carbonation, were 75 and 70%, respectively.

The preparation of 2-(*p*-lithiophenyl)- and 2-(*m*-lithiophenyl)quinoline in such good yields was of particular interest because Summers[2] had attempted earlier to prepare the isomeric 7-(*p*-lithiophenyl)quinoline by treating 7-(*p*-bromophenyl)-quinoline with *n*-butyllithium at −50°, but was

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