

varying degrees of lability of the new species as indicated by the reduction-oxidation cycling recovery of starting material, but incongruous  $E_p$  values. A third combination of these, electrochemical reversibility, but "chemical irreversibility" can be found in systems 51 and 57b, the reduction of  $(\pi\text{-C}_{10}\text{H}_8)\text{Fe}_2(\text{CO})_5$  and  $[(\pi\text{-C}_5\text{H}_5)\text{Ni-SCH}_3]_2$  ( $n = 1$ ) to anions. Both of these systems show small (50 mv) separations of  $E_{p/2}^{\text{anodic}}$  and  $E_{p/2}^{\text{cathodic}}$ . Polarograms immediately after partial reduction show reductive-oxidative wave contributions at the  $E_{1/2}$  value noted. The oxidative component rapidly disappears augmenting a new oxidative wave at more anodic potentials. The electrochemically reversible reduction ( $n = 1$ ) of  $(\pi\text{-C}_5\text{H}_5)_3\text{Mn}_2(\text{NO})_3$  gives an even more unstable anion, no oxidative component being observable after electrolysis. Similar data have been accumulated for the oxidation of  $[(\pi\text{-C}_5\text{H}_5)\text{Ni}(\text{CO})_2]$  (system 56a), a well-defined but unstable reductive component being observable after oxidation. Oscillographic sweeps on single drops in the vicinity of 50 v/sec show that even at this short time some decomposition

is occurring. Apparently here we are encountering the problem of the time scale to judge events by. Over the long run these new species are unstable while over short time periods we may conceive of them as useful entities and even characterize them. The question then arises concerning the entries in Table I for which no oxidation-reduction recovery is listed, but which exhibit related reductive-oxidative peak currents which are formally electrochemically irreversible on triangular voltammetry. These may represent labile materials belonging in a chemically reversible set whose time scale is short. Unfortunately, the difficulty in assigning peaks to definite species, except where models may be predicted and examined, is a distinct barrier. However, it is to this interesting area of short-lived species that the present work is extending.

**Acknowledgments.** The authors wish to acknowledge the support in the form of a grant from the Army Research Office (USA-DA-ARO-131-124). One of them (R. E. D.) acknowledges the encouragement of the Alfred P. Sloan Foundation.

## Addition and Metalation Reactions of Organolithium Compounds. I. Products

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**Abstract:** Reactions of organolithium compounds and diphenylacetylene have been shown to give products arising from addition and/or metalation depending upon the choice of lithium reagent, solvent, and temperature.

This project<sup>3</sup> was prompted by a consideration of the unusual ability of organolithium compounds to polymerize isoprene in hydrocarbon solution to the all-*cis* polymer, natural rubber.<sup>4</sup> Other organoalkali compounds produce a considerably more random structure. The stereospecificity is related to the covalent character of the organolithium bond, and the polymerization must proceed by a series of concerted *cis* additions of growing organometallic chain to monomer. The intimate nature of this addition process is drastically affected by a change to more basic solvents which leads to a random polymer.<sup>4</sup> Stereospecific isoprene polymerization presumably occurs by a series of six-center transition states.<sup>5</sup> It was of interest to determine whether a similar *cis* stereospecific addition to acetylenes might occur, perhaps by a process involving a four-center addition. Acetylenes and organolithium compounds might react to produce vinylic lithium derivatives, and it is known that under the proper

conditions, *i.e.*, low temperature and solvents of low basicity, such compounds retain their configuration.<sup>6</sup> The adduct could then be trapped by carbonation, a process known to proceed with retention of configuration.<sup>6,7</sup>

The literature contains little information concerning the reactions of noncarbonyl conjugated acetylenes with organoalkali metal compounds. In contrast Grignard reagents under the usual conditions do not react with nonterminal alkynes.<sup>8</sup> However, in refluxing xylene-tetrahydrofuran, diphenylacetylene and phenylmagnesium bromide react to form hexaphenylbenzene and octaphenylcyclooctatetraene.<sup>9,10</sup> This is a process which does not involve Grignard addition to the triple bond but rather coordination of the

(6) D. Y. Curtin and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **84**, 1967 (1962), and references cited therein to earlier Curtin papers.

(7) D. Seyferth and L. G. Vaughan, *ibid.*, **86**, 883 (1964).

(8) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954.

(9) H.-P. Thronsen and H. Zeiss, *J. Organometal. Chem.*, **1**, 301 (1964); M. Tsutsui, *Chem. Ind. (London)*, 780 (1962).

(10) The latter compound was originally identified by Tsutsui<sup>9</sup> as a tricyclooctatetraene derivative. It appeared, however, to be identical with a compound tentatively suggested to be octaphenylcubane (H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962)), but more recently shown to be the cyclooctatetraene derivative (G. S. Pawley, W. N. Lipscomb, and H. H. Freedman, *ibid.*, **86**, 4725 (1964)).

(1) From the Ph.D. Thesis of Z. G. Gardlund.

(2) From the M.S. Thesis of S. L. Gardlund.

(3) A preliminary report describing a portion of this work has appeared: J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Am. Chem. Soc.*, **85**, 3897 (1963).

(4) H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 2451 (1957).

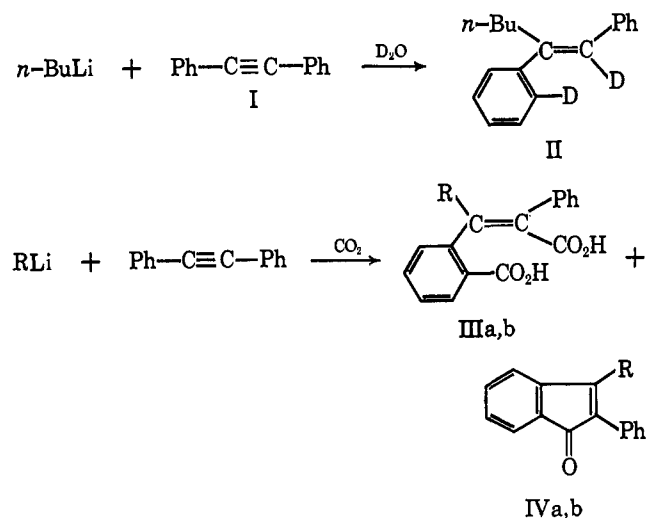
(5) H. Sinn and F. Patat, *Angew. Chem. Intern. Ed. Engl.*, **3**, 93 (1964).

alkyne with magnesium to yield, presumably, a metal coordinated cyclobutadiene derivative which may react with more diphenylacetylene or itself to give the observed products.<sup>9</sup> Lithium being a metal of high coordinating ability, similar coordinative cyclization processes with organolithium compounds could not be ruled out in advance.

One example of the addition of an organosodium reagent to an alkyne has been reported by Ziegler who relates that  $\alpha$ -cumylpotassium adds to diphenylacetylene yielding the corresponding stilbene of unspecified stereochemistry.<sup>11</sup>

## Results and Discussion

*n*-Butyllithium and diphenylacetylene do not react in pentane solution over a period of many hours whereas *n*-butyllithium or ethyllithium react with diphenylacetylene in ethyl ether (24 hr., 30°) to yield the products shown.



IIIa, IVa, R = *n*-Bu  
 IIIb, IVb, R = C<sub>2</sub>H<sub>5</sub>

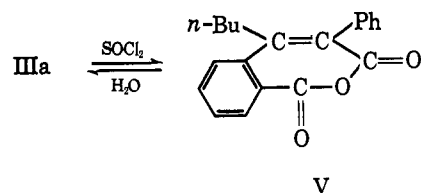
The *trans* nature of the  $\alpha$ -*n*-butylstilbene (II, except that product was obtained by hydrolysis rather than deuterolysis;  $\lambda_{\text{max}}$  225 m $\mu$  ( $\epsilon$  5200), 268 m $\mu$  ( $\epsilon$  16,200) was demonstrated by photoisomerization using a Hanovia mercury arc lamp and isolating, by means of preparative-scale v.p.c., the new component which appears to the extent of approximately 24% after 72 hr. of illumination. The new component *cis*- $\alpha$ -*n*-butylstilbene had  $\lambda_{\text{max}}$  222 m $\mu$  ( $\epsilon$  13,000), 257 m $\mu$  ( $\epsilon$  10,900). In addition to having the expected shorter wavelength maximum in the ultraviolet, the new compound (*cis*) displays olefinic proton resonance at  $\tau$  3.62 in contrast to the unisomerized compound (*trans*) in which the olefinic proton resonance occurs at  $\tau$  3.36. That the higher field olefinic proton resonance is characteristic of the *cis* isomer in this sort of compound has been pointed out by Curtin, Gruen, and Shoulders.<sup>12</sup>

The structures of the dicarboxylic acids (IIIa,b) were in accord with elemental analysis and neutralization equivalents. In the case of III a further elucidation was obtained by conversion to a dimethyl ester of the correct molecular weight for the indicated structure. In the n.m.r. spectrum this ester as well as IIIa and IIIb

(11) K. Ziegler and H. Dislich, *Chem. Ber.*, **90**, 1107 (1957).

(12) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958).

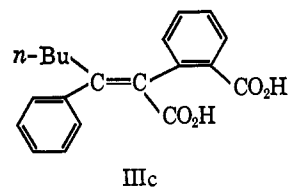
showed eight aromatic protons in the region  $\tau$  2.6–2.7 and another single aromatic proton at a lower field in the  $\tau$  2.0 region, the latter being split into a doublet having coupling constants of 7–10 c.p.s. Both the chemical shift and the coupling constant are of the correct magnitude for an aromatic proton *ortho* to a COO group.<sup>13</sup> Finally the dicarboxylic acid (IIIa) from *n*-butyllithium was converted to its anhydride (V) ( $\nu_{\text{max}}$  CHCl<sub>3</sub> 1785, 1750 cm.<sup>-1</sup>) which in turn was hydrolyzed under mild conditions back to IIIa. This fact confirms the *ortho* nature of the ring carboxyl group and the *trans* disposition of the phenyl rings.



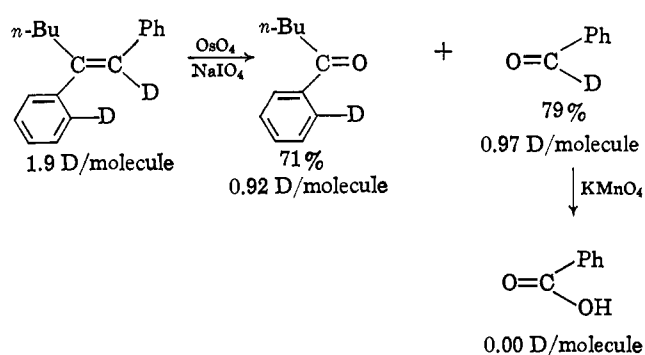
The structures of the indones (IVa,b) were proven by independent syntheses (see the Experimental Section).

Compound V is a seven-membered ring anhydride examples of which, though rare, are not completely unknown in the literature.<sup>14</sup>

Although difficult to rationalize in terms of the indone structures, the evidence so far presented does not definitely rule out a structure such as IIIc for the dicarboxylic acid. Compound IIIc would be expected



to readily dehydrate to a six-membered ring anhydride. Attempts to oxidatively cleave the highly hindered olefinic bond in IIIa (or c) were not successful, but the dideuterated compound II was cleaved with osmium tetroxide and sodium metaperiodate<sup>15</sup> as indicated below.



(13) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956). See also L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 85.

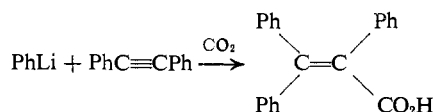
(14) J. W. Hill, *J. Am. Chem. Soc.*, **52**, 4110 (1930); R. Adams and J. L. Andersen, *ibid.*, **73**, 136 (1951); P. Karrer and L. Schneider, *Helv. Chim. Acta*, **30**, 859 (1947); H. K. Hall, Jr., *J. Org. Chem.*, **28**, 2028 (1963). Unfortunately no spectral data are available for these compounds.

(15) R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *ibid.*, **21**, 478 (1956).

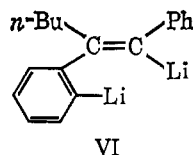
The benzaldehyde- $\alpha$ - $d$  contained 0.97 deuterium atom which was shown to be aldehydic by n.m.r. spectroscopy and oxidation with neutral potassium permanganate to deuterium-free benzoic acid. The deuterium atom in the valerophenone was shown to be in the benzene ring *ortho* to the carbonyl group by the integrated n.m.r. spectrum which indicated the presence of only one low-field *ortho* hydrogen centered at  $\tau$  1.96. (see the discussion above of the n.m.r. spectrum of compound IIIa). By analogy, therefore, the structure of the dicarboxylic acid must be IIIa.

Recovered diphenylacetylene from the *n*-butyllithium deuterolysis reaction contained some deuterium which indicates smaller quantities of a reaction product which could not be detected in the acidic fraction after carbonation.

Methylithium, generally the least reactive of the alkylolithiums, did not react with diphenylacetylene even at 50° in dimethoxyethane. Phenyllithium, in contrast, adds to the alkyne but does not metalate, the product being triphenylacrylic acid (11%). This observation has earlier been made by Eisch and Kaska.<sup>16</sup>



The most interesting observation is the formation of a dicarbanion-like substance from ethyl- or *n*-butyllithium which is specifically metalated in the *ortho* position of the benzene ring. Unfortunately the stereochemistry of the addition process cannot be ascertained from the facts now available inasmuch as the *trans* dilithium compound VI may be the thermodynamic



isomer arising by equilibration. Although the *trans* isomer is certainly the thermodynamic isomer in the case of stilbenyllithium,<sup>6</sup> organolithium compounds are structurally complex,<sup>17</sup> and one cannot easily extrapolate this observation to substance VI, the indicated structure of which is only a stoichiometric representation.

Further work on the factors leading to the dicarbanion, its properties, and the stereochemistry of the addition process is in progress.

## Experimental Section

Melting points are uncorrected. Ultraviolet spectra were determined on a Cary recording spectrophotometer, Model 11, or a Perkin-Elmer spectrophotometer, Model 202, using ethanol as solvent; n.m.r. spectra were determined on a Varian Model A-60 (60 Mc.) spectrometer using tetramethylsilane as internal standard. Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill. Vapor phase chromatography, unless otherwise noted, was carried out on an Aerograph instrument using a column packed with Dow 11 silicone on firebrick. Hydrocarbon solvents (pentane, ligroin) were purified by stirring overnight with sulfuric acid, followed by repeated washing with water, drying over mag-

nesium sulfate, and 24 hr. of reflux over sodium prior to final distillation. *t*-Butyllithium was obtained in pentane solution from the Lithium Corp. of America.

*n*-Butyllithium was prepared from *n*-butyl bromide and lithium in ethyl ether.<sup>18</sup> Prior to use the reaction mixture was filtered through a glass wool plug, and the concentration was determined by the double titration method.<sup>19</sup> Diphenylacetylene was prepared according to published procedures.<sup>20</sup>

Deuterium analyses were performed by Mr. J. Nemeth, Urbana, Ill., using the falling drop method.

***n*-Butyllithium and Diphenylacetylene Hydrolysis.** To 0.67 mole of *n*-butyllithium in 440 ml. of ethyl ether at room temperature under a nitrogen atmosphere, there was added rapidly 50 g. (0.28 mole) of diphenylacetylene in 200 ml. of ethyl ether. A slight temperature rise was observed and over a period of 2 or 3 min. the solution changed from nearly colorless to red. After stirring at room temperature for 24 hr., the reaction mixture was treated slowly with 30 ml. of water while maintaining the temperature at approximately 5° by means of external cooling. An additional 50 ml. of water was added, the ether layer was separated, and after washing again with water, was dried over magnesium sulfate. Removal of ether left 47 g. of an oil, which was shown by vapor phase chromatography to contain two compounds, unreacted diphenylacetylene (45%) and *trans*- $\alpha$ -*n*-butylstilbene (55%), corresponding to a 39% yield of product.

Separation of product from unreacted diphenylacetylene was achieved by four distillations through a small Vigreux column to give 4 g. of  $\alpha$ -*n*-butylstilbene: b.p. 143–144° (0.4 mm.);  $n_{D}^{24}$  1.5878;  $\lambda_{\text{max}}$  268  $\mu$  ( $\epsilon$  16,200), and 225  $\mu$  ( $\epsilon$  5200); n.m.r. (numbers in parentheses indicate relative peak areas) in  $\text{CCl}_4$ ,  $\tau$  2.76 (10), 3.36 (1), 7.34 (2), 8.65 (4), and 9.18 (3). *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}$ : C, 91.47; H, 8.53; mol. wt., 236. Found: C, 91.27; H, 8.63; mol. wt., 232.

**Photoisomerization of *trans*- $\alpha$ -*n*-Butylstilbene.** *trans*- $\alpha$ -*n*-Butylstilbene was irradiated with a Hanovia ultraviolet lamp (temperature about 80°). After 48 hr., a second component with a shorter retention time appeared in the v.p.c. of the mixture. At the end of 72 hr., v.p.c. revealed the presence of only starting material and one additional component, the new product constituting 24% of the mixture.

The two components were separated on a preparative v.p.c. column (diethyleneglycol succinate on firebrick at 190°). The component having the lower retention time was characterized as *cis*- $\alpha$ -*n*-butylstilbene:  $\lambda_{\text{max}}$  257  $\mu$  ( $\epsilon$  10,900) and 222  $\mu$  ( $\epsilon$  13,000); n.m.r. (in  $\text{CCl}_4$ ),  $\tau$  2.83 and 3.02 (10) 3.62 (1), 7.54 (2), 8.66 (4), and 9.12 (3).

***n*-Butyllithium and Diphenylacetylene. Deuterolysis.** To 50 g. of diphenylacetylene (0.28 mole) in 200 ml. of ether was added rapidly 0.368 mole of *n*-butyllithium in 300 ml. of ether, and the solution was stirred at room temperature for 20 hr. The reaction mixture then was maintained at approximately 5° by external cooling as 14.8 g. of deuterium oxide was added slowly. This solution then was stirred at room temperature for 12 hr., followed by the addition of 50 ml. of water. The reaction mixture was treated as described above in the hydrolysis reaction. Distillation of the mixture yielded deuterated diphenylacetylene, b.p. 97–113° (0.3 mm.). After four recrystallizations from 95% ethanol the white needles had m.p. 59.5–60.0°. *Anal.* Calcd. for  $\text{C}_{14}\text{H}_8\text{D}$ : D, 10.0. Found: D, 3.87, 2.85.

A higher boiling fraction was redistilled to yield deuterated  $\alpha$ -*n*-butylstilbene (II): b.p. 156° (0.35 mm.); n.m.r. (in  $\text{CCl}_4$ ),  $\tau$  2.76 (9), 7.38 (2), 8.69 (4), and 9.20 (3). *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{D}_2$ : D, 10.0. Found: D, 8.02, 9.50.

***n*-Butyllithium and Diphenylacetylene. Carbonation.** To 0.32 mole of *n*-butyllithium in 220 ml. of ethyl ether at room temperature and under a nitrogen atmosphere, there was added rapidly 25 g. (0.14 mole) of diphenylacetylene in 100 ml. of ethyl ether. The reaction mixture turned red almost immediately and, after stirring at room temperature for 24 hr., was poured slowly over a large excess of powdered Dry Ice. The product was acidified with 6 *N* hydrochloric acid, and the organic layer then was washed with several portions of water. The aqueous layer was extracted with ether; the ether layers were combined and extracted with aqueous

(18) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *ibid.*, **71**, 1489 (1949).

(19) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(16) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **84**, 1501 (1962).  
(17) T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2135 (1964); Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963).

(20) L. I. Smith and M. M. Falkof, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 350; A. C. Cope, D. S. Smith, and R. J. Colter, *Org. Syn.*, **34**, 42 (1954).

sodium carbonate. The aqueous layer was made slightly acidic with hydrochloric acid and extracted with several portions of ether. After drying over magnesium sulfate the ether was removed under reduced pressure leaving 14 g. of a yellow oil. Trituration with hexane dissolved the valeric acid which was present and causes crystallization of 6.5 g. (14%) of 2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid (IIIa). Three recrystallizations from benzene or ethyl acetate (needles) afforded pure product: m.p. 176–177°;  $\lambda_{\max}$  209 m $\mu$  ( $\epsilon$  20,200), 221 (16,400), and 280 ( $\epsilon$  2110) (shoulder), respectively;  $\nu_{\max}^{\text{CHCl}_3}$  1705 cm $^{-1}$ ; n.m.r. (in dioxane),  $\tau$  2.68 (8) and 2.08 and 1.93 (1, doublet,  $J = 10.4$  c.p.s.). *Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>(COOH)<sub>2</sub>: C, 74.05; H, 6.21; neut. equiv., 162. Found: C, 74.35; H, 6.45; neut. equiv., 166.

The dimethyl ester of 2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid (IIIa) was prepared by treating 5.9 g. (0.018 mole) of an ethereal solution of 2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid (IIIa) with 0.05 mole of diazomethane<sup>21</sup> in 75 ml. of ethyl ether. After standing for 2 hr., excess diazomethane was decomposed with glacial acetic acid and solvent was removed under reduced pressure. The residue was washed with dilute sodium carbonate, taken up in ethyl ether, and dried over magnesium sulfate; after removal of ether there remained 2.9 g. (45%) of a slightly yellow oil which showed a single peak on v.p.c.

The oil was distilled to give the dimethyl ester of 2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid: b.p. 162° (0.2 mm.);  $n_D^{20}$  1.5568;  $\lambda_{\max}$  225 m $\mu$  ( $\epsilon$  15,340), 227 (4110) (shoulder), and 312 (1640) (shoulder); n.m.r. (in CCl<sub>4</sub>),  $\tau$  1.96 and 2.09 (1), 2.63 (8), 6.17 (3), 6.78 (3), 7.69 (2), 8.83 (4), and 9.32 (3). *Anal.* Calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>: C, 74.98; H, 6.86; mol. wt., 352. Found: C, 75.20; H, 6.90; mol. wt., 349.

The hexane extract of the acidic fraction (above) was washed with a large amount of water to remove as much valeric acid as possible. After drying over magnesium sulfate, the hexane was removed under reduced pressure leaving a small amount of an orange-yellow oil which was recrystallized four times from hexane to give a few milligrams of an impure solid, m.p. 80–92°, neut. equiv. 290. The neutralization equivalent and the integrated n.m.r. spectrum of this compound were consistent with the structure *n*-BuCPh=CPhCO<sub>2</sub>H, 2,3-diphenyl-2-heptenoic acid.

The neutral layer from the carbonation product of *n*-butyllithium and diphenylacetylene was dried over magnesium sulfate. After removal of the ether there remained 21 g. of a red oil. Vapor phase chromatography indicated the presence of diphenylacetylene (56%), 5-nonanone (16%), and 2-phenyl-3-*n*-butylindone (28%). Distillation through a small column yielded a 6.2-g. (16%) mixture of 2-phenyl-3-*n*-butylindone plus a small amount of an unidentified compound which proved difficult to separate: boiling point of mixture, 178–180° (0.3 mm.);  $n_D^{20}$  1.6039;  $\nu_{\max}^{\text{CCl}_4}$  1715 cm $^{-1}$ ;  $\lambda_{\max}$  254 m $\mu$  ( $\epsilon$  22,500).

A dinitrophenylhydrazone of the indone was obtained in the usual manner, and after recrystallization from 95% ethanol-ethyl acetate had m.p. 176–178°. *Anal.* Calcd. for C<sub>25</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 67.86; H, 5.29; N, 12.66. Found: C, 67.42; H, 5.04; N, 12.38.

A mixture melting point with the 2,4-dinitrophenylhydrazone derivative of an authentic sample (see below) showed no depression, and the infrared and ultraviolet spectra were identical,  $\lambda_{\max}$  250 m $\mu$  ( $\epsilon$  21,000) and 392 m $\mu$  ( $\epsilon$  20,800).

**Preparation of 2-Phenyl-3-*n*-butylindone (IVa).** 2-Phenyl-3-*n*-butylindone was prepared by a procedure used in the synthesis of 2-phenyl-3-ethylindone.<sup>22</sup> 2-Phenyl-1,3-indanedione (17.5 g., 0.0795 mole) in 450 ml. of anhydrous benzene was added in one portion under a helium atmosphere to a vigorously stirred *n*-butyl Grignard reagent in diethyl ether. The Grignard reagent was prepared from *n*-butyl bromide (26.4 ml., 0.25 mole) and magnesium (6.0 g., 0.25 g.-atom). The bright red color which developed when the first indanedione was added soon disappeared. The resulting brown mixture first was stirred with refluxing for 2 hr. and then at room temperature for 2 hr. The ice-cooled ether-benzene solution was hydrolyzed with 75 ml. of cold 5 *N* sulfuric acid. The aqueous layer was removed and extracted with 100 ml. of ethyl ether. The organic layers were combined and washed successively with two 100-ml. portions of dilute aqueous sodium carbonate solution and two 100-ml. portions of water. The ether-benzene solution then was dried with anhydrous sodium sulfate, filtered, and evaporated down to 20 ml. under aspirator vacuum. Distillation yielded 14.8 g. of 2-phenyl-3-*n*-butylindone, b.p. 170° (0.30 mm.),  $n_D^{20}$  1.6148.

The orange, crystalline 2,4-dinitrophenylhydrazone of the indone had a melting point of 173–174° after one recrystallization from ethyl acetate.

**Preparation of Anhydride (V) of 2-Phenyl-3-(*o*-carboxyphenyl)-2-heptenoic Acid (IIIa).** 2-Phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid (5.00 g., 0.015 mole) was suspended in 100 ml. of anhydrous carbon tetrachloride with rapid stirring. Thionyl chloride (11.70 g., 0.0985 mole) was added in one portion and the mixture was heated under reflux for 4 hr.

The clear, yellow solution was allowed to cool to room temperature, poured into 75 ml. of 6 *N* hydrochloric acid, and stirred for 1 hr. before standing overnight. The aqueous layer was extracted with ethyl ether and the organic layers were combined. The ether-carbon tetrachloride solution then was extracted with three 25-ml. portions of aqueous, saturated sodium carbonate to remove any unreacted acid. Subsequent acidification of the basic aqueous layer with 6 *N* hydrochloric acid and extraction with ethyl ether yielded 0.15 g. of unreacted acid. The ether-carbon tetrachloride solution was dried over anhydrous magnesium sulfate, and the solvent was evaporated. The anhydride was obtained as a viscous yellow oil in 70% yield. Five recrystallizations from hexane produced white crystals: m.p. 87.5–88.0°;  $\nu_{\max}^{\text{CHCl}_3}$  1785, 1750 cm $^{-1}$ . *Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>3</sub>: C, 78.40; H, 5.92; mol. wt., 306. Found: C, 78.34; H, 5.98; mol. wt., 331.

The anhydride (0.02 g.,  $8.3 \times 10^{-5}$  mole) was suspended in 3 ml. of water and stirred for 5 days at 28–30°. The suspension was filtered and dried to give 0.02 g. of 2-phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid, m.p. 168–170°. A mixture melting point with an authentic sample of the acid showed no depression.

**Ethyllithium and Diphenylacetylene. Carbonation.** Diphenylacetylene (20.0 g., 0.112 mole) was added in one portion to a solution of ethyllithium (0.148 mole) in 240 ml. of ethyl ether. The cloudy green solution became yellow-green in 3 min. and was bright yellow after 19.5 hr. of stirring at room temperature. The bright yellow reaction mixture was carbonated by decantation over Dry Ice after 27 hr. of reaction time to give a bright orange mixture.

After work-up in the manner described for *n*-butyllithium, distillation of the neutral fraction gave 59% diphenylacetylene and 11.5% 2-phenyl-3-ethylindone (IVb): b.p. 165–173° (0.8 mm.); m.p. 97.5–98° after four recrystallizations from 100% ethanol (lit.<sup>23</sup> m.p. 97–98°); mixture melting point with authentic sample, 97–98°; n.m.r. (20% in CCl<sub>4</sub>),  $\tau$  2.67 and 2.87 (8,8), 7.33 (1,8), and 8.73 (3,4);  $\nu_{\max}^{\text{CCl}_4}$  1717 cm $^{-1}$ ;  $\lambda_{\max}$  256 m $\mu$  ( $\log \epsilon$  4.56). The 2,4-dinitrophenylhydrazone had m.p. 225–228° after one recrystallization from ethanol-ethyl acetate, mixture melting point with authentic sample, 225–226°; phenylhydrazone m.p. 96–97° after two recrystallizations from ethanol (lit.<sup>22</sup> m.p. 96–97°).

The acid fraction of the reaction mixture yielded 11.9% 2-phenyl-3-(*o*-carboxyphenyl)-2-pentenoic acid (IIIb); m.p. 191–192° after three recrystallizations from ethanol; n.m.r. (10% in NaOD-D<sub>2</sub>O),  $\tau$  2.49 (8,8), 7.68 (1,8), and 9.21 (3,4). *Anal.* Calcd. for C<sub>16</sub>H<sub>14</sub>(COOH)<sub>2</sub>: C, 72.96; H, 5.44; neut. equiv., 148. Found: C, 73.13; H, 5.48; neut. equiv., 148, 151.

When the reaction was run in ethyl ether at –70° for 429 hr. before carbonation, 97% diphenylacetylene was recovered along with 0.07 g. of acidic material, m.p. 70–87°.

If the reaction is carried out under the same conditions, but carbon dioxide is bubbled through the solution, there is obtained 6.95% 2-phenyl-3-(*o*-carboxyphenyl)-2-pentenoic acid (IIIb), and 27% 2-phenyl-3-ethylindone (IVb). Diphenylacetylene (23.4%) also was recovered along with 8 g. of undistillable tar.

If the reaction was run under the same conditions but the reaction mixture was diluted fourfold before carbonation, which was carried out over a period of 7 hr., there was obtained 15.4% 2-phenyl-3-(*o*-carboxyphenyl)-2-pentenoic acid (IIIb) and 30% 2-phenyl-3-ethylindone (IVb). Diphenylacetylene was recovered in 17% yield.

**Preparation of 2-Phenyl-3-ethylindone (IVb).** Using the procedure of Frank,<sup>22</sup> 2-phenyl-3-ethylindone (IVb) was synthesized from 2-phenyl-1,3-indanedione and ethylmagnesium bromide. Two recrystallizations from 100% ethanol gave red needles, m.p. 96.5–97.5° (lit.<sup>22</sup> m.p. 97–98°). A 2,4-dinitrophenylhydrazone of the product had m.p. 225–226° (lit.<sup>22</sup> m.p. 206–207°).

**Phenyllithium and Diphenylacetylene. Carbonation.** Diphenylacetylene (18.0 g., 0.100 mole) was added in one portion to a vigorously stirred solution of phenyllithium (0.232 mole) in 232 ml. of ethyl ether. The solution was stirred at room temperature

(21) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(22) R. L. Frank, *et al.*, *J. Am. Chem. Soc.*, **66**, 1 (1944).

(23) D. Y. Curtin and W. A. Richardson, *ibid.*, **81**, 4724 (1959).

for 24 hr. before carbonation by decantation. The tan carbonation mixture yielded 14.1 g. of acidic material and 24.7 g. of neutral material after work-up in the manner described above. The acidic material was suspended in 650 ml. of boiling water<sup>24</sup> and filtered hot to give 1.2 g. of triphenylacrylic acid, m.p. 219.5–220° after three recrystallizations from ethanol (lit.<sup>28</sup> m.p. 216–217.5°), mixture melting point with an authentic sample, 216–218°.

The neutral fraction was distilled to give 23 g. of a mixture, b.p. 100–125 (0.6 mm.),  $\nu_{\text{max}}^{\text{C}^{14}}$  1667  $\text{cm}^{-1}$ , which probably consists of diphenylacetylene and benzophenone (lit.<sup>25</sup>  $\nu_{\text{max}}^{\text{C}^{14}}$  for benzophenone 1664  $\text{cm}^{-1}$ ). The undistilled portion was recrystallized from ethanol to give 8.2% (based on phenyllithium) of triphenylcarbinol.

**Oxidative Cleavage of Dideuterated *trans*- $\alpha$ -*n*-Butylstilbene (II).** The procedure was that of Pappo, Allen, Lemieux, and Johnson.<sup>15</sup> A solution of 9.0 g. (0.038 mole) of II and 0.193 g. (0.00076 mole) of osmium tetroxide in 150 ml. of purified dioxane and 50 ml. of water was stirred for 5 min. during which time the solution became purple in color. While maintaining a temperature of 24–26°, a total of 34.2 g. (0.16 mole) of sodium metaperiodate was added over a period of 1 hr. The purple solution was stirred at room temperature for 60 hr. with little change in color. Heating for 15 min. at 60° resulted in a color change to pale yellow. The mixture

(24) Curtin and Richardson<sup>28</sup> separated benzoic acid and triphenylacrylic acid by employing the difference in solubilities in boiling water. Benzoic acid is soluble in water to the extent of 2.2 g./100 ml. at 75°. Triphenylacrylic acid dissolves in boiling water to the extent of 2.8 mg./ml. of water. Therefore 650 ml. of boiling water will dissolve 1.82 g. of triphenylacrylic acid but 14.3 g. of benzoic acid. The total yield (11%) of triphenylacrylic acid is then 3.02 g., 1.2 g. isolated and 1.82 g. lost due to solubility in boiling water.

(25) N. Fuson, M. L. Josein, and E. M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954).

was extracted with diethyl ether, and the combined organic layer (about 600 ml.) was filtered through anhydrous sodium sulfate. The solution was concentrated to 150 ml. and a calculated slight excess of saturated aqueous sodium bisulfite was added. The precipitate was collected on a filter, acidified with dilute hydrochloric acid, extracted with diethyl ether, dried over sodium sulfate, and distilled to yield 3.21 g. (79%) of benzaldehyde- $\alpha$ -*d*, pure by v.p.c. No aldehydic hydrogen appeared in the low-field area of the n.m.r. spectrum. *Anal.* Calcd. for  $\text{C}_7\text{H}_5\text{DO}$ : D, 16.67 atom %. Found: D, 16.15 atom %.

A portion of benzaldehyde- $\alpha$ -*d* was oxidized with sodium hydroxide–potassium permanganate<sup>26</sup> to give benzoic acid (identical with an authentic sample) which contained 0.00 atom % deuterium. Other workers have shown that under these conditions deuterium bound to the aryl ring would not be exchanged.<sup>27</sup>

The remaining solution, after the sodium bisulfite treatment was distilled through a Vigreux column to yield 4.34 g. (71%) of valero-phenone-*o*-*d*, b.p. 78–80° (0.4 mm.), pure by v.p.c. *Anal.* Calcd. for  $\text{C}_{11}\text{H}_{13}\text{DO}$ : D, 7.14 atom %. Found: D, 6.60 atom %.

In addition to having the correct infrared and n.m.r. spectra (see Discussion), a 2,4-dinitrophenylhydrazone of the product had m.p. 169.0–169.5° (lit.<sup>26</sup> m.p. 166°).

**Acknowledgment.** It is a pleasure to thank the Socony-Mobil Oil Company and the Air Force Office of Scientific Research, Grant No. AF-AFOSR 270-65, for support of this research.

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(27) F. Jones, M. Zinn, and C. Hauser, *J. Org. Chem.*, **28**, 663 (1963)

## Fluorocarbon Nitroxides

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Contribution from Texaco, Inc., Beacon, New York. Received October 1, 1965

**Abstract:** Nitroxides with fluorocarbon substituents have been found to form isolable, stable free radicals. Bis(2-chlorotetrafluoroethyl) nitroxide has been synthesized and characterized successfully. Evidence is presented for the existence of additional stable nitroxides containing fluorinated alkyl substituents. Nitroxide radicals with two difluoromethylene groups bonded to the nitrogen atom are believed to form a general class of stable radical species. The electron spin resonance spectra of these radicals is discussed.

Nitroxide radicals ( $\text{R}_2\text{NO}$ ) stabilized by fluorocarbon substituents have been known for a very short time with the first example, bis(trifluoromethyl) nitroxide, being reported in 1965.<sup>1</sup> The corresponding hydrocarbon radical ( $(\text{CH}_3)_2\text{NO}$ ) as well as other nitroxides having hydrogen on the carbon adjacent to the nitrogen have never been isolated. Dimethyl nitroxide and its deuterated analog were observed as major fragments in the mass cracking pattern of a mass spectroscopic study of the reaction of methyl and deuteriomethyl radicals with nitric oxide.<sup>2</sup> Although it was not detected,  $(\text{CH}_3)_2\text{NO}$  was proposed as the intermediate in the formation of the trimethylhydroxylamine. Stable nitroxide radicals containing hydrocarbon substituents require a tertiary carbon atom adjacent to the nitrogen ( $\alpha$ -carbon) such as in the case of di-*t*-butyl nitroxide<sup>3</sup> or aromatic substituents such as in diphenyl

nitroxide.<sup>4</sup> A number of such radicals has been made. The stabilizing factors in these cases are reported to be resonance delocalization in the aromatic substituents and steric effects in the case of the alkyl substituents. Three-electron bond formation in compounds containing the N–O linkage has also been considered to lend stability to the radical structures.<sup>5</sup>

Paramagnetic species have been detected in liquid nitroso fluorocarbons by electron spin resonance (e.s.r.) spectroscopy.<sup>6</sup> The spectra obtained were reported to be consistent with fluorocarbon nitroxides which were postulated to be reactive intermediates in the copolymerization of nitroso fluorocarbons and tetrafluoroethylene. The subsequent synthesis and isolation of  $(\text{CF}_3)_2\text{NO}$  indicated that fluorocarbon nitroxides

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(5) R. B. Briere, H. Lemaire, and A. Rassat, *Tetrahedron Letters*, 1775 (1964).

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(2) A. Maschke, B. Shapiro, and F. W. Lampe, *ibid.*, **86**, 1929 (1964).