Carbanions. X. The Preferential Migration of *p*-Biphenylyl in 2-*m*-Biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium[1,2]

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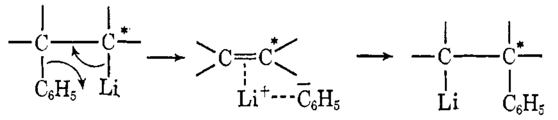
Abstract: Reaction of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with lithium in tetrahydrofuran at −65° yields 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium as shown by carbonation to give 3-*m*-biphenylyl-3,3-bis(*p*-biphenylyl)propanoic acid. When the solution of 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium is warmed to 0° and held at this temperature 3 hr before carbonation, the crude acid obtained consists of at least 98.6 ± 0.4% of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid. The much higher migratory aptitude of *p*-biphenylyl than of *m*-biphenylyl is taken to indicate that migration of an aryl group in such organolithium compounds occurs in a carbanion by way of a cyclic or bridged transition state or intermediate such as I. Analogies are pointed out to certain related rearrangements involving 1,2 shifts of vinyl, carbonyl, and trimethylsilyl groups, and it is suggested that the area of carbanion rearrangements is more general than usually supposed.

In a previous paper[3] it was shown that 2,2,2-triphenylethyllithium in tetrahydrofuran solution undergoes rearrangement to 1,1,2-triphenylethyllithium in the presence of benzyllithium or phenyllithium-C^{14} without detectable incorporation of benzyl or radioactive phenyl groups. These experiments demonstrate that the 1,2 shift of phenyl occurs without the formation and readdition of kinetically free phenyl radical, phenyl anion, or phenyllithium.[4] The rearrangement was thereby concluded to occur by an intramolecular process. These experiments, however, did not eliminate the possibility[5] that 2,2,2,-triphenylethyllithium undergoes elimination of phenyl anion (or radical) but that phenyl anion (or radical) and 1,1-diphenylethene (or corresponding radical anion) exist in a solvent "cage" and recombine before radioactive phenyllithium or benzyllithium can diffuse into the "cage." The possibility that ordinary phenyllithium and 1,1-diphenylethene could exist in such a solvent "cage" and combine before radioactive phenyllithium or benzyllithium could diffuse into the "cage" can be dismissed since phenyllithium was found[3] to add to 1,1-diphenylethene only slowly under the reaction conditions. An attractive variation[6] of the cage-recombination mechanism is that rearrangement of 2,2,2-triphenylethyllithium occurs with elimination of phenyllithium as an ion pair to which 1,1-diphenylethene is bound as a ligand of the lithium ion; the ion pair-olefin complex then collapses to final product before an external organolithium compound can attack the 1,1-diphenylethene in the complex (eq 1).

While such elimination-readdition mechanisms may appear attractive in light of the proof[3,5] of occurrence of an intermolecular elimination-readdition mechanism for rearrangement of 2,2,3-triphenylpropyllithium, in earlier work it was proposed that phenyl migration[7] proceeded by way of a cyclic transition state or reaction intermediate such as I for rearrangement of 2,2,2-triphenylethyllithium; similar transition states of intermediates were proposed by Zimmerman and Zweig[8] for migration of phenyl in 2,2-diphenylpropyllithium and phenyl or *p*-tolyl in 2-phenyl-2-(*p*-tolyl)-propyllithium.



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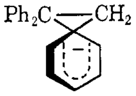

I

The present investigation was undertaken in order to try to distinguish between the proposed intramolecular elimination-readdition mechanisms of phenyl migration and the intramolecular cyclic mechanism of migration by way of an intermediate or transition state such as I. Such a distinction appears possible since in the elimination-readdition process the unshared electron pair in the phenyl anion or the unpaired electron in the phenyl radical is in an sp^2 orbital which is orthogonal to the aromatic π orbitals of the migrating phenyl group; hence the presence of a substituent at the *meta* or *para* position of the phenyl group would not be expected to greatly affect the rate of elimination of that group as an anion or radical. For comparison, Streitwieser and Lawler[9] have found that the rate of deuterium exchange in biphenyl with lithium cyclohexylamide in cyclohexylamine is for a *para* position only 2.3 times that of a single position in benzene and for a *meta* position 3.7 times that of a position in benzene; similar partial rate factors were reported by Shatenshtein[10] for exchange with potassium amide in

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(1) Abstracted from the Ph.D. thesis of G. Wentworth, Georgia Institute of Technology, 1966.

(2) Presented in part before the Division of Organic Chemistry at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 13, 1966.

(3) Part IX: E. Grovenstein, Jr., and G. Wentworth, *J. Am. Chem. Soc.*, **89**, 1852 (1967).

(4) By "kinetically free" we mean that the phenyl radical, phenyl anion, or phenyllithium had sufficient lifetime to diffuse into the surrounding solvent away from the 1,1-diphenylethene (or 1,1-diphenylethene radical anion). It is assumed here that kinetically free phenyl radicals (or anions) would undergo very rapid lithium atom (or lithium cation) transfer reactions with benzyllithium or phenyllithium-C^{14}.

(5) E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **85**, 3305 (1963).

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 237.

(7) E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Am. Chem. Soc.*, **83**, 2537 (1961).

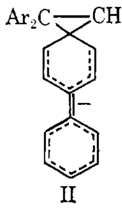
(8) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(9) A. Streitwieser, Jr., and R. G. Lawler, *ibid.*, **85**, 2854 (1963); **87**, 5388 (1965).

(10) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 187 (1963).

liquid ammonia. For rearrangement of a 2,2,2-triarylethyllithium proceeding by elimination of an aryl anion (*cf.* eq 1), a *m*-biphenylyl anion would be expected to be eliminated somewhat more readily than a *p*-biphenylyl anion and thus *m*-biphenylyl should migrate somewhat more readily than *p*-biphenylyl.

On the other hand if rearrangement of 2,2,2-triarylethyllithium proceeds by way of an intermediate such as I, a *p*-biphenylyl group should migrate more readily than a *m*-biphenylyl group because the intermediate II from *p*-biphenylyl migration should have greater charge delocalization than that of III from *m*-biphenylyl migration since the mesomeric effect of the substituent phenyl group is not conveyed nearly as effectively from a *meta* as from a *para* position. In a system of somewhat similar electrical demand, *m*- and *p*-phenyl as substituent groups increase the ionization constant of phenol[11] according to the usual linear Hammett relationship if substituent constants of +0.124 and +0.205, respectively, are assigned[12] these groups.



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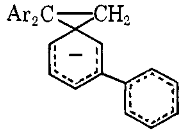


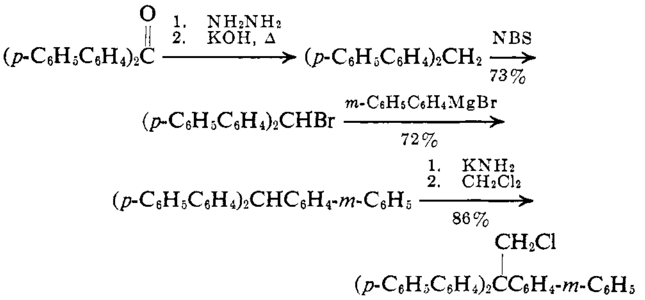
III

Accordingly 2-*m*-biphenyl-2,2-bis(*p*-biphenylyl)ethyllithium was prepared by reaction of 2-chloro-1-*m*-biphenyl-1,1-bis(*p*-biphenylyl)ethane with lithium, and the relative migratory aptitude of *m*-biphenylyl *vs.* *p*-biphenylyl was determined.

Results

Synthesis of 2-Chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane. Initially it was intended to prepare this compound from chloro-*m*-biphenylylbis(*p*-biphenylyl)methane according to the procedure used for preparation[13] of 2-chloro-1,1,1-triphenylethane from chlorotriphenylmethane. *m*-Biphenylylbis(*p*-biphenylyl)carbinol was prepared by reaction of 3-lithiobiphenyl with 4,4′-diphenylbenzophenone in tetrahydrofuran; however attempts to convert this carbinol to the chloride by reaction with acetyl chloride according to the procedure[14] for conversion of triphenylcarbinol to chlorotriphenylmethane gave a halogen-free product. While reaction of the carbinol with thionyl chloride and pyridine[15] gave a chlorine-containing product, the material in our hands proved difficult to purity. Accordingly the procedure in Scheme I was adopted.

Scheme I



Reduction of 4,4′-diphenylbenzophenone by the modified Wolff–Kishner procedure of Huang-Minlon[16] gave an almost quantitative yield of bis(*p*-biphenylyl)methane, whereas Clemmenson reduction under either the acidic or alkaline conditions of Martin[17] resulted in almost quantitative recovery of unreacted ketone (possibly because of the very low solubility of the ketone in aqueous media). Bromobis(*p*-biphenylyl)methane was prepared by reaction of bis(*p*-biphenylyl)methane with N-bromosuccinimide according to a general procedure of Zervas and Dilaris[18] except that benzoyl peroxide was employed as catalyst. A preliminary attempt to couple bromobis(*p*-biphenylyl)methane with 3-lithiobiphenyl in tetrahydrofuran solution resulted in a 74% yield of 1,1,2,2-tetrakis(*p*-biphenylyl)ethane, possibly by way of a halogen–metal interchange.[19] The reaction of bromobis(*p*-biphenylyl)methane with 3-*m*-biphenylylmagnesium bromide in tetrahydrofuran also gave 1,1,2,2-tetrakis(*p*-biphenylyl)ethane in some 84% yield. While halogen–metal interchange in reactions of Grignard reagents has been reported[20] to be more facile in tetrahydrofuran than in ethyl ether, the high yield of symmetrical coupling product under the present conditions is unusual. When the coupling of bromobis(*p*-biphenylyl)methane with 3-*m*-biphenylmagnesium bromide was run in ethyl ether, the desired *m*-biphenylylbis(*p*-biphenylyl)methane was obtained; the best yield of this compound (some 72%) was obtained in ethyl ether–benzene solution[21] along with 18% yield of 1,1,2,2-tetrakis(*p*-biphenylyl)ethane. Reaction of *m*-biphenylylbis(*p*-biphenylyl)methane with potassium amide in ammonia–ether solution gave a deeply colored solution of the corresponding triarylmethylpotassium which reacted readily with an excess of methylene chloride to give 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane. The over-all yield of this chloride from 4,4′-diphenylbenzophenone was about 43%.

Synthesis of Carboxylic Acids. In order to characterize the products of carbonation of the organolithium compounds from 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane, it was necessary to synthesize all of the likely carboxylic acids.

3-*m*-Biphenylyl-3,3-bis(*p*-biphenylyl)propanoic acid was prepared by reaction of *m*-biphenylylbis(*p*-biphenylyl)carbinol with malonic acid. This reaction is modeled after the procedure of Hellerman[22] for preparation of 3,3,3-triphenylpropanoic acid from triphenylcarbinol; however in the present case after the reactants were heated at a bath temperature of 220° for 12 hr, the starting carbinol was recovered almost quantitatively. Also heating of the reactants with acetic anhydride according to the modification of Hellerman's procedure

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(11) F. Kieffer and P. Rumpf, *Compt. Rend.*, **238**, 360 (1954).

(12) These σ values were calculated from the reported[11] pK_a values of *m*-phenyl- and *p*-phenylphenol and a plot of pK_a *vs.* σ for other phenols [L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963); A. Bryson and R. W. Matthews, *Australian J. Chem.*, **16**, 401 (1963)].

(13) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957).

(14) W. E. Bachmann in "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 841.

(15) R. H. Clark and H. R. L. Streight, *Trans. Roy. Soc. Canada, Sect. III*, [3] **23**, 77 (1929).

(16) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(17) E. L. Martin, *ibid.*, **58**, 1438 (1936).

(18) L. Zervas and I. Dilaris, *ibid.*, **77**, 5354 (1955).

(19) *Cf.* R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 350 (1951).

(20) L. I. Zakharkin, O. Yu. Okhlobystin, and K. A. Bilevitch, *J. Organometal. Chem.* (Amsterdam), **2**, 309 (1964).

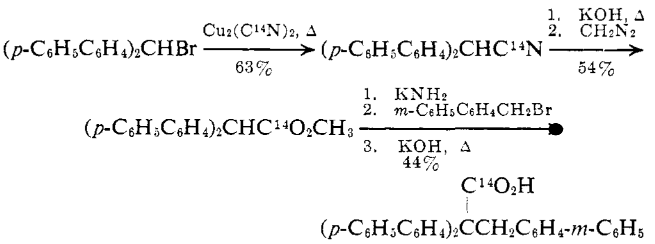
(21) *Cf.* W. E. Bachman, *J. Am. Chem. Soc.*, **55**, 2135 (1933).

(22) L. Hellerman, *ibid.*, **49**, 1735 (1927).

suggested by Gagnon[23] failed to give any of the desired carboxylic acid. Evidently because of the high melting point of *m*-biphenylylbis(*p*-biphenylyl)carbinol, malonic acid decomposes before an effective melt of the reactants can be obtained even in presence of acetic anhydride (bp 140°); however in the presence of higher boiling *n*-butyric anhydride (bp 198°), 3-*m*-biphenylyl-3,3-bis-(*p*-biphenylyl)propanoic acid was obtained though in only 17% yield.

3-*m*-Biphenylyl-2,2-bis(*p*-biphenylyl)propanoic acid-1-C^{14} was synthesized according to the method of Scheme II. Reaction of bromobis(*p*-biphenylyl)methane with cuprous cyanide at 160° gave the expected nitrile; however attempts to obtain this nitrile by reaction of the same bromide with sodium cyanide in acetone or in dimethyl sulfoxide[24] were unsuccessful. In the latter solvent, after addition of water 4,4′-diphenylbenzophenone (27% yield) was isolated in addition to bis(*p*-biphenylyl)carbinol. The carbinol doubtlessly arose from hydrolysis of the bromide while the ketone possibly arose from O-alkylation of the solvent, followed by base-catalyzed elimination. Attempts to hydrolyze bis(*p*-biphenylyl)ethanenitrile with dilute potassium hydroxide[25] in diethylene glycol at 80° resulted in essentially quantitative recovery of starting nitrile, while at 160° a 94% yield of bis(*p*-biphenylyl)methane arose, doubtlessly by decarboxylation of the desired acid. At 120° bis(*p*-biphenylyl)ethanoic acid was obtained in some 60% yield. Methyl bis(*p*-biphenylyl)ethanoate was alkylated with 3-(bromomethyl)biphenyl in moderate yield by a procedure similar to that of Hauser;[26] saponification of the product gave the desired 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)propanoic acid-1-C^{14} in an over-all yield of some 15% from bromobis(*p*-biphenylyl)methane.

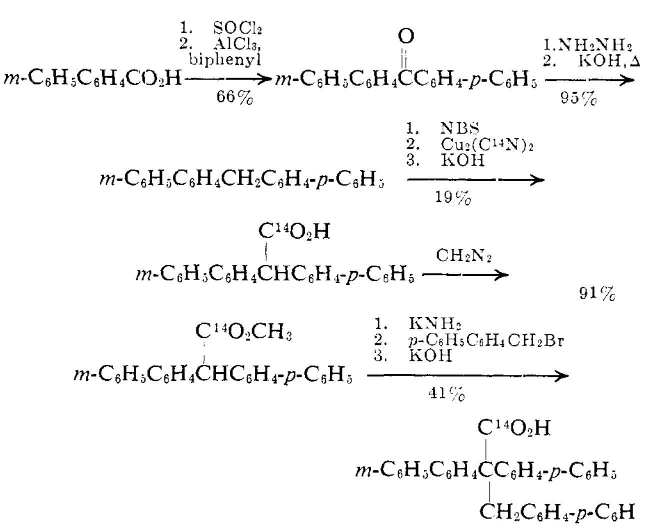
Scheme II



2-*m*-Biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid-1-C^{14} was synthesized according to the method of Scheme III. While all of the products from the reactions shown in Scheme III are new compounds, the reactions are quite similar to those which have been discussed earlier (Schemes I and II).

Reaction of 2-Chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with Lithium. The reaction of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with lithium in tetrahydrofuran at −65° followed by carbonation gave a carboxylic acid which was found to be identical with the sample of 3-*m*-biphenyl-3,3-bis(*p*-biphenylyl)propanoic acid (mp 226.4–228.1°) whose synthesis is reported above. Thus this reaction with lithium gave the expected organolithium compound and provides conformation of the structure of the starting chloride.

Scheme III



In contrast reaction of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with lithium in tetrahydrofuran at 0° gave according to Gilman's double-titration technique[27] a 45% yield of organolithium compound and, after carbonation, a 30% yield of crude acid of mp 208.0–209.5°. This acid was essentially identical with the sample of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid-1-C^{14} (mp 209.0–210.0°) prepared by Scheme III. According to an isotope-dilution analysis with this radioactive acid, 98.1 ± 0.5% of the crude acid was 2-*m*-biphenyl-2,3-bis(*p*-biphenylyl)propanoic acid. From this result it is obvious that a *p*-biphenylyl group has undergone a 1,2 shift during the reaction of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with lithium at 0° some time prior to carbonation.

In order to provide more information concerning the nature of this rearrangement, the reaction of the chloride was repeated as before with lithium at −65°. After the usual 3-hr stirring period at this temperature, titration indicated a 39% yield of organolithium compound. The solution was then allowed to warm to 0° and stirred at this temperature for 4 hr before carbonation. The crude acid was obtained in 38% yield and according to isotope-dilution analysis contained 98.6 ± 0.4% of 2-*m*-biphenyl-2,3-bis(*p*-biphenylyl)propanoic acid. This result together with the first reaction at −65° implies that reaction of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with lithium in tetrahydrofuran at −65° yields 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium and that upon increase of temperature to 0° this organolithium compound rearranges to 1-*m*-biphenylyl-1,2-bis(*p*-biphenylyl)ethyllithium. Attempts to analyze the crude reaction product for 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl) propanoic acid (the product expected for migration of the *m*-biphenylyl group) were unsuccessful; the 98.6 ± 0.4% yield of 2-*m*-biphenyl-2,3-bis(*p*-biphenylyl)propanoic acid corresponds to the *minimum* amount of *p*-biphenylyl migration in the product acid since the remainder of the crude product may have been an impurity (solvent, stopcock grease, etc.).

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[23] P. Gagnon, *Ann. Chim.* (Paris), [10] 12, 299 (1929).

[24] *Cf.* A. C. Cope and A. S. Mehta, *J. Am. Chem. Soc.*, **86**, 5626 (1964).

[25] *Cf.* F. S. Prout, *et al.*, in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 95.

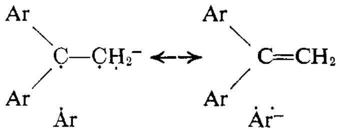
[26] W. G. Kenyon, R. B. Meyer, and C. R. Hauser, *J. Org. Chem.*, **28**, 3108 (1963).

[27] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

Discussion

The present demonstration that in the rearrangement of 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium the *p*-biphenylyl group migrates, after statistical correction for unequal numbers of biphenylyl groups, more than 24.5 times more readily than the *m*-biphenylyl group provides strong evidence against rearrangement proceeding by elimination of a biphenylyl anion and readdition of this anion to the resulting 1,1-bis(biphenylyl)ethene according to any of the detailed paths which have been previously discussed. This argument is on the basis that a *m*-biphenylyl anion should be eliminated more readily than a *p*-biphenylyl anion if analogies with the relative ease of formation[9,10] of *m*- and *p*-biphenylyl anions during base-catalyzed hydrogen exchange upon biphenyl are pertinent and if, as expected, a 1,1-bis(*p*-biphenylyl)ethene moiety is somewhat more stable than a 1-*m*-biphenylyl-*p*-biphenylyl moiety in the transition state for the elimination.

With less certainty, the present migratory aptitudes also rule out migration by way of a biphenylyl radical and 1,1-bis(biphenylyl)ethene radical anion. This conclusion is based on the probable argument that the 1,1-bis(*p*-biphenylyl)ethene radical anion is somewhat more stable (thanks to greater electron delocalization) and therefore more readily formed than 1-*m*-biphenylyl-1-*p*-biphenylylethene radical anion and also that *m*-biphenylyl radical is likely more readily formed than *p*-biphenylyl radical because of greater contribution from the polar structure V in the transition state for cleavage. Structure V should be more stable when the group being cleaved is *m*-biphenylyl rather than *p*-biphenylyl because of the greater stability of a *m*-biphenylyl than *p*-biphenylyl anion, which is implied by the greater ease of formation of the former. For rearrangement proceeding by way of cleavage into a biphenylyl radical and 1,1-bis(biphenylyl)ethene radical anion we would, therefore, anticipate that *m*-biphenylyl radical would cleave and hence appear to migrate more readily than *p*-biphenylyl radical, a result contrary to the observed migratory aptitudes.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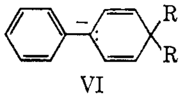
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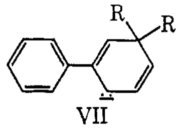
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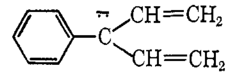
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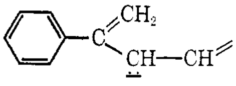
IX

The observed migratory aptitudes are in good agreement with rearrangement proceeding by way of a cyclic transition state or intermediate such as II or III. The portions of II and III which are of significant energetic difference are contained in structures VI and VII, respectively, which are illustrated for simplicity by single canonical structures. In the simple Hückel LCAO molecular orbital approximation, the energies of structures VI and VII are the same as those of structures VIII and IX, respectively. Calculations[28] show that VIII is more stable than IX by 0.97 $|\beta|$ unit. While $|\beta|$ must be regarded as an empirical parameter, a value of 35 kcal/mole has been found[29] for attachment of a proton upon a benzenoid ring to give a cationic σ complex. If this value of $|\beta|$ is assumed in the present case, the equilibrium ratio of VI to VII (or of II to III after statistical correction for unequal numbers of migrating groups) is calculated to be 525; if $|\beta|$ is 20 kcal/mole, the calculated ratio is 36. These calculations suffice to show that transition states or intermediates II and III differ sufficiently in energy to account for the observed highly preferential migration of *p*-biphenylyl over *m*-biphenylyl.

While we believe that the present migratory aptitudes are best accommodated by rearrangement occurring in a carbanion by way of II or III, it might be noted that preferential migration of *p*-biphenylyl over *m*-biphenylyl would also be expected if the rearrangement occurred in the corresponding free radical through transition states or intermediates differing from II or III by one less electron each. Previously it has been argued that the greater migratory aptitude of benzyl over phenyl in rearrangement of 2,2,3-triphenylpropyllithium provides evidence for rearrangement occurring in a carbanion rather than a free radical.[7] While this general argument still appears correct, the conclusion is restricted to migration of benzyl and is not applicable to migration of phenyl in 2,2,2-triphenylethyllithium since migration of benzyl occurs by an intermolecular process while migration of phenyl occurs by an intramolecular process.[3,5] It has also been argued that rearrangement of phenyl in 2,2-diphenylpropyllithium occurs in a carbanion rather than a free radical, because *inter alia* rearrangement of 2-*p*-tolyl-2-phenylpropyllithium occurs with preferential migration of phenyl over *p*-tolyl;[8] in this argument it was assumed on general grounds that *p*-tolyl would migrate more readily than phenyl for rearrangement of a free radical. More recently, however, it has been demonstrated that phenyl migrates more readily than *p*-tolyl in rearrangement of free radicals.[30] While for 1,2 shifts of phenyl and other aryl groups occurring during rearrangements of organolithium compounds, the evidence in favor of rearrangement occurring in a carbanion rather than a free radical is not as strong as once supposed; the general evidence[8,31] can still be most simply accommodated on the view that these are rearrangements of carbanions.

Finally it is of interest to note that intramolecular rearrangements of carbanions or organometallic compounds have been observed for 1,2 shifts of vinyl[32] and carbonyl[33] as well as aryl. These reactions,

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(28) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press Inc., New York, N. Y., 1965, pp 92 and 94.

(29) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 342.

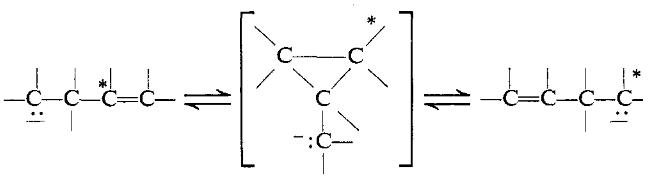
(30) C. Rüchardt and R. Hecht, *Tetrahedron Letters*, 961 (1962).

(31) E. Grovenstein, Jr., and L. P. Williams, Jr., *J. Am. Chem. Soc.*, **83**, 412 (1961).

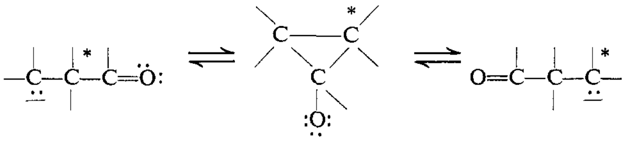
(32) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. Sidder, *ibid.*, **86**, 2247 (1964); M. L. Silver, P. R. Shafer, J. E. Norlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

(33) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3544 (1966); A. Nickon, J. L. Lambert, and J. E. Oliver, *ibid.*, **88**, 2787 (1966); A. Nickon and J. L. Lambert, *ibid.*, **88**, 1905 (1966); J. P. Freeman and J. H. Plonka, *ibid.*, **88**, 3662 (1966).

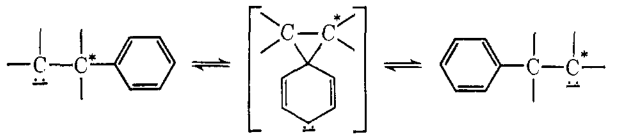
stripped of complicating details such as the role of the metallic cation and solvent, can be represented in the simplified form



X



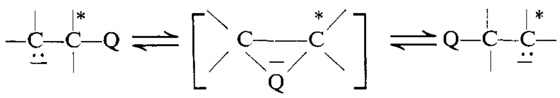
XI



XII

The remarkable similarity of these three rearrangements does not appear to have received adequate emphasis. While it is not known whether the species (X and XII) shown in brackets are transition states or reaction intermediates, at least cyclopropylcarbinyllithium and magnesium derivatives are stable under certain experimental conditions.[32]

Vinyl, carbonyl, and aryl groups have in common an unsaturated character which permits these groups to accept additional electrons during the course of rearrangement as illustrated by the fairly classical structures of the proposed intermediates (X, XI, XII). It seems reasonable also that groups which are "unsaturated" because of the presence of vacant d or p orbitals on the atom Q to which the carbanionic center becomes attached (see XIII) should have high migratory aptitudes



XIII

in carbanion rearrangements.[34] A pertinent example in the field of nitrogen chemistry is provided by the recent report of facile base-catalyzed 1,2 shift of the trimethylsilyl group in various hydrazines;[35] here a vacant 3d orbital of silicon is likely utilized during rearrangement. These considerations imply that the area of carbanion rearrangements is more general than usually supposed and that additional research in this area is desirable. Thus carbanion rearrangements involving a 1,2 shift of an acetylenic group (*e.g.*, C≡CPh) appear likely. Also numerous possibilities involving hetero atoms (Zn, B, Al, Si, Ge, Sn, P) centrally located in the group Q appear promising. In some of these the intermediate XIII may be isolable; in others polymerization, elimination, or other side reactions may occur in place of rearrangement.

Experimental Section[36]

***m*-Biphenylylbis(*p*-biphenylyl)carbinol.** Into a 1000-ml Morton flask equipped with a high-speed stirrer[37] and dropping funnel, 42.0 g (0.180 mole) of 3-bromobiphenyl was added slowly onto 3.33 g (0.480 g-atom) of finely cut lithium and 0.1 ml of methyl iodide in 550 ml of tetrahydrofuran (freshly distilled from $NaAlH_4$) at 5° under an atmosphere of dry nitrogen. After addition of about one-third of the bromide, the reaction temperature was lowered to −25°, and the remainder of the bromide was added. After addition of the bromide was completed, the deep purple solution was stirred for 1 hr at −25°. Gilman titration[27] indicated the formation of 105 mmoles (58% yield) of 3-lithiobiphenyl. The solution was siphoned through a glass-wool filter (to remove unreacted lithium) under a nitrogen atmosphere into a 3-l. Morton flask. A solution of 30.1 g (0.090 mole) of 4,4′-diphenylbenzophenone[38] in 1500 ml of dry tetrahydrofuran was added at a flask temperature of 5°, over a period of 1 hr, and the resulting green solution was stirred vigorously at room temperature for 1 hr. The reaction mixture was acidified with 400 ml of 5% hydrochloric acid and the tetrahydrofuran removed on a rotating evaporator. The remaining aqueous suspension of solid was extracted with ether. A quantity of off-white solid (7.8 g), which was insoluble in both aqueous and ether phases, was isolated by filtration and dried *in vacuo*. The ether extract upon evaporation to dryness yielded an orange solid residue which was washed with cyclohexane to remove biphenyl. The total weight of crude white and orange product was 20.6 g (mp 201–229°) of a mixture of the desired carbinol and unreacted ketone. Repeated recrystallizations from benzene removed most of the ketone and gave 11.0 g (0.022 mole or 25% yield based on starting ketone) of white powder of mp 227–231°. A 2.00-g sample of this powder was subjected to vacuum sublimation at 230° (0.02 mm), and the sublimate was recrystallized four times from benzene to give 0.83 g of compound, mp 231–233°. This product upon admixture with 4,4′-diphenylbenzophenone (mp 235–237°) had mp 203–222°; moreover the infrared spectrum of the product was substantially different from that of the ketone (O–H absorption at 2.75 μ and absence of carbonyl absorption at 6.1 μ).

Anal. Calcd for $C_{37}H_{28}O$: C, 90.95; H, 5.78. Found: C, 90.93, 90.90; H, 5.79, 5.88.

Reaction of a portion of the carbinol with acetyl chloride[14] gave, after recrystallization of the product from benzene, a white solid, mp 128–133° dec. A portion of the sample in ethanol failed to give a precipitate when treated with acidified silver nitrate (triphenylmethyl chloride under these conditions gave an instantaneous white precipitate) and the sample also gave a negative sodium fusion test for halogen. The infrared spectrum of the product showed strong absorption at 7.9 μ (C–O stretching frequency), and the nmr spectrum showed aromatic but no aliphatic hydrogens. The product is likely bis[*m*-biphenylylbis(*p*-biphenylyl)methyl] ether.

Bis(*p*-biphenylyl)methane. To a solution of 4,4′-diphenylbenzophenone (75.0 g, 0.224 mole) in 2000 ml of triethylene glycol containing 38 g of potassium hydroxide at 120° was added 44.7 g (0.90 mole) of hydrazine hydrate, and the mixture was heated at gentle reflux (175°) for 3 hr. Excess hydrazine-water was then allowed to distil from the reaction mixture until a flask temperature of 210° was attained and the mixture was maintained at this temperature for 26 hr. The mixture was cooled to room temperature, diluted with an equal volume of water, and filtered. The precipitate was washed well with water and this white solid after drying amounted to 69.8 g (97% yield) of product of mp 157–161°. One recrystallization from absolute ethanol (the product was placed in the cup of a Soxhlet extraction apparatus and extracted with ethanol in order to avoid use of a large quantity of solvent) gave 63.0 g of white crystalline product of mp 162–163° [lit.[39] bis(*p*-biphenylyl)methane

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[34] A similar conclusion has been arrived at independently and communicated to us recently by Professor Robert West.

[35] R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **88**, 4648 (1966); R. E. Bailey and R. West, *ibid.*, **86**, 5369 (1964).

[36] Melting points were taken on a Mel-Temp apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined on a Varian Associates A-60 instrument. Infrared spectra were determined on a Perkin-Elmer Infracord Model 137 spectrophotometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Bernhardt Microanalytical Laboratory, Mülheim, West Germany. The technique of combustion and counting of radioactive compounds was the same as that described earlier [E. Grovenstein, Jr., S. Chandra, C. E. Collum, and W. E. Davis, Jr., *J. Am. Chem. Soc.*, **88**, 1275 (1966)].

[37] A. A. Morton and L. M. Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

[38] C. Calzolari and C. Furlani, *Ann. Triest. Cura Univ. Trieste, Sez. 2*, **22–23**, 63 (1953); *Chem. Abstr.*, **49**, 938*g* (1955).

[39] J. Weiler, *Chem. Ber.*, **7**, 1188 (1874).

mp 162°]. The average yield of crude product from five similar preparations was 96%.

Bromobis(*p*-biphenylyl)methane. A solution of 11.0 g (0.0343 mole) of bis(*p*-biphenylyl)methane, 6.71 g (0.0377 mole) of N-bromosuccinimide, and 0.05 g of dibenzoyl peroxide in 300 ml of carbon tetrachloride was heated at reflux 76 hr. Three additional 0.05-g portions of dibenzoyl peroxide were added periodically to the reaction mixture. The solution was allowed to cool to room temperature and succinimide was removed by filtration. The filtrate was evaporated to dryness on a rotating evaporator and the light-tan solid residue, after a recrystallization from benzene–petroleum ether, gave 10.5 g (0.0264 mole, 77% yield) of off-white crystals, mp 138–141°. After further recrystallization from benzene–petroleum ether the product had mp 142–144° [lit.[40] bromobis(*p*-biphenylyl)methane mp 143°]. The average yield of six such preparations was 73%.

1,1,2,2-Tetrakis(*p*-biphenylyl)ethane. A. Preparation with 3-Lithiobiphenyl. From the reaction of 9.3 g (0.040 mole) of 3-bromobiphenyl with 0.61 g (0.088 g-atom) of lithium in the usual Morton apparatus, a solution of 24 mmoles (60% yield by Gilman titration[27]) of 3-lithiobiphenyl in 300 ml of tetrahydrofuran was prepared at −20°. A solution of 8.0 g (0.020 mole) of bromobis(*p*-biphenylyl)methane in 50 ml of tetrahydrofuran was added to the organolithium compound at −20° over a period of 20 min. The resulting mixture was stirred for 10 min and then forced onto solid carbon dioxide. To the carbonated mixture was added 200 ml of 5% hydrochloric acid, and the mixture was extracted with five 100-ml portions of ether. A quantity of solid, which remained suspended in the ether layers, was isolated by filtration and dried to give 3.96 g of product, mp 260–270°. An additional 0.67 g of the same product [a total of 74% yield of crude 1,1,2,2-tetrakis(*p*-biphenylyl)ethane] was isolated from the ether extract together with 0.59 g of 3-biphenylcarboxylic acid and 2.6 g of biphenyl. A 1.5-g portion of the hydrocarbon, mp 260–270°, was heated at 260° (0.03 mm) to remove 0.05 g of volatile impurity. The residue after two recrystallizations from chloroform and two recrystallizations from toluene amounted to 0.83 g of white crystals, mp 275–279° [lit.[40] 1,1,2,2-tetrakis(*p*-biphenylyl)ethane mp 276–279°].

Anal. Calcd for $C_{50}H_{38}$: C, 94.00; H, 6.00. Found: C, 93.81, 93.87; H, 6.17, 5.97.

B. Preparation with *m*-Biphenylylmagnesium Bromide. A solution of *m*-biphenylylmagnesium bromide was prepared by dropwise addition of 13.3 g (0.057 mole) of 3-bromobiphenyl in 50 ml of tetrahydrofuran to 2.53 g (0.104 g-atom) of magnesium turnings suspended in 500 ml of tetrahydrofuran at reflux temperature in the usual Morton apparatus. After 4 hr of vigorous stirring, the mixture was cooled to 25° and a solution of 11.4 g (28.6 mmoles) of bromobis(*p*-biphenylyl)methane in 100 ml of tetrahydrofuran was added dropwise over a period of 20 min and stirring was continued for another 20 min before addition of 100 ml of 5% hydrochloric acid. The organic layer was separated, the aqueous layer was extracted with ether, and the ether extract was combined with the organic layer. Evaporation to dryness gave a gummy solid which when washed with chloroform gave 6.2 g of white powder, mp 269–277°. Concentration of the chloroform solution and addition of ethanol gave upon chilling 2.0 g of solid which when heated at 245° (0.02 mm) gave 0.38 g of sublimate, mp 192–207°. The residue upon recrystallization from toluene afforded 1.3 g of product, mp 270–276°. The total yield of high-melting product was therefore 7.5 g (83% yield). After recrystallization from toluene the product had mp 274–278°; the infrared absorption spectrum of this product was identical with that of the previous sample of 1,1,2,2-tetrakis(*p*-biphenylyl)ethane prepared from 3-lithiobiphenyl. The sublimate after recrystallization from chloroform–ethanol had mp 205–208° and is likely *m*-biphenylylbis(*p*-biphenylyl)methane. It was thought possible that the large excess of magnesium used in this reaction might have been responsible for the formation of the coupling product of bromobis(*p*-biphenylyl)methane. Hence the reaction was repeated but the solution of *m*-biphenylylmagnesium bromide was filtered through a glass-wool plug in order to remove unreacted magnesium metal before addition of bromobis(*p*-biphenylyl)methane; however, an 84% yield of crude 1,1,2,2-tetrakis(*p*-biphenylyl)ethane, mp 271–277°, was obtained.

***m*-Biphenylylbis(*p*-biphenylyl)methane.** The Grignard reagent of 3-bromobiphenyl was prepared in 500 ml of ethyl ether by reaction of 18.6 g (0.080 mole) of 3-bromobiphenyl with 2.04 g (0.084 g-atom) of magnesium turnings at the boiling point of ether with stirring in the usual Morton apparatus for 6 hr. To the solution of *m*-biphenylylmagnesium bromide in refluxing ether was added over a 30-min period a slurry of 16.0 g (0.040 mole) of bromobis(*p*-biphenylyl)methane in 200 ml of ether, and the mixture was stirred for 30 min before decomposition with 100 ml of 5% hydrochloric acid. A white solid (12.1 g), insoluble in both aqueous and ether phases, was isolated by filtration and had mp 203–227°. The ether phase was condensed to about 150 ml and yielded 2.46 g of white solid, mp 201–229°. The two fractions, after a loss of 4.0 g of the first fraction during an attempt at recrystallization from toluene, were combined and sublimed at a bath temperature of 210–230° (0.03 mm). The sublimate amounted to 8.3 g (44% yield) of product, mp 202–210°. Another vacuum sublimation and two recrystallizations from chloroform–ethanol gave 7.5 g of white solid, mp 205–211°. A chloroform solution of this solid was extracted with several portions of 94% sulfuric acid. The chloroform solution after addition of ethanol and cooling deposited 5.9 g of white solid, mp 211–213°. Vacuum sublimation gave 4.9 g of a white powder, mp 212–213.5°.

Anal. Calcd for $C_{37}H_{28}$: C, 94.03; H, 5.97; mol wt, 472. Found: C, 93.71, 93.87; H, 6.18, 6.02; mol wt, 508.

A more convenient synthesis of *m*-biphenylylbis(*p*-biphenylyl)methane utilized benzene to dissolve the bromobis(*p*-biphenylyl)methane. From the reaction of 11.65 g (0.050 mole) of 3-bromobiphenyl with 1.22 g (0.050 g-atom) of magnesium turnings, a solution of 0.040 mole (80% yield) of *m*-biphenylylmagnesium bromide in 250 ml of ethyl ether was prepared. (The quantitative analysis[41] of the Grignard reagent was carried out by hydrolyzing an aliquot with water, acidifying with dilute sulfuric acid, adjusting the pH to 10 with an ammonium hydroxide–ammonium chloride buffer, and titrating for magnesium ion with a solution of the disodium salt of ethylenediaminetetraacetic acid to an end point marked with Eriochrome Black T. For confirmation a portion of the original acidified hydrolysate was titrated potentiometrically for bromide ion with standardized silver nitrate solution.) A solution of 14.0 g (0.035 mole) of bromobis(*p*-biphenylyl)methane in 100 ml of dry benzene was added to the stirred solution of Grignard reagent at room temperature over a period of 30 min, and the resulting mixture was heated at reflux for 1 hr. The reaction mixture was decomposed by addition of 150 ml of 5% hydrochloric acid. A quantity of solid, insoluble in both aqueous and organic phases, was removed by filtration and after drying weighed 14.3 g, mp 193–229°. This material was subjected to vacuum sublimation (0.05 mm); the fraction collected at a bath temperature of 225–240° weighed 11.9 g (72% yield) and had mp 203–208°. The brown residue from the sublimation weighed 2.05 g (18% yield of crude product) and after recrystallization from toluene had mp 272–277°; this material is identified as 1,1,2,2-tetrakis(*p*-biphenylyl)ethane and had the same infrared absorption spectrum as the previous more highly purified sample. The ether–benzene phase was evaporated to dryness and the residue extracted with 200 ml of cyclohexane; the undissolved solid consisted of 1.3 g (11% yield) of a substance of mp 147–150°, which was identified as bis(*p*-biphenylyl)methanol on the basis of the identity of its infrared absorption spectrum with that of an authentic sample. The 11.9 g of hydrocarbon after another vacuum sublimation and two recrystallizations from chloroform–ethanol gave 8.1 g of white crystals, mp 208–211°. Two further such crystallizations and a final vacuum sublimation gave 5.9 g of product, mp 212–214°, as obtained earlier for *m*-biphenylylbis(*p*-biphenylyl)ethane.

2-Chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane. Potassium amide was prepared in a 500-ml Morton flask equipped with a Morton stainless steel, high-speed stirrer and a Dry Ice–acetone condenser, from the reaction of 3.91 g (0.100 g-atom) of potassium with 200 ml of anhydrous ammonia containing a small crystal of ferric nitrate. After the blue color of the solution of potassium metal had changed to gray-brown a slurry of 4.72 g (0.010 mole) of *m*-biphenylylbis(*p*-biphenylyl)methane in 100 ml of dry ether was added and the resulting mixture stirred vigorously at reflux for 8 hr. The deep purple-blue solution was siphoned under an atmosphere of dry nitrogen into a flask containing 30 ml of freshly distilled methylene chloride at −30°. The blue color disappeared after the mixture was stirred for 15 min. Unreacted potassium amide was destroyed by addition of 5.35 g (0.100 mole) of solid ammonium chloride; then 200 ml of water and 250 ml of methylene chloride was added. The organic phase was separated, dried over

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[40] W. Schlenk, J. Renning, and G. Racky, *Chem. Ber.*, **44**, 1178 (1911).

[41] We are indebted to Dr. E. C. Ashby for this procedure.

anhydrous magnesium sulfate, and evaporated to dryness on a rotating evaporator. The light tan solid residue was recrystallized from methyl ethyl ketone to give 4.61 g of nearly white powder, mp 219–223° (88.5% yield). This material after five recrystallizations from methyl ethyl ketone gave 3.3 g of white product, mp 223.2–224.3°.

Anal. Calcd for $C_{38}H_{29}Cl$: C, 87.59; H, 5.61; Cl, 6.80. Found: C, 87.41, 87.35; H, 5.81, 5.67; Cl, 7.10, 6.97.

In a similar preparation an 84% yield of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane, mp 218–222°, was obtained.

3-*m*-Biphenylyl-3,3-bis(*p*-biphenylyl)propanoic Acid. In an unsuccessful experiment modeled after the procedure of Hellerman,[22] 2.44 g (5.0 mmoles) of *m*-biphenylylbis(*p*-biphenylyl)carbinol was ground up in a mortar and pestle with 2.6 g (25 mmoles) of malonic acid and then the mixture was heated at a bath temperature of 225° under a nitrogen atmosphere under conditions such that volatile products could distil from the reaction mixture. Additional 2.6-g portions of malonic acid were added at three 3-hr intervals, and after 12 hr of heating the reaction mixture was ground with an excess of potassium hydroxide and then thoroughly stirred with 500 ml of hot water. Undistilled solid (2.27 g, mp 225–233°) was isolated and identified as unreacted carbinol by its infrared spectrum; acidification of the filtrate failed to yield detectable carboxylic acid. An experiment in which *m*-biphenylylbis(*p*-biphenylyl)carbinol was heated at reflux with a molecular equivalent of acetic anhydride and 25% excess of malonic acid for 3 hr and then, after removal of acetic anhydride (*in vacuo*), heating was continued at reflux for 6 hr with 1 molar equiv of propionic anhydride, gave an 86% recovery of unreacted carbinol and a dark resin which yielded none of the desired carboxylic acid upon attempted crystallization. In a successful experiment, to an intimate mixture of *m*-biphenylylbis(*p*-biphenylyl)carbinol (1.00 g, 2.05 mmoles) and malonic acid (2.13 g, 20.5 mmoles) was added 0.35 g (2.2 mmoles) of *n*-butyric anhydride, and the mixture was heated rapidly in an oil bath at 200° until gas evolution had ceased (15 min). After workup as in the first experiment, 0.73 g of unreacted carbinol was recovered and 0.198 g (16.7% yield) of acid, mp 223–227°. After three recrystallizations from ethanol white crystals, mp 226–228.1°, were obtained.

Anal. Calcd for $C_{39}H_{30}O_2$: C, 88.27; H, 5.70. Found: C, 88.13, 88.01; H, 5.69, 5.60.

Bis(*p*-biphenylyl)ethanenitrile-1-C^{14}. In a preliminary experiment a solution of 0.98 g (0.020 mole) of sodium cyanide and 4.0 g (0.010 mole) of bromobis(*p*-biphenylyl)methane in 300 ml of dimethyl sulfoxide (Baker Analyzed Reagent) was warmed at about 60° with stirring for 36 hr while protected from atmospheric moisture by a drying tube filled with anhydrous $CaSO_4$. The solution was diluted with 800 ml of water and the solid which separated was isolated by filtration. Recrystallization of the solid from ethanol gave 0.90 g (27% yield) of a product, mp 234–236°, which was identified as 4,4′-diphenylbenzophenone according to infrared spectral comparisons. From the mother liquors was isolated 2.4 g (72% yield) of a compound, mp 145–150°, which was primarily bis(*p*-biphenylyl)carbinol according to its infrared spectrum.

In another experiment 0.98 g (0.020 mole) of sodium cyanide and 4.0 g (0.010 mole) of bromobis(*p*-biphenylyl)methane in 250 ml of acetone (freshly distilled from P_2O_5) was heated at reflux with stirring for 72 hr with protection from atmospheric moisture. After dilution with water, only impure bis(*p*-biphenylyl)carbinol (2.6 g, 77% yield) was recovered.

In a successful experiment cuprous cyanide-C^{14} was prepared from sodium cyanide-C^{14} (from Tracerlab, Inc.; activity of 9.8 μcuries/mmole) according to the procedure[42] for nonradioactive compounds. Freshly dried cuprous cyanide (0.737 g, 8.25 mequiv) was mixed with 2.98 g (7.48 mmoles) of bromobis(*p*-biphenylyl)methane and the mixture heated at 160° under an atmosphere of dry nitrogen for 12 hr. The organic product was extracted from the cooled melt with acetone, the acetone extract evaporated to dryness, and the residue subjected to vacuum sublimation (0.05 mm). The fraction collected at a bath temperature of 150–160° weighed 0.73 g (29% yield) and had mp 146–149°; this was identified as impure bis(*p*-biphenylyl)carbinol by its infrared spectrum. The fraction collected at 175–200° weighed 1.83 g (71% yield) and had mp 182–186°. A recrystallization of this material from ethanol gave 1.62 g of white crystals, mp 184–186°. In three such preparations the average yield of crude bis(*p*-biphenylyl)ethanenitrile was 63%. The analytical sample after another recrystallization from ethanol and another vacuum sublimation had mp 185.8–187.2°.

Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.42, 90.37; H, 5.74, 5.74; N, 3.75, 3.78.

Methyl Bis(*p*-biphenylyl)ethanoate-1-C^{14}. In a preliminry experiment bis(*p*-biphenylyl)ethanenitrile (0.89 g, 2.6 mmoles) was heated with 125 ml of 0.082 *N* KOH in diethylene glycol at 80° for 10 hr; however, upon cooling to room temperature and dilution with water, the starting nitrile was precipitated (99% recovery). When this experiment was identically repeated except that the temperature was 160° for 8 hr, dilution with water gave 0.77 g (94% yield) of a compound, mp 159–161°, which was identified as bis(*p*-biphenylyl)methane by mixture melting point and infrared spectral comparisons. The following procedure was the most successful of a number of others tried for hydrolysis of the nitrile to the corresponding carboxylic acid. A solution of 32 g (0.50 mole) of potassium hydroxide in 100 ml of water was added to a solution of 2.00 g (5.80 mmoles) of bis(*p*-biphenylyl)ethanenitrile in 400 ml of diethylene glycol and the resulting solution heated at 120 ± 10° for 48 hr. The solution was cooled to room temperature, diluted with 1.0 l. of water, and filtered to give 0.75 g of precipitate. Vacuum sublimation of this material at a bath temperature of 155–185° (0.05 mm) gave 0.170 g (9.1% yield) of bis(*p*-biphenylyl)methane (mp 160–162°) and at 170–190° 0.45 g (22% recovery) of bis(*p*-biphenylyl)ethanenitrile. Acidification of the alkaline filtrate with concentrated hydrochloric acid and filtration gave 1.29 g (61% yield) of acid, mp 201–206°. Two recrystallizations from 95% ethanol gave 0.99 g of white crystals, mp 206.5–207.5° [lit.[43] bis(*p*-biphenylyl)ethanoic acid mp 208°]. Repetition of this hydrolysis with bis(*p*-biphenylyl)ethanenitrile-1-C^{14} gave 60% yield of bis(*p*-biphenylyl)ethanoic acid-1-C^{14}. Reaction of an ethereal solution of 0.82 g (2.25 mmoles) of bis(*p*-biphenylyl)ethanoic acid-1-C-^{14} with an excess of diazomethane in ether at 0° gave, after evaporation of the ether and recrystallization of the residue from methanol, 0.76 g (89% yield) of methyl ester, mp 125–127°. After two further recrystallizations from methanol the product had mp 126.3–127.8°.

Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 86.00, 85.76; H, 5.67, 5.73.

3-(Bromoethyl)biphenyl. A solution of 75.0 g (0.446 mole) of 3-methylbiphenyl (Aldrich Chemical Co.), 87.2 g (0.490 mole) of N-bromosuccinimide, and 0.2 g of dibenzoyl peroxide in 400 ml of carbon tetrachloride was heated at reflux. After 3 hr, an additional 0.2 g of dibenzoyl peroxide was added, and then the mixture was heated at reflux for an additional 22 hr. Insoluble succinimide was removed by filtration, solvent was removed on a rotating evaporator, and the residue distilled *in vacuo*. The fraction boiling at 165–180° (1.5 mm) weighed 82.3 g (75% yield) and solidified upon standing. This orange solid, after three recrystallizations from petroleum ether, gave off-white crystals, mp 56.5–58.0°.

Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.48; Br, 32.34. Found: C, 63.13; 63.33; H, 4.49, 4.55; Br, 32.48, 32.60.

3-*m*-Biphenylyl-2,2-bis(*p*-biphenylyl)propanoic Acid-1-C^{14}. In a 500-ml Morton flask equipped with a stainless-steel Morton high-speed stirrer and Dry Ice–acetone condenser was condensed 200 ml of anhydrous ammonia. Under an atmosphere of dry nitrogen, 0.340 g (8.7 mg-atoms) of potassium and a small crystal of ferric nitrate was added, and the solution stirred for 1 hr. To the resulting solution of potassium amide was added 2.08 g (5.5 mmoles) of methyl bis(*p*-biphenylyl)ethanoate-1-C^{14} in 50 ml of anhydrous ether, and the solution stirred for 2 hr. A solution of 1.43 g (5.8 mmoles) of 3-(bromomethyl)biphenyl in 50 ml of anhydrous ether was added over a period of 30 min and the resulting solution stirred for 30 min at reflux. Ammonium chloride (1.0 g) was added, and the ammonia was allowed to evaporate from the mixture. After 100 ml of water was added, the ether phase was separated and allowed to evaporate to dryness. The yellow solid residue was heated at reflux for 15 hr with 250 ml of 15% aqueous potassium hydroxide. A small amount of undissolved, brown solid was removed by filtration and the filtrate acidified with hydrochloric acid. The white solid (2.17 g) which separated from the solution was isolated by filtration and had mp 182–200°. This material was subjected to partial vacuum sublimation at a bath temperature of 200–220° (0.04 mm). The sublimate, after recrystallization from aqueous ethanol, weighed 0.238 g (12% yield) and had mp 205–207°. This substance was identified as bis(*p*-biphenylyl)ethanoic

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(42) J. V. Supniewski and P. L. Salzbera, "Organic Syntheses," Coll. Vol. I., A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p 46.

(43) E. Shilow and S. Burmistrow, *Chem. Ber.*, **68**, 582 (1935).

acid by infrared spectral comparisons. The residue from the sublimation, after two recrystallizations from absolute ethanol, gave 1.28 g (44% yield) of white solid, mp 202–204.5°. After two more recrystallizations from ethanol the melting point was 203.5–204.5°.

Anal. Calcd for $C_{39}H_{30}O_2$: C, 88.27; H, 5.70. Found: C, 88.22, 88.34; H, 5.60, 5.68.

3-Biphenylcarboxylic Acid. A solution of *m*-biphenylylmagnesium bromide in 250 ml of ether was prepared by the reaction of 23.3 g (0.100 mole) of 3-bromobiphenyl (K and K Laboratories, Inc.) with 2.55 g (0.105 g-atom) of magnesium turnings. The Grignard reagent was siphoned onto a large excess of solid carbon dioxide and after the usual work-up 10.6 g (53% yield) of acid, mp 160–163°, was obtained. After two recrystallizations from ethanol 8.7 g of white crystals was obtained, mp 162–163° (lit.[44] mp 160°).

3,4′-Diphenylbenzophenone. This ketone was synthesized by a procedure like that used for 4,4′-diphenylbenzophenone.[38] Reaction of 18.0 g (0.091 mole) of 3-biphenylcarboxylic acid and 150 g (1.26 moles) of thionyl chloride at reflux temperature for 2 hr gave *m*-phenylbenzoyl chloride, to which, after removal of excess thionyl chloride by distillation, was added 250 ml of carbon disulfide, 14.6 g of anhydrous aluminum chloride, and 28.1 g (0.182 mole) of biphenyl. After the initial vigorous reaction had subsided the mixture was heated at reflux with stirring for 3 hr. The black tarlike adduct, after standing overnight, was isolated by filtration, washed with carbon disulfide (to remove unreacted biphenyl), and decomposed with ice-cold concentrated hydrochloric acid. The ketone was separated by filtration and washed well with water and then 95% ethanol. The crude product (26.9 g, mp 131–136°) after recrystallization from benzene–petroleum ether amounted to 20.2 g (66% yield) of white crystals, mp 138–141°. Two recrystallizations from ethanol gave 15.5 g of crystals of mp 142–144°. An analytical sample after two further crystallizations from ethanol and a vacuum sublimation [at a bath temperature of 150° (0.02 mm)] had mp 143.8–145.0°.

Anal. Calcd for $C_{25}H_{18}O$: C, 89.79; H, 5.43. Found: C, 89.62; H, 6.05.

***m*-Biphenylyl-*p*-biphenylylmethane.** A solution of 14.2 g (0.0425 mole) of 3,4′-diphenylbenzophenone, 8.5 g (0.17 mole) of hydrazine hydrate, and 8.4 g (0.128 mole) of potassium hydroxide pellets in 600 ml of triethylene glycol was heated at 175° for 2 hr. The excess hydrazine was allowed to distil from the reaction mixture, whereupon the temperature was raised to 205° and maintained at that temperature for 36 hr. The solution was cooled to room temperature, diluted with 1500 ml of water, and extracted with six 500-ml portions of ether. The ether extract yielded 13.0 g (95% yield) of white solid, mp 92–96°. After two recrystallizations from ethanol and a distillation in a sublimation apparatus [bath temperature 120° (0.03 mm)], 9.2 g of hydrocarbon, mp 99.3–100.4°, was obtained.

Anal. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29. Found: C, 93.61, 93.55; H, 6.43, 6.31.

Bromo-*m*-biphenylyl-*p*-biphenylylmethane. A solution of 9.10 g (28.5 mmoles) of *m*-biphenylyl-*p*-biphenylylmethane, 5.35 g (31.3 mmoles) of N-bromosuccinimide, and 0.1 g of dibenzoyl peroxide in 250 ml of carbon tetrachloride was heated at reflux for 48 hr. An additional 0.05 g of dibenzoyl peroxide was added after the first 12 hr of reaction. Insoluble succinimide, formed in the reaction, was removed by filtration and the filtrate evaporated to dryness on a rotating evaporator. The residue upon recrystallization from 200 ml of cyclohexane gave 3.2 g of yellow powder, mp 142–144°; recrystallization of this product gave 2.7 g of nearly white solid, mp 143.5–145°, which was identified as 3,4′-diphenylbenzophenone according to its infrared spectrum. Evaporation of the mother liquor from the cyclohexane crystallization gave 6.2 g of nearly white powder, mp 94–100°; three recrystallizations of this material from cyclohexane gave 4.9 g of white product, mp 102–103.5°. A small portion of this product upon two further recrystallizations from cyclohexane had mp 103.4–104.7°; since the infrared spectrum of this substance showed appreciable contamination with 3,4′-diphenylbenzophenone, the crude bromide was not submitted for analysis but was employed for synthesis of the following acid.

***m*-Biphenylyl-*p*-biphenylylethanoic Acid-1-C^{14}.** A mixture of 4.14 g (*ca.* 10 mmoles) of crude bromo-*m*-biphenylyl-*p*-biphenylylmethane (mp 102–103.5°) and 1.02 g (11.4 mequiv) of cuprous cyanide-C^{14} (radioactivity was 9.8 μcuries/mmole) was heated at 160° for 20 hr under an atmosphere of dry nitrogen. The organic product was extracted from the cooled melt with chloroform, the chloroform extract evaporated to dryness, and the residue distilled in an apparatus for vacuum sublimation at a bath temperature of 150–195° (0.03 mm). The product amounted to 3.27 g, mp 135–148°. Recrystallization from ethanol gave 3.0 g of white solid of mp 135–148°, whose infrared spectrum indicated that it was a mixture of *m*-biphenylyl-*p*-biphenylylethanenitrile and 3,4′-diphenylbenzophenone. This mixture was dissolved in 200 ml of diethylene glycol and a solution of 16 g (0.25 mole) of potassium hydroxide pellets in 50 ml of water was added and the solution heated at 110–120° for 24 hr. The solution was diluted with 300 ml of water and a precipitate (1.26 g) was isolated by filtration of the cool solution. This precipitate, mp 137–141°, was identified as somewhat impure 3,4′-diphenylbenzophenone according to its infrared spectrum. Acidification of the filtrate with hydrochloric acid gave 1.66 g (4.6 mmoles) of acid, mp 168–173°. Two recrystallizations from aqueous ethanol gave 1.31 g of white crystals, mp 172–174°.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.88, 85.94; H, 5.63, 5.63.

Methyl *m*-Biphenylyl-*p*-biphenylylethanoate-1-C^{14}. An ethereal solution of *m*-biphenylyl-*p*-biphenylylethanoic acid-1-C^{14} (1.03 g, 2.83 mmoles) was treated at 0° with excess diazomethane. The solution was evaporated to dryness and the residue crystallized from methanol to give 0.98 g (2.59 mmoles, 91% yield) of ester, mp 87–90°. The analytical sample after two further recrystallizations from methanol had mp 89.5–90.5°.

Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 85.71, 85.87; H, 5.78, 5.85.

2-*m*-Biphenylyl-2,3-bis(*p*-biphenylyl)propanoic Acid-1-C^{14}. 4-Methylbiphenyl was synthesized from *p*-toluidine by the procedure of Gomberg and Pernert[45] and converted to 4-(bromomethyl)biphenyl, mp 85–87°, by the method of Zervas and Dilaris[18] (but with traces of dibenzoyl peroxide used as catalyst). In a 500-ml Morton flask equipped with a stainless steel Morton high-speed stirrer and a Dry Ice–acetone condenser, 200 ml of anhydrous ammonia was condensed. Potassium (0.415 g, 10.6 mg-atoms) and then a small crystal of ferric nitrate were added and the solution was stirred for 1 hr (under an atmosphere of dry nitrogen throughout this and the following reactions in liquid ammonia solution). A solution of 0.950 g (2.51 mmoles) of methyl *m*-biphenylyl-*p*-biphenylylethanoate-1-C^{14} in 75 ml of anhydrous ether was added and the resulting solution stirred for 2 hr. A solution of 0.945 g (3.8 mmoles) of 4-(bromomethyl)biphenyl in 25 ml of anhydrous ether was then added over a period of 10 min and the solution stirred for 30 min. Unreacted potassium amide was destroyed by adding 0.54 g (10 mmoles) of solid ammonium chloride, and the ammonia was allowed to evaporate from the mixture. Dilute hydrochloric acid was added, the ether phase was separated, and the aqueous layer extracted once with ether. Evaporation of the combined ether phases yielded a solid residue which was heated at reflux for 24 hr with 250 ml of 15% aqueous potassium hydroxide. A quantity of dark brown, undissolved solid was removed by filtration and the filtrate acidified with hydrochloric acid. The white solid (0.545 g, 41% yield) was isolated by filtration and had mp 205–209.5°. After four recrystallizations from ethanol, this material yielded 0.28 g of white crystals, mp 209.0–210.0°.

Anal. Calcd for $C_{39}H_{30}O_2$: C, 88.27; H, 5.70. Found: C, 88.22, 88.39; H, 5.60, 5.58.

Reaction of 2-Chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane with Lithium. A. Reaction at −65°. To a 500-ml Morton flask (previously flame dried under a stream of dry nitrogen) equipped with a high-speed stirrer[37] and dropping funnel was added 150 ml of tetrahydrofuran (freshly distilled from $NaAlH_4$), 0.153 g (22.1 mg-atoms) of lithium, about 2% of a solution of 3.00 g (5.75 mmoles) of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane in 100 ml of dry tetrahydrofuran, and 0.05 ml of methyl iodide. The reactants were kept under an atmosphere of dry nitrogen throughout all of the following reactions with lithium. The solution was stirred vigorously at 0 ± 5° until a faint purple color appeared (2 hr); the reaction temperature was then lowered to −65 ± 5° and the remainder of the chloride added over a period of 30 min. The solution was stirred at −65° for 3 hr; Gilman double titration[27] of four 5-ml aliquots of this solution indicated that the yield of organolithium compound was 50 ± 10%. The deep purple solution was forced onto a large excess of solid carbon dioxide. To the carbonated mixture, after sublimation of unreacted carbon dioxide, was added 200 ml of 10% sulfuric acid. The acidified mixture was extracted with ether and the organic phase was evaporated to dryness.

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(44) H. Schmidt and G. Schultz, *Ann. Chem.*, **203**, 133 (1880).

(45) M. Gomberg and J. C. Pernert, *J. Am. Chem. Soc.*, **48**, 1372 (1926).

The solid residue was stirred vigorously (3 hr) with 500 ml of 2% aqueous potassium hydroxide. Undissolved solid (2.1 g, mp 190–225°) was separated by filtration. Acidification of the filtrate brought about the precipitation of 0.722 g (24% yield) of solid, mp 225–228°. This acid after three recrystallizations from ethanol amounted to 0.489 g of white crystals, mp 226.5–228°. This acid gave no depression of melting point when mixed with the sample of 3-*m*-biphenylyl-3,3-bis(*p*-biphenylyl)propanoic acid synthesized above from *m*-biphenylylbis(*p*-biphenylyl)carbinol. Moreover, the infrared spectra of the acid and the synthetic sample were identical.

B. Reaction at 0°. This reaction was run in the same apparatus and by the same general technique as that for the reaction at −65°. To 0.133 g (19.2 mg-atoms) of lithium and 200 ml of tetrahydrofuran was added 0.05 ml of methyl iodide and about 10% of a solution of 2.50 g (4.80 mmoles) of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane in 50 ml of tetrahydrofuran. The solution was stirred vigorously at 0 ± 5° until a purple color appeared (1 hr). Then the remainder of the chloride was added over a period of 30 min at 0° and the solution stirred at this temperature for 6 hr before carbonation. The color of the solution just before carbonation was blue black; Gilman's double titration[27] indicated the presence of 45% yield of organolithium compound. After the usual work-up, 1.88 g of neutral product (mp 109–177°) and 0.995 g (39% yield) of crude acid, mp 208.0–209.5°, were obtained. This acid showed no melting point depression when mixed with a sample of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid synthesized previously according to Scheme III. Mixtures (about 50:50) of the acid with 3-*m*-biphenylyl-3,3-bis(*p*-biphenylyl)propanoic acid and with 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)propanoic acid (synthesized according to Scheme II) had mp 201–219° and 180–202°, respectively. The infrared spectrum of the acid (in carbon disulfide) was identical with the infrared spectrum of the independently synthesized sample of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid; however, the infrared spectrum of 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)propanoic acid was almost identical with these spectra except that the absorptions at 13.4 and 14.4 μ were broader.

The remaining crude acid (0.9861 g, mp 208.0–209.5°) was diluted with 0.1386 g of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid-1-C^{14} (mp 209.0–210.0°, specific activity 9.793 ± 0.002 μcuries/mmole from Scheme III). The mixture was recrystallized to constant specific activity. After four recrystallizations from ethanol and one from benzene, the acid had mp 209.0–210.0° and specific activity 1.227 ± 0.005 μcuries/mmole. From these data, it follows that 98.1 ± 0.5% of the crude acid was 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid.

C. Reaction at −65° and Rearrangement at 0°. Reaction between 0.106 g (15.3 mg-atoms) of lithium and 2.00 g (3.84 mmoles) of 2-chloro-1-*m*-biphenylyl-1,1-bis(*p*-biphenylyl)ethane in 250 ml of tetrahydrofuran at −65 ± 5° was run as in the first run at −65°. After the 3-hr stirring period at this low temperature, Gilman's double titration[27] indicated a 39% yield of organolithium compound. The solution was then allowed to warm to 0 ± 5° and stirred at this temperature for 4 hr before carbonation. After the usual work-up 1.33 g of neutral product (mp 79–132°) and 0.781 g (38% yield) of acid, mp 205–208°, were isolated. This acid gave no depression of melting point and had an infrared spectrum identical with that of a sample of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)-propanoic acid (synthesized by Scheme III), while this acid on admixture with the synthetic samples of 3-*m*-biphenylyl-3,3-bis(*p*-biphenylyl)propanoic acid and with 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)propanoic acid gave mixtures which melted with considerable depression of melting point. The crude acid (0.7802 g), mp 205–208°, was mixed with 0.1400 g of 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid-1-C^{14} (activity of 9.793 ± 0.002 μcuries/mmole, mp 209.0–210.0°) and the mixture recrystallized to constant radioactivity. After four recrystallizations from ethanol and two recrystallizations from benzene, the acid had mp 209.2–210.1° and activity of 1.508 ± 0.005 μcuries/mmole. From these data it can be calculated that 98.6 ± 0.4% of the crude acid was 2-*m*-biphenylyl-2,3-bis(*p*-biphenylyl)propanoic acid.

In an attempt to analyze the crude carboxylic acid from this run and the preceding run at 0° for any 3-*m*-biphenylyl-2,2-bis(*p*-phenylyl)propanoic acid, the combined mother liquors from recrystallization of the crude acid from these two runs were evaporated to dryness to give 0.053 g of acid, mp 207–208.5°. To this acid was added 0.50 g of pure 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)-propanoic acid-1-C^{14}. After one recrystallization from benzene, crystals, mp 175–196°, were obtained; the melting point of this material was not altered after two more recrystallizations from benzene. Benzene was removed from the mother liquors and the residue combined with the recrystallized material. After four recrystallizations from ethanol, crystals, mp 180–197°, were obtained. Since only impure acid was obtained by any of the procedures tried, isotope-dilution analysis for 3-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)-propanoic acid was abandoned.

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