

to give a yield of 64%. Pure product, mp 174–5°C, was obtained by two successive recrystallizations from propanol, charcoal being used in the last recrystallization. About 50 ml of solvent per gram of product was necessary. Benzene was also a satisfactory recrystallization solvent.

E. Transesterification Attempt. Dimethyl tetrachloroterephthalate, 25 grams (0.075 mole), was dissolved in a solution of 135 ml *n*-propanol, 35 ml benzene, and 2 grams *p*-toluenesulfonic acid. Intermittent heating and reflux over 8 days were accompanied with the addition of 60 ml benzene, 20 ml propanol, and acid (3 × 0.5 gram). Crystals obtained upon cooling were starting material, mp 157–8.5°C. Two additional crops from the reaction mixture were substantially the dimethyl ester.

Comparable attempts at transesterification with sodium propoxide and titanium isopropoxide as catalysts also failed.

F. Attempted Saponification. A mixture of 1 gram (0.003 mole) dimethyl tetrachloroterephthalate, 75 ml absolute ethanol, and 25 ml of 0.44*N* KOH was refluxed 3 hr. After it cooled, 50 ml of water and 25 ml of 0.1*N* HCl were added. Titration, using 0.1*N* HCl, to the phenolphthalein end point gave a neutralization equivalent, after blank correction, of 242 (theory is 166). The same procedure was used, and a saponification equivalent for di-*n*-propyl tetrachlorophthalate of 197 was found (calcd 194). Longer time and variants of this procedure with aliphatic tetrachloroterephthalates still did not give a satisfactory saponification equivalent. Substantially more drastic treatment resulted in an attack on the aromatic nucleus. Profft and Timm (10) do not report such an attack in their saponification procedure.

G. Complexation Studies. Previously described procedures did not give complexes of hexamethylbenzene with aliphatic tetrachloroterephthalates as were obtained with tetrachlorophthalate and tetrabromophthalate esters (8). With dimethylaniline, colors were observed with dipropyl (pale yellow), dibutyl (pale yellow), dioctyl (greenish yellow),

and bis-pentafluorophenyl (dark yellow) tetrachloroterephthalates. Other observations are reported in the discussion.

H. Infrared Spectra. All were taken at 0.66% concentration in KBr pellets.

I. Elemental Analyses. All were made by Spang Microanalytical Laboratories of Ann Arbor, Mich. Analyses were in satisfactory agreement with calculated values and were made available to reviewers.

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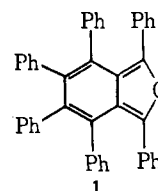
Derivatives of Hexaphenylisobenzofuran

FEREIDUN RAZMARA and MALCOLM P. STEVENS¹

Department of Chemistry, American University of Beirut, Beirut, Lebanon

Diels-Alder adducts have been prepared from hexaphenylisobenzofuran and a variety of dienophiles, including benzyne. Benzyne adduct was the only one of those prepared that did not decompose by retrograde Diels-Alder reaction upon heating. Attempted aromatization reactions of adducts are described.

Hexaphenylisobenzofuran (1), a yellow-green fluorescent compound, was first reported in 1961 by Reid and Bonnichausen (6). It has not been investigated in any detail apart from some studies of its absorption and fluorescence spectra (8). Our interest in 1 stemmed from its potential as a precursor to some highly phenyl-substituted naphthalenes, compounds we desired for studying effects of steric crowding on thermal properties. While we were not successful in obtaining the latter by this route, we report here some aspects of the Diels-Alder chemistry of 1.



In general, hexaphenylisobenzofuran undergoes the Diels-Alder reaction readily with olefinic or acetylenic dienophiles if the latter are not substituted with phenyl groups. For example, dienophiles which failed to react after several days in refluxing toluene or benzene or upon fusing with 1 include *trans*-stilbene, diphenylacetylene, cinnamaldehyde, cinnamionitrile, and α -phenylcinnamionitrile. Also, unexpectedly, fu-

¹ Home address and to whom correspondence should be sent: Department of Chemistry, University of Hartford, West Hartford, Conn. 06117.

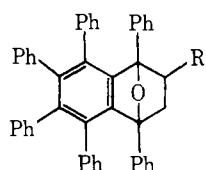
Table I. Diels-Alder Adducts of Hexaphenylisobenzofuran

Dienophile	Adduct ^a	Reaction conditions	Yield, %	mp, °C ^b
Acrolein	2	c	94	250-2
Methyl vinyl ketone	3	c	94	229-30
Acrylonitrile	4	c	93	269-71
Maleic anhydride	5	c	80	273-5
N-Phenylmaleimide	6	c	91	292-3
Dibenzoylacetylene	7	c	94	247
Benzyne	8	d	85	268

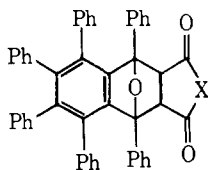
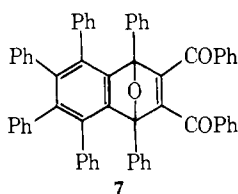
^a Elemental analyses (C, H or C, H, N) in agreement with calculated values submitted for review. ^b All melted with decomposition except 8. ^c In refluxing benzene. ^d Benzyne formed from anthranilic acid and isoamyl nitrite.

maric acid formed no adduct. Adducts were formed in refluxing benzene with acrolein, methyl vinyl ketone, acrylonitrile, maleic anhydride, N-phenylmaleimide, and dibenzoylacetylene. Benzyne adduct was formed using either anthranilic acid or 2-phenyliodonobenzoate as precursor. In addition, fumaryl chloride reacted rapidly at room temperature in benzene solution; however, attempts to hydrolyze the product to dicarboxylic acid resulted in reoccurrence of the intense green fluorescence of 1. Fumaric acid may have the wrong geometry for reaction and fumaryl chloride may have formed a molecular complex with 1.

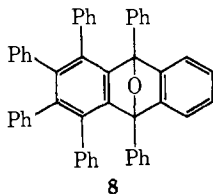
Structures of the various adducts are given (2-8), and pertinent experimental data are summarized in Table I. All the products, with the exception of benzyne adduct (8), were thermally unstable and decomposed upon melting to regenerate 1.



- 2 R = CHO
3 R = COCH₃
4 R = CN

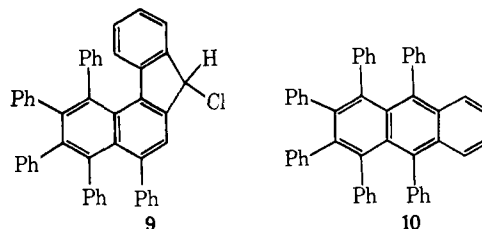


- 5 X = O
6 X = NPh



Removal of the oxygen bridge of acrolein, methyl vinyl ketone, and acrylonitrile adducts (2-4) to form the corresponding naphthalene derivatives was attempted at low temperatures to avoid decomposition. When gaseous hydrogen chloride was bubbled into an acetic acid suspension of acrolein adduct (2), the fluorene derivative (9) was formed by intramolecular chloroalkylation (?). Similar treatment of methyl vinyl ketone adduct (3) with hydrogen chloride gave rise to an isomeric product, possibly the exo epimer (5), but no aromatization. Unlike adduct 3, the isomer did not decompose upon melting. Acrylonitrile adduct (4) was unreactive under these conditions. Attempts to simultaneously aromatize and furanize dibenzoylacetylene adduct (7) to give the fully phenylated analog of 1,3-diphenylnaphtho-[2,3-c]furan (8) resulted only in a reverse Diels-Alder reaction.

Under more vigorous conditions (zinc in refluxing acetic acid), benzyne adduct (8) was deoxygenated to 1,2,3,4,9,10-hexaphenylantracene (10), a compound exhibiting blue fluorescence under ultraviolet light.



The ultraviolet spectrum of 10 (λ_{\max} of the longest wavelength band, 335 nm) displays a blue shift relative to anthracene (376 nm) whereas 9,10-diphenylantracene displays a red shift (392 nm). This is consistent with 1,2,3,4-tetraphenylnaphthalene (296 nm) and 1,4,5,8-tetraphenylnaphthalene (1) (334 nm) which exhibit blue and red shifts, respectively, relative to naphthalene (312 nm).

EXPERIMENTAL

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Ir spectra were run in Nujol on a Perkin-Elmer Model 257 grating spectrophotometer. Uv spectra were recorded in ethanol on a Perkin-Elmer Ultraviolet-Visible Model 202 spectrophotometer. Analyses were done by F. Pascher Mikroanalytische Laboratorium, Bonn, Germany.

Diels-Alder Reactions of Hexaphenylisobenzofuran.

Dienophiles Other Than Benzyne. A solution of 5 mmol of hexaphenylisobenzofuran (6) (2.87 grams) and 6 mmol of dienophile in 20 ml of benzene was refluxed until the intense green fluorescence disappeared. The solution was then evaporated to about half its volume and 20 ml of ethanol were added. The solution was left overnight to allow crystallization and the product was recrystallized from benzene-ethanol. With fumaryl chloride, refluxing was not necessary as reaction occurred in a few minutes at room temperature to give a product, mp (unpurified) 190-220°C. Attempted hydrolysis of the product resulted in regeneration of the green fluorescence of hexaphenylisobenzofuran.

Benzyne (4). To a refluxing mixture of 5 mmol of hexaphenylisobenzofuran (2.87 grams) and 15 mmol (2.06 grams) of anthranilic acid in 50 ml of dimethoxyethanol was added dropwise during 2 min a solution of 2 grams of isoamyl nitrite in 50 ml of dimethoxyethanol. Refluxing was continued for 2 hr and, after cooling, a solution of 5 grams of potassium hydroxide in 100 ml of 50% ethanol was added. The crude product crystallized out in 10 min. The crystals were collected, washed with ethanol, and recrystallized from benzene-ethanol to give white needles in 85% yield.

The product was also prepared using 2-phenyliodonobenzoate in diglyme as benzyne precursor (2), but the yield was only 20%.

Melting points and percentage yields of adducts are given in Table I.

2-Phenyl-3,4-(tetraphenylbenzo)-9-chlorofluorene (9). Compound 9 was reported earlier (?) but no experimental details were provided.

Hydrogen chloride was bubbled into a suspension of 2 grams of 2 in 200 ml of acetic acid at room temperature. After 4 hr the mixture became deep orange and all the solid dissolved. The solution, saturated with hydrogen chloride, was left for 8 hr, then 50 ml of water were added. The resulting precipitate was dried and recrystallized (benzene-ethanol) to give 1.0 gram (50%) of orange crystals, mp 193° dec (with evolution of HCl); ir 1600, 1182, 1075, 1029, 920, 887, 855, 820, 769, 742, 714, 706, 700, 691 cm⁻¹; nmr (CS₂) δ 5.83 (s), 6.4-7.5 (m), approx. ratio 1:30.

Epimerization of Methyl Vinyl Ketone Adduct. When adduct 3 was treated with hydrogen chloride as described above, the epimer was formed in 85% yield; mp 238-9°C; ir 1702, 1600, 1270, 1295, 1222, 1200, 1150, 1132, 1078, 1050, 1030, 1005, 950,

912, 818, 757, 730, and 700 cm^{-1} (ir of **3**: 1716, 1600, 1318, 1296, 1200, 1172, 1160, 1070, 1030, 1015, 1000, 950, 912, 895, 862, 840, 820, 780, 760, 730, 720, 700 cm^{-1}). Elemental analyses (C, H) in agreement with calculated value were submitted for review.

1,2,3,4,9,10-Hexaphenylanthracene (**10**). A mixture of 0.5 gram of benzyne adduct (**8**) and 0.5 gram of activated zinc dust was refluxed 1½ hr in 25 ml of acetic acid. The hot solution was filtered, and 10 ml of water was added to precipitate the crude yellow product. Recrystallization (ether) gave a 40% yield of pale yellow crystals which exhibited blue fluorescence under an ultraviolet lamp; mp 285–90°C; ir 1600, 1160, 1072, 1030, 768, 760, 745, 700 cm^{-1} ; uv λ_{max} of longest wavelength band (ethanol) 335 nm. Recrystallization and chromatography (alumina) failed to remove completely unreacted **8** as indicated by unsatisfactory analyses.

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Condensation of Acetylenic Esters with Biphenyl Compounds Having Active Methylene Groups

HIKMAT N. AL-JALLO

Department of Chemistry, Nuclear Research Institute, Atomic Energy Commission, Tuwaittha, Baghdad, Iraq

Biphenyl derivatives of acetylenic B-diketone, B-keto-ester, and B-keto-cyanide were prepared by the interaction of ethyl phenylpropiolate and 4-acetylbiphenyl, ethyl 4-biphenylacetate, and 4-biphenylacetonitrile, respectively. The acetylenic B-diketone was converted to 4-pyrone, 4-thiopyrone, and 1-hydroxy-4-pyridone. In addition, ethyl phenylpropiolate reacted with 4-biphenylacetamide to give the substituted glutaconimide.

The acetylenic diketone, 1-(4-biphenyl)-5-phenylpent-4-yne-1:3-dione (**III**), was prepared by the interaction of ethyl phenylpropiolate (**I**) and 4-acetylbiphenyl in the presence of sodium ethoxide. The diketone (**III**) was converted to 4-pyrone (**IV**) upon heating over its melting point. In addition, partial conversion was affected even during recrystallization from benzene when boiled for a few minutes. Reactions of the diketone (**III**) or 4-pyrone (**IV**) with hydroxylamine hydrochloride or phosphorus pentasulfide gave the corresponding hydroxy pyridone (**V**) and thiopyrone (**VI**), respectively. Such diketone (**III**) is considered as a new sensitive complexing ligand. It forms intense yellow and greenish-blue complexes with uranium and copper metals, respectively. The acetylenic diketone could not be isolated in the case of 2,6-diphenylpyrone (**5**). Moreover, the acetylenic B-keto-cyanide (**VII**), B-keto-ester (**VIII**), and glutaconimide (**IX**) were obtained from the reaction between ethyl phenylpropiolate (**I**) and nitrile (**IIb**), ester (**IIc**) and amide (**IId**), respectively, as shown in Figure 1. The infrared spectra of compounds **VII** and **VIII** indicate their presence in the enol-forms. Compounds **VII** and **IX** were obtained by the modification of the reported procedure for the phenyl analog (**1**).

EXPERIMENTAL

Infrared spectra were obtained with a Beckman IR-10 spectrophotometer and nmr spectra with a Varian A-60 instrument, with TMS as internal standard. Compounds were analyzed at the Max Planck Institute, Ruhr, West Germany. Light petroleum had a bp of 33–40°C.

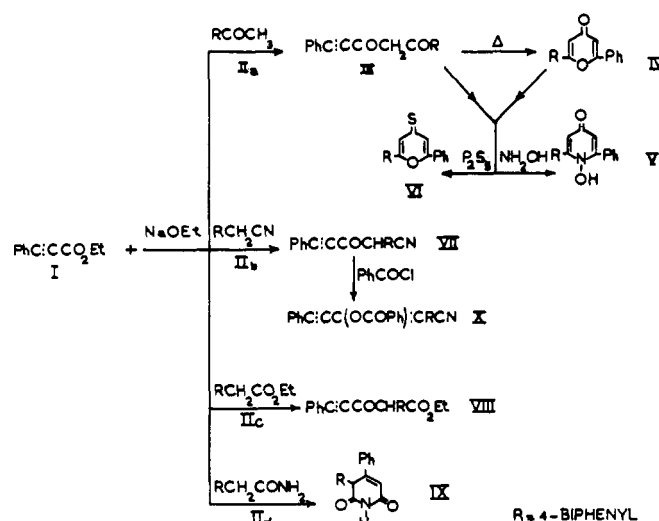


Figure 1. Reactions of ethyl phenylpropiolate with different 4-biphenyl compounds

1-(4-Biphenyl)-5-phenylpent-4-yne-1:3-dione (III). 4-Acetylbiphenyl (**IIa**, 8.0 grams) and ethyl phenylpropiolate (**I**, 7.0 grams) were added successively to an ice-cold suspension of sodium ethoxide (from 1.0 gram of sodium and 2 ml of absolute ethanol). The reaction mixture was left at 0°C for two days and then poured into water (200 ml). The solid which separated out was filtered and proved to