As the temperature was raised, the reaction became even more complex and more profound cleavage products were formed so that, at 135° (in refluxing diglyme), the ultimate cleavage product, tin metal, was formed. The higher temperatures may promote the disproportionation of the intermediate tributyltin lithium.[11]

$$Bu_3SnLi \longrightarrow Bu_2Sn + BuLi$$

Air oxidation of the dibutyltin during work-up would lead to the product actually found, dibutyltin oxide, but the origin of the tin metal is obscure.

The reaction of hexaphenylditin with excess lithium aluminum hydride is also complex. As shown in Table II, at lower temperatures, the product isolated is diphenyltin oxide while, at elevated temperatures, tin metal is the product. No triphenyltin hydride could be detected in either reaction. It is difficult to explain the cleavage products as arising from the disproportionation of the intermediate triphenyltin lithium, since Tamborski[12] has indicated that the above intermediate is stable in refluxing tetrahydrofuran for 24 hr. No degradation of hexaphenylditin was noted in an experiment when the ditin was refluxed in tetrahydrofuran for 21 hr.; 98% of the ditin was recovered unchanged.

TABLE II

REACTION OF HEXAPHENYLDITIN WITH LITHIUM ALUMINUM HYDRIDE

Solvent	Temp., °C.	Time, hr.	Products (%)
Ether	35	18	Diphenyltin oxide (85), hexaphenylditin (5) (remainder tar)
Tetrahydrofuran	64	21	Tin metal (75) (residue unidentified tar containing 10% tin by analysis)

A preliminary experiment showed that tetraphenyltin is also cleaved by lithium aluminum hydride. The reaction was run at 0° for 6.5 hr. in tetrahydrofuran. Approximately 87% of starting material was recovered, but a trace of diphenyltin oxide was also found, and the presence of benzene was detected in the solvent distillate by vapor phase chromatography.

Experimental

Reaction of Hexabutylditin with Lithium Aluminum Hydride.—All of the reactions reported in Table I were run by the typical procedure shown below. In a typical run, 91 g. (0.157 mole) of hexabutylditin which had been freshly distilled (b.p. 180–200° at 1 mm.) was dissolved in 100 ml. of dry tetrahydrofuran and added dropwise under nitrogen to a slurry of 8.0 g. (0.84 equiv.) of lithium aluminum hydride in 400 ml. of tetrahydrofuran. The mixture warmed slightly and turned dark green after 1 hr. It was then refluxed and stirred for 18 hr. The mixture was then hydrolyzed with sodium potassium tartrate according to the procedure of van der Kerk,[13] but an incomplete separation occurred. The aqueous layer was, therefore, extracted with three 200-ml. portions of ether; the ethereal layer was combined with tetrahydrofuran layer formed on hydrolysis. The extracts were dried over exsiccated magnesium sulfate, and the mixed solvents were distilled through a 25-cm. Vigreux column. The still residue was then distilled through a small 10-cm. Vigreux column and there was obtained 17.0 g. (0.0585 mole, 18.5% yield) of tributyltin hydride, b.p. 75–85° (0.025 mm.), $n^{30}\text{D}$ 1.4682, lit.[14] $n^{22}\text{D}$ 1.4720; and 70.0 g. (0.121 mole, 77% recovery) of hexabutylditin, b.p. 156–160° (0.025 mm.), $n^{25}\text{D}$ 1.5100, lit.[14] $n^{25}\text{D}$ 1.5090.

The infrared spectrum of the tributyltin hydride was superimposible upon the spectrum of an authentic sample of tributyltin hydride prepared by reduction of bis(tributyltin oxide) with lithium aluminum hydride.

Preparation and Hydrolysis of Tributyltin Lithium.—Tributyltin lithium was prepared by the method of Gilman and Rosenberg[8] using 25.6 g. (0.135 mole) of stannous chloride and 173 g. of a 15% solution of *n*-butyllithium in hexane (0.405 mole of *n*-butyllithium). The mixture was hydrolyzed for 15 min. after preparation with saturated ammonium chloride solution, and then was worked up in the usual manner to yield 15 g. (0.052 mole) of tributyltin hydride, b.p. 123° (1.5 mm.), infrared spectrum and vapor phase chromatogram identical with an authentic sample; and 18.5 g. (0.075 mole) of di-*n*-butyltin oxide.

Anal. Calcd. for $(C_4H_9)_2SnO$: Sn, 47.8. Found: Sn, 47.65.

Reaction of Hexaphenylditin with Lithium Aluminum Hydride.—This reaction was carried out in a fashion similar to that described above. In a typical run, 90 g. (0.128 mole) of recrystallized hexaphenylditin [m.p. 230–231° (uncor.)] was mixed under nitrogen with a slurry of 15.0 g. (1.6 equiv.) of lithium aluminum hydride in 400 ml. of dry tetrahydrofuran. The initial dark green color turned dark brown on refluxing for 21 hr. The mixture was worked up as with hexabutylditin to yield 22.7 g. (0.191 mole, 74.3% yield) of metallic tin in the form of small spheres.

Anal. Calcd.: Sn, 100.0. Found: Sn, 99.0 (emission spectrograph shows all Sn lines).

There was also isolated 20 g. of an unidentified dark red-brown material from evaporation of the mixed solvents, probably polymeric diphenyltin. This material, on standing in air, slowly decolorized and formed a white powder which was probably impure diphenyltin oxide.

Anal. Calcd. for $(C_6H_5)_2SnO$: Sn, 41.2. Found: Sn, 41.0. Considerable quantities of benzene were identified in the mixed solvent distillate by vapor phase chromatography, thus indicating phenyl–tin cleavage.

Reaction of Hexaphenylditin with Tetrahydrofuran.—Fifty grams (0.714 mole) of hexaphenylditin (m.p. 233–234°) was refluxed under nitrogen with 200 ml. of tetrahydrofuran for 21 hr. The ditin dissolved in the hot solution and reprecipitated when the solution was cooled. The filtrate was evaporated to 30 ml. and cooled; additional material precipitated. Both crops of crystals had m.p. 232–234°, and a mixture melting point with the starting material of 232–234°, thus confirming the identity of the recovered material as substantially pure starting material. The yield of recovered material was 49.1 g. (98%, substantially quantitative).

Reaction of Tetraphenyltin with Lithium Aluminum Hydride.—Seventy-five grams (0.15 mole) of tetraphenyltin was treated with 15 g. (0.394 mole) of lithium aluminum hydride in 400 ml. of tetrahydrofuran at 0° for 6.5 hr. under nitrogen. After work-up in the usual manner there was recovered 65.5 g. (87.4% recovery) of tetraphenyltin, m.p. and m.m.p. (with starting material) 222–224°.

A trace of diphenyltin oxide was also found as a precipitate in the mixed solvent–water layers after hydrolysis, and the presence of benzene was detected in the tetrahydrofuran layer by vapor phase chromatography.

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(11) See ref. 9.

(12) C. Tamborski, F. Ford, and E. Soloski, *J. Org. Chem.*, **28**, 181 (1963).

(13) See ref. 2, p. 93.

(14) C. Tamborski, F. Ford, and E. Soloski, *J. Org. Chem.*, **28**, 237 (1963).

Dicarbenes. Some Isolable Bisdiazoalkanes

ROBERT W. MURRAY AND ANTHONY M. TROZZOLO

Bell Telephone Laboratories, Inc.,
Murry Hill, New Jersey

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In connection with a study of species containing two divalent carbon atoms we have reported[1] the prepara-

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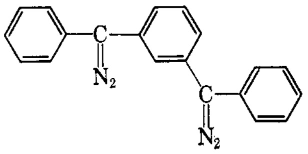
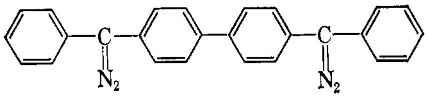
(1) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

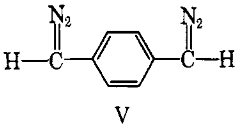
tion of 1,4-bis(α-diazobenzyl)benzene (I). Use of the low temperature glass technique[2,3] has permitted the assignment of a triplet ground state to a number of divalent carbon species.[4] More recently[5] this technique was used to demonstrate that the photolysis of I produces *p*-phenylenebis(phenylmethylene) (II), a dicarbene derivative possessing a triplet ground state. Since the examination of other dicarbenes promises to be of considerable importance, the synthesis of some additional dicarbene precursors including one in which the divalent carbon atoms are *meta* to one another was undertaken. The bisdiazo compounds, 1,3-bis(α-diazobenzyl)benzene (III) and 4,4'-bis(α-diazobenzyl)biphenyl (IV), were prepared by the manganese dioxide oxidation of the appropriate dihydrazone. Similarly, mercuric oxide oxidation of the dihydrazone of terephthalaldehyde led to 1,4-bis(α-diazomethyl)benzene (V).



III

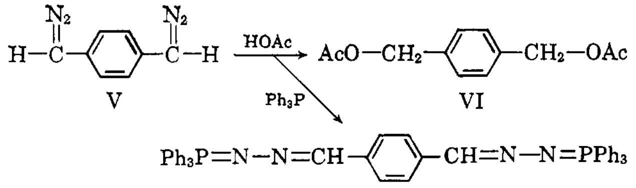


IV



V

Structural differences influence the stability of the bisdiazo compounds. Compounds III and IV are red solids which decompose at their melting points. A satisfactory elementary analysis can be obtained on III while IV appears to decompose slowly at room temperature. Compound V, a reddish orange solid, is rather unstable at room temperature. The infrared spectra of these substances all have the characteristic diazo band at 4.7–4.9 μ. The reaction of V with acetic acid leads to the known diacetate, α,α'-*p*-xylenediol diacetate (VI). Staudinger and Meyer[6] have shown that phosphazines, from the reaction of diazo compounds with phosphines, can be useful derivatives for the diazo compounds. In this work, this reaction has been extended to the bisdiazo compounds. Thus V can be converted to a crystalline bisphosphazine (VII), a material which is somewhat sensitive to moisture and oxidation. The bisphosphazines can be analyzed to demonstrate the presence of the 2 moles of nitrogen in the less stable bisdiazo compounds.



VII

The crystals of all of the bisdiazo compounds described are strongly dichroic. There was a variation in the selective absorption of light depending upon the direction of polarization. Thus, when viewed with polarized light, some of the crystals appeared to be red while others were colorless. A study of this interesting phenomenon and an application to possible crystal structure assignments has been described elsewhere.[7]

Experimental[8]

1,3-Dibenzoylbenzene was prepared by the procedure given[1] for 1,4-dibenzoylbenzene using 38 g. (0.29 mole) of aluminum chloride, 30 g. (0.15 mole) of isophthaloyl chloride, and 250 ml. of dry benzene. The crude product was recrystallized from 95% ethanol to give white crystals (31.6 g., 74.8%), m.p. 104–105°, lit.[9] m.p. 99–101°.

1,3-Dibenzoylbenzene Dihydrazone.—A solution of 30 g. (0.105 mole) of 1,3-dibenzoylbenzene in 150 ml. of absolute ethanol was heated under reflux for 15 hr. with 202 g. of 95% hydrazine (192 g. hydrazine, 6.0 moles). Water was added to the cloud point and the solution was stored in the refrigerator. The yellow, sticky crystals which formed were collected and recrystallized from 95% ethanol to give white crystals (4.71 g., 14.3%), m.p. 157–160°; infrared spectrum: 6.25, 6.14, and 2.95 μ.

Anal. Calcd. for $C_{20}H_{18}N_4$: C, 76.4; H, 5.8; N, 17.8. Found: C, 76.4; H, 5.9; N, 17.6.

1,3-Bis(α-diazobenzyl)benzene (III).—An erlenmeyer flask was charged with 0.251 g. (0.80 mmole) of 1,3-dibenzoylbenzene dihydrazone, 2 g. of sodium sulfate, 0.702 g. (8.0 mmoles) of manganese dioxide, 125 ml. of anhydrous ether, and 0.5 ml. of a saturated solution of potassium hydroxide in ethanol. Addition of the potassium hydroxide catalyst caused an instantaneous formation of the red color of the bisdiazo compound. The reaction mixture, which was protected from light by an aluminum foil wrapper, was stirred vigorously for 4 hr. and filtered; the ether was evaporated to give a quantitative yield of red crystals. The analytical sample was prepared by recrystallization from cyclohexane, m.p. 125–126° dec.

Anal. Calcd. for $C_{20}H_{14}N_4$: C, 77.4; H, 4.6; N, 18.0. Found: C, 77.8; H, 4.8; N, 17.8.

Terephthalaldehyde Dihydrazone.—A solution of 13.4 g. (100 mmoles) of terephthalaldehyde, 300 ml. of absolute ethanol, and 135.2 g. of 95% hydrazine (128.2 g. hydrazine, 4.0 moles) was prepared and allowed to stand at room temperature for 11 days. The solution then was concentrated, water was added to the cloud point, and the solution was refrigerated. The white solid which formed was filtered off and had m.p. 165°,[10] lit.[11] m.p. 165°. The yield was 13.4 g. (83.2%).

1,4-Bis(α-diazomethyl)benzene (V).—An erlenmeyer flask was charged with 0.324 g. (2 mmoles) of terephthalaldehyde dihydrazone, 125 ml. of benzene, 2 g. of sodium sulfate, 2.16 g. (10 mmoles) of yellow mercuric oxide, and 0.5 ml. of ethanol saturated with potassium hydroxide. The reaction mixture was stirred vigorously for 100 min. at which time all of the dihydrazone had reacted as determined by the infrared spectrum. The benzene was evaporated to give a sticky red solid which decomposed slowly at room temperature. The red solid had a strong diazo band in the infrared (4.76 μ) and had $\lambda_{\max}^{\text{benzene}}$ 318 and 500 mμ.

α,α'-*p*-Xylenediol Diacetate (VI).—A benzene solution of 1,4-bis(α-diazomethyl)benzene (from 0.648 g., 4 mmoles of di-

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[2] W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

[3] J. H. van der Waals and M. S. DeGroot, *Mol. Phys.*, **2**, 233 (1959); **3**, 191 (1960).

[4] R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962); A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

[5] A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *ibid.*, **85**, 2526 (1963).

[6] H. Staudinger and S. Meyer, *Helv. Chim. Acta*, **2**, 619 (1919).

[7] R. W. Murray and A. M. Trozzolo, Proceedings of the 1961 International Symposium on Microchemical Techniques, Interscience Publishers, Inc., New York, N. Y., 1962, p. 233.

[8] Infrared spectra were determined by means of a Perkin-Elmer Infracord infrared spectrophotometer. Melting points were taken by the Köfler method and are uncorrected; ultraviolet spectra were obtained on a Beckman DK-2 spectrophotometer.

[9] E. Ador, *Ber.*, **13**, 320 (1880).

[10] This melting point value is observed only when the melting point is taken very rapidly. A yellow, high melting solid is formed when the dihydrazone is heated.

[11] R. Adams, J. E. Bullock, and W. C. Wilson, *J. Am. Chem. Soc.*, **45**, 526 (1923).

hydrazone) was added, with stirring, to a solution of 2 ml. of glacial acetic acid in 5 ml. of benzene. The red color of the bisdiazo compound was discharged instantaneously. The reaction mixture was extracted twice with aqueous sodium bicarbonate and the aqueous layers were backwashed with ether. The ether–benzene solution was dried (magnesium sulfate) and evaporated to give a yellow oil which solidified upon standing in the refrigerator. This solid was recrystallized from pentane to give white crystals with an infrared band at 5.70 μ and m.p. 45–49°, lit.[12] m.p. 47°. The yield was 0.10 g. (11.4%).

1,4-Bis(α-diazomethyl)benzene Bisphosphazine (VII).—A solution of 1,4-bis(α-diazomethyl)benzene (prepared from 0.958 g., 5.9 mmoles of dihydrazone) in 125 ml. of benzene was added, over a period of 5 hr., to a solution of 3.04 g. (11.5 mmoles) of triphenylphosphine in 50 ml. of benzene. The system was under a nitrogen atmosphere and the reaction solution was magnetically stirred. The bisphosphazine, which precipitated as a yellow solid, was filtered off and washed with dry ether. A nitrogen atmosphere was maintained over the filter funnel to prevent moisture from decomposing the bisphosphazine. The solid was recrystallized from ether–chloroform and dried *in vacuo;* it had m.p. 192–195° dec. The yield was 1.20 g. (30%).

Anal. Calcd. for $C_{44}N_{36}N_4P_2$: C, 77.5; H, 5.3; N, 8.22. Found: C, 77.7; H, 5.4; N, 7.82.

4,4′-Dibenzoylbiphenyl.—To a stirred slurry of 79.8 g. (0.6 mole) of aluminum chloride in 150 ml. of carbon disulfide, heated to gentle reflux, was added dropwise a solution of 69.2 ml. (84.6 g., 0.6 mole) of benzoyl chloride in 50 ml. of carbon disulfide. A solution of 20 g. (0.13 mole) of biphenyl in 60 ml. of carbon disulfide then was added to the stirred mixture over a period of 6 hr. The dark-colored reaction mixture then was poured into ice-cold concentrated hydrochloric acid. The reaction mixture was extracted with methylene chloride. The extracts were washed with dilute aqueous sodium hydroxide, dried (magnesium sulfate), and evaporated to give a white solid. This solid was recrystallized from ethanol to give pearl-white plates, m.p. 214–216°, lit.[13] m.p. 216°. The yield was 2.34 g. (4.96%). The major product of the reaction mixture was monobenzoyl biphenyl.

4,4′-Dibenzoylbiphenyl Dihydrazone.—A solution of 1.94 g. (5.38 mmoles) of 4,4′-dibenzoylbiphenyl, 125 ml. of absolute ethanol, and 33.7 g. of 95% hydrazine (32.0 g., 1.0 mole hydrazine) was refluxed under argon for 24 hr. The solution was concentrated on the rotary evaporator and stored in the refrigerator. The tan-colored solid which formed was filtered off and recrystallized from benzene–cyclohexane. The white crystals formed had m.p. 200–203° (taken rapidly).

Anal. Calcd. for $C_{26}H_{22}N_4$: C, 80.0; H, 5.7; N, 14.4. Found: C, 80.4; H, 5.9; N, 14.0.

4,4′-Bis(α-diazobenzyl)biphenyl (IV).—An erlenmeyer flask was charged with 0.39 g. (1 mmole) of 4,4′-dibenzoylbiphenyl dihydrazone, 100 ml. of anhydrous ether, 5 g. of sodium sulfate, 0.86 g. (10 mmoles) of manganese dioxide, and 0.5 ml. of ethanol saturated with potassium hydroxide. The reaction mixture was stirred vigorously for 70 min. The reaction mixture was filtered and the ether was evaporated to give a sticky red solid, which when triturated with methylene chloride gave red crystals, m.p. 132–134° dec. The crystals were dichroic and had a strong infrared band at 4.81 μ.

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(13) W. Schlenk and M. Brauns, *Ber.*, **48**, 716 (1915).

Reactions of Indoles with Benzyne

MARTIN E. KUEHNE AND TSUNEHIRO KITAGAWA

The Department of Chemistry of the University of Vermont,
Burlington, Vermont

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The postulation of benzyne has led to numerous investigations designed to prove the existence of this short-lived intermediate and to establish factors which affect is generation from precursors such as monohalobenzenes, *o*-dihalobenzenes, diphenyliodonium salts, *o*-benzenediazonium carboxylate, 1,2,3-benzothiadiazole 1,1-dioxide, di-*o*-iodophenylmercury, and *o*-chlorobenzophenone.[1] However, less attention has been given to the exploration of benzyne chemistry from the point of view of arylation reactions on carbon, which might be of synthetic interest. Thus, the only reports are on the arylation of carbanions derived from compounds with acidic hydrogen,[2] particularly in cyclization reactions,[3] the addition to olefins,[4] acetylenes,[5] and reactive dienes,[6] and the benzyne arylation of enamines.[7] This paper describes a partially successful attempt to extend this aspect of benzyne chemistry.

Indoles, like enamines, present a bidentate system to electrophiles, which may be attacked on nitrogen or on carbon at the 3-position. When benzyne (I) was generated from bromobenzene with sodium amide in liquid ammonia in the presence of the sodium salt of indole (IIa), N-phenylindole (III, 5%) and 3-phenylindole (IV, 15%) were formed, together with aniline, diphenylamine, and triphenylamine. Under the same conditions, benzyne formation in the presence of N-methylindole (V) did not lead to any N-methyl-3-phenylindole (VI) but only to the aryl amines derived from reaction of benzyne with the solvent.

The reaction products were identified by thin layer and vapor phase chromatographic comparison with authentic samples. Isolation of 3-phenylindole (IV), triphenylamine, and aniline (as picrate) was accomplished by preparative column chromatography.

Benzyne arylation of the indole sodium salt on nitrogen and predominantly on carbon may be contrasted with the corresponding methylation which leads only to nitrogen alkylation under the same conditions.

When the indole lithium salt (IIb) was treated with benzyne (I), generated from *o*-bromofluorobenzene and magnesium in tetrahydrofuran, N-phenylindole (III, 0.5%), 3-phenylindole (IV, 1%), and 2,3-phenylenedihydroindole (VII, 8%) were formed. N-Methylindole (V) and benzyne, generated under the same conditions, produced N-methyl-3-phenylindole (VI, 4%).

In the absence of a proton source, nucleophilic attack of the phenyl anion on the indolenine system of the intermediate VIII leads to the more stable anilide anion, corresponding to 2,3-phenylenedihydroindole (VII), which is then protonated on work-up. With the N-methyl immonium salt IX, abstraction of a more acidic proton and generation of 3-phenylindole (VI) is preferred over cyclization to a dihydroindole.

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