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Dicarbenes. The Preparation and Some Reactions of 1,4-Bis[α-diazobenzyl]benzene[1]

ROBERT W. MURRAY AND ANTHONY M. TROZZOLO

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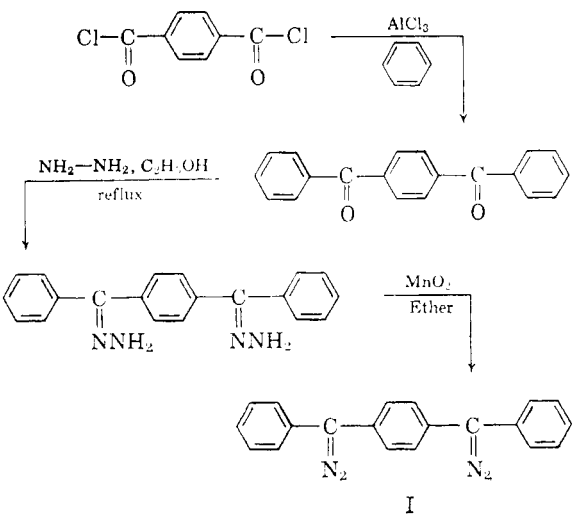
The preparation of 1,4-bis[α-diazobenzyl]benzene (I) is reported. The reaction of I with oxygen, with acetic acid, as well as its thermal decomposition in toluene is described. The possibility of a diradical intermediate in the thermal and photochemical decomposition of I is discussed. Preliminary ESR measurements indicate the presence of free radicals in the thermal decomposition of I.

This paper reports the synthesis and some of the properties of 1,4-bis[α-diazobenzyl]benzene (I). The bisdiazoalkanes have received comparatively little attention with most of the investigations of this class of compounds occurring in recent years.[2] To date, all of the preparations of bisdiazoalkanes have been performed *in situ*. We have begun a study of bisdiazoalkanes containing aryl groups. These compounds, which are expected to have increased stability, have particular interest as potential dicarbene precursors.

The Friedel-Crafts reaction of terephthaloyl chloride and benzene was used to prepare 1,4-dibenzoylbenzene[3] which was then converted to its dihydrazone.[4] Attempts to oxidize the dihydrazone to the bis-diazo compound by the usual method, using yellow mercuric oxide,[5] gave only small yields of I. When silver oxide was used as the oxidizing agent more I was produced but further reaction took place to give back 1,4-dibenzoylbenzene. The oxidation was finally accomplished very satisfactorily using active manganese dioxide.[6] This method caused the immediate appearance of the purple color of I and gave good yields of product free of dihydrazone and diketone. This preparation is shown on Chart I.

CHART I



I

When an ethereal or chloroform solution of I was slowly evaporated the product could be obtained as small, purple crystals. These crystals decomposed with loss of nitrogen at 114–116°. The solid material slowly decomposed at room temperature and consequently could not be satisfactorily analyzed. When examined with the polarizing microscope the crystals of I were found to exhibit pleochroism—that is, 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 purple in color and some colorless. When the microscope stage was rotated, the purple colored crystals became colorless and vice versa. A striking consequence of this phenomenon was observed when crystals of I were irradiated with intense incandescent light on the microscope stage. The purple-colored crystals began to decompose rapidly giving off nitrogen bubbles. The colorless crystals exposed to the same irradiation remained unchanged. When the stage was rotated, the colorless crystals became purple and immediately began to decompose.

The assignment of the structure I to the purple compound rests on its method of preparation, its infrared spectrum (diazo band at 4.91 μ,[7] no car-

(1) Presented before the Division of Organic Chemistry, 139th National Meeting, American Chemical Society, St. Louis, Mo., March, 1961.

(2) (a) Petersen, U. S. Dept. of Commerce, Office of Technical Service Report PB 694 (1941); (b) H. Lettre and U. Brose, *Naturwiss.*, **36**, 57 (1949); (c) T. Lieser and G. Beck, *Chem. Ber.*, **83**, 137 (1950); (d) C. M. Samour and J. P. Mason, *J. Am. Chem. Soc.*, **76**, 441 (1954); (e) C. D. Gutsche, T. D. Smith, M. F. Sloan, J. J. Q. van Ufford, and D. E. Jordan, *J. Am. Chem. Soc.*, **80**, 4117 (1958); (f) H. Reimlinger, *Chem. Ber.*, **92**, 970 (1959); (g) C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

(3) F. Münchmeyer, *Ber.*, **19**, 1845 (1886).

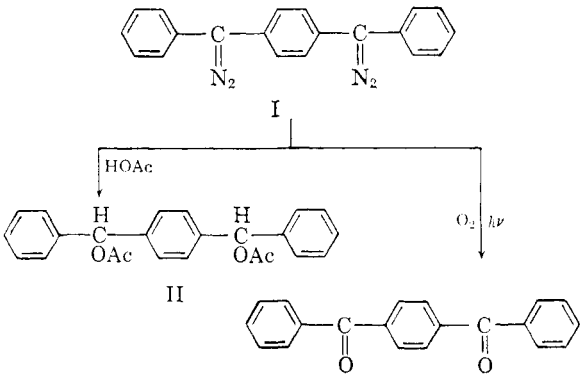
(4) F. Klages, E. Mergenthaler, and H. Haury, *Chem. Ber.*, **81**, 400 (1948).

(5) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

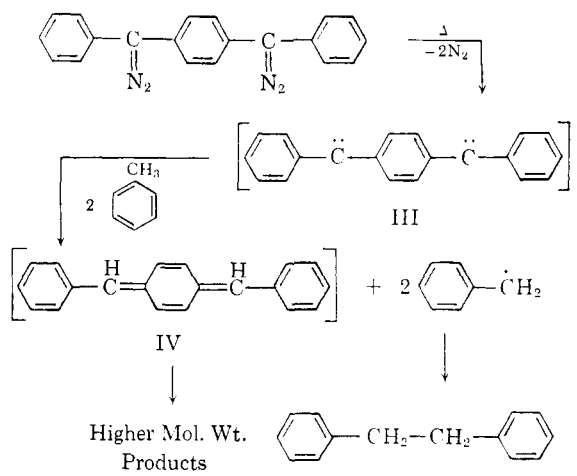
(6) J. Attenburrow *et al.*, *J. Chem. Soc.*, 1094 (1952). The authors wish to thank Dr. E. A. Chandross of these laboratories for this helpful suggestion as well as for a generous supply of active manganese dioxide.

(7) P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, **79**, 5756 (1957).

bonyl band), and the following reactions. When I was photolyzed in the presence of oxygen, 1,4-dibenzoylbenzene was regenerated. This reaction is analogous to that observed by Kirmse and co-workers[8] who have shown that diphenylmethylene from the photolysis of diphenyldiazomethane reacts with oxygen to given benzophenone. The reaction of I with acetic acid gave 1,4-bis[α-acetoxybenzyl]-benzene (II) (acetate band in infrared, 5.73 μ[9]; m.p. 145–146.5°, reported[10] m.p. 143–144°). These data establish the structure of I.



In the case of diphenyldiazomethane a number of workers have reported products which presumably arise from a hydrogen abstraction reaction of the intermediate, triplet diphenylmethylene, with the solvent. Thus, Kirmse and co-workers[8] found that 1,1,2,2-tetraphenylethane was produced when diphenyldiazomethane was photochemically decomposed in the presence of cyclohexane or cyclohexene, for example. They ascribed this product to a hydrogen abstraction reaction of diphenylmethylene, followed by dimerization of the resultant diphenylmethyl radicals. Likewise, Parham[11] found that 1,1,2,2-tetraphenylethane was produced when diphenyldiazomethane was thermally decomposed in petroleum ether. Bamford and Stevens[12] have observed that diphenylmethylene in the presence of benzyl methyl ether gave 1,1,2,2-tetraphenylethane and 1,2-diphenyl-1,2-dimethoxyethane. These products can be explained by an abstraction reaction followed by dimerization of the resultant radicals. When diphenyldiazomethane was thermally decomposed in toluene, 1,1,2,2-tetraphenylethane was again produced,[13] probably *via* the same sort of abstraction reaction. When I was thermally decomposed in refluxing toluene and the crude product chromatographed, dibenzyl(1,2-diphenylethane) was isolated. In addition a colorless oil and a yellow oil were obtained. These oils appeared to be polymeric in nature becoming brittle solids when cooled but reverting to oils when warmed. It is likely that the intermediate from I abstracts hydrogen atoms from toluene and the benzyl radicals thus produced dimerize to give dibenzyl. If the diradical intermediate, III, were produced by the decomposition of I, it might be expected to abstract two hydrogen atoms to give α,α′-diphenyl-*p*-xylylene (IV), a species previously reported to be nonisolable by Thiele.[14]

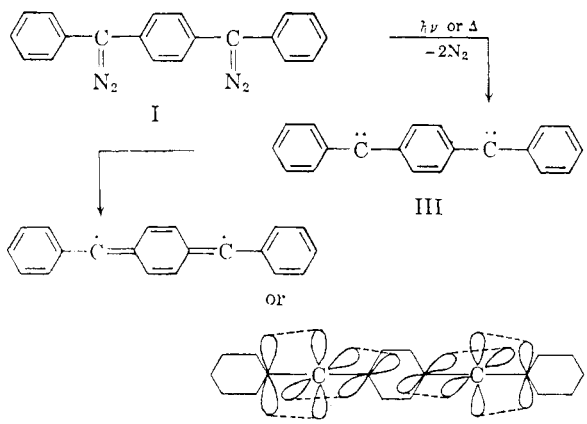


The possibility that the thermal and photochemical decomposition of I might involve the intermediate, III, is an especially interesting one. Evidence has been presented[8,15] that diphenylmethylene, unlike most other divalent carbon intermediates, should be assigned a triplet, rather than a singlet configuration. Presumably the triplet configuration is favored in the case of diphenylmethylene because each of the two unshared electrons present can interact with a different benzene ring in a structure approximating two resonance-stabilized benzyl radicals which are at least partially insulated from each other.[15] The intermediate, III, has two such triplet configurations in the same molecule and can have two of the four initially unpaired electrons available paired in a quinoid structure, while each of the remaining two electrons is interacting with one of the end benzene rings and thus completely prevented from pairing with the other. This species might be expected to have the properties of a diradical. A pictorial representation of III is shown in Chart II.

In order to gain more insight into the nature of the intermediate produced by the photolytic or thermal decomposition of I, we have begun a series of electron spin resonance (ESR) experiments. It is not known, for example, whether the reactions and products described are due to consecutive or

(8) W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).
(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 180.
(10) A. Wehnen, *Ber.*, 9, 310 (1876).
(11) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).
(12) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952).
(13) R. W. Murray, unpublished results.
(14) J. Thiele and H. Balhorn, *Ber.*, **37**, 1463 (1904).
(15) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

CHART II



simultaneous loss of the two molecules of nitrogen. Simultaneous loss of nitrogen would lead to III. However, the production of the diketone from I in the photochemical reaction with oxygen might be explained by consecutive reactions without ever involving III. This latter possibility is made less likely by the observation that when I was partially decomposed by photolysis in the presence of oxygen the crude product contained 1,4-dibenzoylbenzene and unchanged I, but no diazoketone as determined by the infrared spectrum.[16] If I had decomposed stepwise, the intermediate diazocarbene produced should have reacted with oxygen to give some diazoketone. Preliminary ESR measurements have shown that when I is thermally decomposed a resonance absorption is obtained with a g value near the free spin value. It is planned to conduct similar ESR experiments with other diazo compounds including 1,3-bis[α-diazobenzyl]benzene (V). Since the intermediate resulting from loss of two molecules of nitrogen from V cannot assume a configuration such as III, ESR experiments in this case should facilitate the identification of the species responsible for the resonance absorption in the case of I.

EXPERIMENTAL[17]

1,4-Dibenzoylbenzene. The procedure of Münchmeyer[3] was followed with some modifications. To a stirred slurry of 56 g. (0.42 mole) of aluminum chloride in 150 ml. of benzene, heated to very gentle reflux, was added, dropwise, a solution of 40 g. (0.19 mole) of terephthaloyl chloride in 250 ml. benzene. When addition was complete, the flask contents were heated to reflux for 0.25 hr. The reaction mixture was allowed to cool and then was stirred in an ice bath while water was cautiously added. The reaction mixture was extracted with methylene chloride and the extract was washed with dilute, aqueous sodium hydroxide, dried (magnesium sulfate), and evaporated to give a white solid (49.8 g., 88.3 %). This material was recrystallized from 95% ethanol to give white crystals of 1,4-dibenzoylbenzene (30.5 g., 54%), m.p. 160–161°, lit.[3] m.p. 159–160°.

1,4-Dibenzoylbenzene dihydrazone. A solution of 30 g. (0.105 mole) of 1,4-dibenzoylbenzene in 150 ml. absolute alcohol was heated under reflux with 202 g. of 95% hydrazine hydrate (192 g. hydrazine, 6.0 moles) for 15 hr. The reaction mixture was then refrigerated. The yellow crystals present were filtered off, water was added to the filtrate and the solution was again stored in the refrigerator. The additional solid which formed was filtered off. Total yield of crude product was 30.4 g. (92.1%). The crude material was recrystallized from dioxane to give 27.3 g. (82.8%) of a pale yellow solid, m.p. 194–200° dec., reported[4] m.p. 190–195°.

1,4-Bis[α-diazobenzyl]benzene (I). An Erlenmeyer flask was charged with 0.250 g. (0.80 mmole) of 1,4-dibenzoylbenzene dihydrazone, 0.705 g. (8.11 mmoles) of manganese dioxide, and 125 ml. of anhydrous ether. The flask was stoppered and the flask contents stirred rapidly with a magnetic stirrer. A saturated solution (0.5 ml.) of potassium hydroxide in ethanol was then added. The reaction was continued for 2 hr. The optimum reaction time was determined by following the consumption of dihydrazone. Infrared spectra of aliquots removed during the reaction were used to determine the amount of dihydrazone present. Longer reaction times led to partial decomposition of I. The solid material was filtered off and the filtrate was evaporated to give a reddish-purple crystalline solid (0.228 g., 92.4%). The infrared spectrum of the final solid showed the absence of dihydrazone and, in most runs, no diketone was present. In some cases a trace amount of ketone was indicated to be present, probably due to partial decomposition of I.

The minimum purity of the solid product was determined by a nitrogen evolution experiment. A satisfactory analysis could not be obtained because the compound decomposed slowly at room temperature. The product was dissolved in 15 ml. of chlorobenzene and added, dropwise, to 25 ml. of chlorobenzene which was being stirred rapidly and was exposed to irradiation from a Westinghouse Co. 275 watt sun lamp. The entire system had been thoroughly flushed with nitrogen before starting the photolysis in order to prevent any errors which would arise from reaction of the intermediate with oxygen. The nitrogen evolved was collected in a gas burette and indicated that the solid was at least 71% bisdiazo compound, I. This percentage figure is considered a minimum since any reaction of the intermediate, III, from I, with more of I to give azine-type products would reduce the amount of available nitrogen.

When an ethereal or chloroform solution of I was evaporated slowly, small, purple crystals were obtained. These crystals were dried *in vacuo* at room temperature and found to decompose rapidly with loss of nitrogen at 114–116°. When these crystals were examined with a polarizing microscope, they were found to exhibit pleochroism. The crystals showed a selective absorption of light depending upon the direction of polarization. When viewed with polarized light, some of the crystals appeared reddish-purple while others appeared colorless. When the microscope stage was rotated the reddish-purple crystals became colorless and vice versa.

When this preparation was carried out using yellow mercuric oxide as oxidizing agent, the yield of I was very low. When silver oxide was used as the oxidizing agent, more bisdiazo compound was produced, but it was always accompanied by a large amount of 1,4-dibenzoylbenzene. Either the silver oxide was oxidizing I further to the diketone or it was catalyzing the decomposition of I, with subsequent reaction of the intermediate from I with oxygen to give the diketone.

Electron spin resonance (ESR) *measurements.*[18] ESR measurements were carried out using a Varian electron para-

(16) P. Yates[7] *et al.* have shown that in α-diazo ketones the ketone band is shifted up in wave length from its normal position while the diazo band is shifted down.

(17) Infrared spectra were determined by means of a Perkin-Elmer Infracord infrared spectrophotometer. Melting points are uncorrected.

(18) The authors wish to acknowledge the valuable assistance of Mr. W. A. Yager in the electron spin resonance measurements.

magnetic resonance spectrometer using 100 kc. modulation. In a typical experiment an ESR sample tube containing *ca.* 5 mg. of solid I was placed in a variable temperature cavity which had been preheated to *ca.* 125°. The sample tube was flushed with nitrogen throughout the entire experiment. The spectrum which was obtained showed a resonance absorption with a *g* value near the free spin value and a line width of approximately 9 gauss. Similar experiments using evacuated sample tubes gave the same resonance absorption.

Reaction of I *with oxygen.* A flask containing 100 ml. of benzene was fitted with an oxygen inlet attached to a fritted disk. Oxygen was bubbled vigorously through the benzene for 0.5 hr. The flask was then irradiated with a Westinghouse Co. 275 watt sun lamp while maintaining a vigorous stream of oxygen through the benzene. A solution of 0.34 g. (1.1 mmoles) of I in 30 ml. of benzene was added dropwise to the irradiated benzene and the purple color of I was slowly discharged. When addition was complete and no purple color remained, the solvent was removed by evaporation leaving a yellow oil which solidified upon standing. The infrared spectrum of this material was essentially identical to that of 1,4-dibenzoylbenzene. The solid weighed 310 mg. (99%). Despite the clean infrared spectrum, this material was difficult to recrystallize, probably because of the presence of polymeric material from the decomposition of I. The solid was recrystallized twice from ethanol and once from cyclohexane to give white plates of 1,4-dibenzoylbenzene, m.p. 161–163°, mixed m.p. 157–162°.

Reaction of I *with acetic acid.* Solid bisdiazo compound, (I), prepared as described above from 1.57 g. (0.005 mole) of 1,4-dibenzoylbenzene dihydrazone, was dissolved in a minimum amount of ether and added dropwise to a solution of 3 ml. of acetic acid in 25 ml. of ether. The purple color of I slowly disappeared. When addition was complete the reaction mixture was stirred (*ca.* 10 hr.) until the purple color was completely gone. The ether solution was then extracted with aqueous sodium bicarbonate, dried (magnesium sulfate), and evaporated to give a yellow oil. The infrared spectrum of this oil indicated that it was mostly acetate (carbonyl band at 5.73 μ) with a small amount of diketone present. The oil was triturated with ethanol and cooled in Dry Ice. Upon warming to room temperature the oil solidified. This solid (0.17 g., m.p. 136–142°) was recrystallized twice from ethanol to give white crystals of 1,4-bis[α-acetoxybenzyl] benzene (II), m.p. 145–146.5°, lit.[10] m.p. 143–144°. The mother liquors from all crystallizations were combined and concentrated to give an oil which slowly solidified on standing. Total solid obtained was 0.285 g. (15.2%), based on dihydrazone).

Thermal decomposition of I *in toluene.* The bisdiazo compound, I (3.04 g., 98.2%), prepared from 3.14 g. (10 mmoles) of 1,4-dibenzoylbenzene dihydrazone, was dissolved in a minimum amount of toluene and this solution was added dropwise to *ca.* 30 ml. of refluxing toluene. The reaction was carried out in a nitrogen atmosphere and the toluene had been refluxing under nitrogen for 0.5 hr. before addition was started. The purple color of I was discharged slowly. The toluene was distilled off through a fractionating column at atmospheric pressure. The residue was a thick, viscous, yellow oil which was fluorescent in ultraviolet light. A portion (500 mg.) of this oil was chromatographed on a column of *ca.* 65 g. of Woelm, activity grade I, neutral alumina. Elution of the column with carbon tetrachloride gave 70 mg. of a white solid which was sublimed to white plates, m.p. 50.5–52.5° (mixed m.p. 50.5–51.5°). The infrared spectrum of this material was identical to that of authentic dibenzyl. Elution of the column with benzene–carbon tetrachloride (40:60) gave a colorless oil (180 mg.) which had a bluish fluorescence in ultraviolet light. Finally elution of the column with chloroform-benzene (30:70) gave a yellow oil (230 mg.). Attempts to crystallize the colorless and yellow oils failed. These oils appear to be polymeric in nature.

MURRAY HILL, N. J.

[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, DOW CHEMICAL CO.]

The Cracking and Rearrangement of Diallyl Ketals to α-Allyl Ketones

N. B. LORETTE AND W. L. HOWARD

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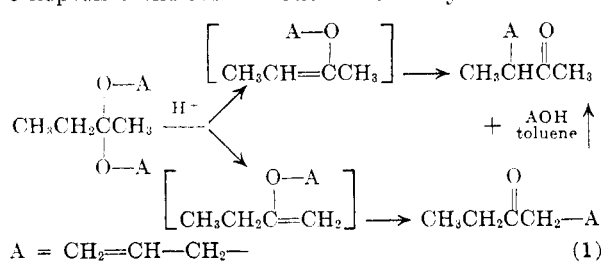
Several diallyl ketals were cracked in the presence of acid and rearranged to *alpha* allyl-substituted ketones in high yields. The use of 2,2-dimethoxypropane made possible the preparation of *alpha* allyl-substituted ketones from ketones and allyl alcohol without isolation of the intermediate diallyl ketals.

The cracking of acetone diallyl ketal to allyl isopropenyl ether and the subsequent quantitative Claisen rearrangement of the ether to 5-hexen-2-one (allylacetone) was reported by Hurd and Pollack[1] in 1938. No reference was found on the use of this procedure for the preparation of other ketones substituted with allyl groups at the *alpha* carbon atoms.

By a modification of the procedure of Hurd and Pollack we have obtained excellent yields of several *alpha* allyl-substituted ketones by the cracking and rearrangement of the corresponding diallyl ketals. The diallyl ketals are easily prepared[2] by alcohol and ketone interchange reactions with 2,2-dimethoxypropane which is commercially available.[3]

The reaction may be illustrated (Equation 1) by the preparation of 3-methyl-5-hexen-2-one and 6-hepten-3-one from 2-butanone diallyl ketal. The



A = CH_2=CH—CH_2— (1)

(1) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1909 (1938).

(2) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).

(3) The Dow Chemical Co.