Reactions of Diphenyldiazomethane and 2-Diazopropane with Zinc Iodide

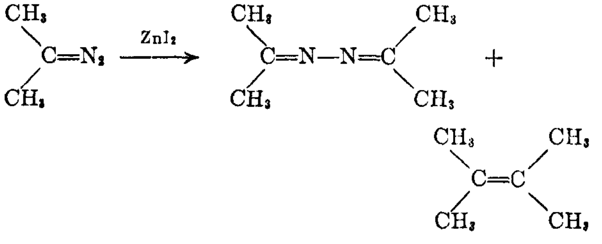
Douglas E. Applequist and Harry Babad[1]

Received August 31, 1961

The great utility of iodomethylzinc iodide as a reagent for the preparation of cyclopropane derivatives,[2] and the reported formation of that reagent from diazomethane and zinc iodide[3] have led us to investigate the reactions of some secondary diazoalkanes with zinc iodide.

Anhydrous 2-diazopropane in ether at −60° to −25° reacted quickly with zinc iodide in trace amounts or in large excess to give primarily acetone azine accompanied by 11–36% yields of tetramethylethylene. Propene was not formed in detectable amounts. The presence of a large excess of added propene in the reaction mixture did not lead to detectable amounts of 1,1,2-trimethylcyclopropane, although trace amounts of a substance having the same vapor phase chromatographic retention time as the latter were formed, with or without added propene. To ensure that the conditions of the reaction were comparable with those employed by Wittig and Schwarzenbach,[3] their preparation of norcarane from cyclohexene, diazomethane, and zinc iodide was repeated. It was found necessary to maintain anhydrous conditions to obtain norcarane.

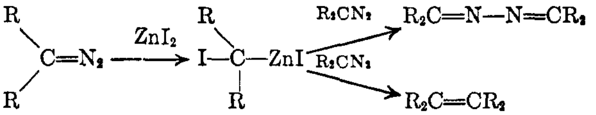
Decomposition of the diazo compound at −15° in the presence of silver oxide and silver (remaining from the preparation from acetone hydrazone and silver oxide) gave mainly acetone azine and less than 1% of tetramethylethylene (based on hydrazone), establishing that tetramethylethylene formation is induced by zinc iodide, and is not just an incidental decomposition or side reaction. Reaction of the diazo compound with acetic acid gave 9–45% yields of tetramethylethylene and 35–52% yields of isopropyl acetate.[4]



$$(CH_3)_2C{=}N_2 \xrightarrow{ZnI_2} (CH_3)_2C{=}N{-}N{=}C(CH_3)_2 + (CH_3)_2C{=}C(CH_3)_2$$

Decomposition of diphenyldiazomethane with trace or excess amounts of zinc iodide in solvents ranging from pure cyclohexane to 60% ether–40% cyclohexane gave high yields of benzophenone azine (as shown in part by isolation of the benzophenone formed by hydrolysis in the isolation procedure). Small amounts (*ca.* 1%) of tetraphenylethylene were obtained in some cases. The presence of a large excess of cyclohexene did not change the products appreciably, but when the solvent consisted of 9% bicyclo[2.2.1]heptadiene, 55% ether, and 36% cyclohexane (by volume), the yields of tetraphenylethylene were increased to 8–10%. In no case could addition products from the olefins be found. Neither could benzhydrol or tetraphenylethane be found in the product mixtures (after hydrolytic isolation procedures).

The simplest interpretation of these results is that the diazo compound reacts with zinc iodide to give the iodoalkylzinc iodide (or some closely analogous species) in the same manner that diazomethane reacts, but that the reagents thus formed are unstable with respect to two alternative fast reactions with the diazo compound, one to give azine and one to give tetrasubstituted ethylene. The insensitivity of the product mixture to zinc iodide concentration speaks against any mechanism for olefin formation by bimolecular reaction of two iodoalkylzinc iodides or of carbenes derived therefrom. Evidence against the participation of carbenes in the formation of either type of product lies in the failure to form tetraphenylethane and cyclohexene from diphenyldiazomethane in cyclohexane, since photolysis of diphenyldiazomethane in cyclohexane forms these products.[5] The possibility that the photochemical reaction forms the triplet state of diphenylcarbene,[6] while the zinc iodide reaction forms the lowest singlet cannot be ruled out from our evidence. This seems highly unlikely, however, as it would be contrary to expectations from the spectroscopic selection rules and would require that interconversion of the two states be slow in solution relative to the chemical reactions, which show high selectivity in both cases.



$$R_2C{=}N_2 \xrightarrow{ZnI_2} I{-}CR_2{-}ZnI \xrightarrow{R_2CN_2} R_2C{=}N{-}N{=}CR_2 \quad;\quad I{-}CR_2{-}ZnI \xrightarrow{R_2CN_2} R_2C{=}CR_2$$

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[1] Taken from the Ph.D. dissertation of Harry Babad, University of Illinois, 1961.

[2] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

[3] G. Wittig and K. Schwarzenbach, *Angew. Chem.*, **71**, 652 (1959).

[4] It is of interest that 2,2-diiodopropane reacts with zinc-copper couple in ether-cyclohexene to give only tetramethylethylene and propene, no cyclopropanes being observed (personal communication from H. E. Simmons and R. D. Smith).

[5] W. Kirmse, L. Horner, and H. Hoffmann, *Ann.*, **614**, 19 (1958).

[6] R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

[7] Melting points are corrected. Infrared spectra were determined in part by Mr. P. E. McMahon and Mrs. M. Verkade. Microanalyses were done by Mr. J. Nemeth, Mrs. A. S. Bay, and Miss J. Liu. Analytical gas chromatography was done on a Perkin-Elmer Model 154B vapor fractometer, using the method of Eastman[8] for quantitative estimation. Samples were collected for identification on an F and M Model 202 gas chromatograph.

EXPERIMENTAL[7]

2-Diazopropane. Acetone hydrazone was prepared from acetone azine[9] and hydrazine by the method of Staudinger and Gaule.[10] Silver oxide was prepared by reaction of 108 g. (0.68 mole) of silver nitrate with 30 g. (0.75 mole) of sodium hydroxide in water. The resulting precipitate was filtered; washed with water, absolute ethanol, and anhydrous ether; and dried for 12 hr. at 50 mm. pressure. To a stirred suspension of 0.34 mole of the silver oxide thus prepared in 250 ml. of anhydrous ether at −60° was added 20 g. (0.34 mole) of freshly distilled acetone hydrazone. The mixture was allowed to warm slowly to about −23°, at which temperature it was kept for 15 min., and then cooled back down to −60°. (Reaction temperatures above −20° resulted in the rapid decomposition of the deeply red diazo compound.) The cold, red solution was filtered onto potassium hydroxide pellets, and the silver–silver oxide residue was washed with cold anhydrous ether. The filtrate was stable for 30 min. at −20°, as shown by the volume of nitrogen evolved when an aliquot was treated with acetic acid. Final drying was accomplished by decanting the solution into a dispersion of sodium hydride in ether and allowing the resulting dispersion to stand at −25° for 1 hr. Suspended sodium hydride and sodium hydroxide were removed by gravity filtration. The resulting solution was stable for several hours at −20° and contained 20–30% yields of diazo compound as shown by nitrogen evolution with acetic acid.

Attempts to prepare 2-diazopropane from acetone hydrazone and mercuric oxide as described by Staudinger and Gaule[10] failed to give detectable yields. Temperatures were varied from −25° to room temperature, solvents were xylene or ethyl ether, and the mercuric oxide was freshly prepared or commercial material.

1,1,2-Trimethylcyclopropane. Trimethylethylene was prepared by dehydration of *t*-amyl alcohol in refluxing benzene with a *p*-toluenesulfonic acid catalyst. After the theoretical amount of water had been collected in an azeotropic distillation tube, the mixture was fractionated through a 4-ft. spinning-band column to give a fraction with b.p. 37.5–38.5° (lit.[11] b.p. 38.4°), which showed only one peak upon gas chromatography through a didecyl phthalate column.

1,1,2-Trimethylcyclopropane was prepared from trimethylethylene and iodomethylzinc iodide by the method of Simmons and Smith,[2] using a zinc-copper couple prepared according to Shank and Shechter.[12] The product was isolated by fractional distillation through the spinning-band column. A fraction of b.p. 54–55° (lit.[13] b.p. 54–54.7°) amounted to a 38% yield and showed only one peak upon gas chromatographic analysis (didecyl phthalate). The infrared spectrum (in carbon tetrachloride) showed no C═C stretching bands, but did show absorptions at 3080 and 1020 cm.$^{-1}$

Tetramethylethylene was prepared by the dehydration of dimethylisopropylcarbinol in refluxing benzene with a *p*-toluenesulfonic acid catalyst. The reaction mixture was fractionated through a 4-ft. spinning-band column to give a fraction with b.p. 72.5–73.5° (lit.[14] b.p. 73°), which showed a single peak upon gas chromatographic analysis (didecyl phthalate). The infrared spectrum was like one in the literature,[15] but contained an additional medium intensity band at 890 cm.$^{-1}$, which suggests some contamination by 2,3-dimethyl-1-butene, whose $C{=}CH_2$ out-of-plane deformation would appear in that region.

Bicyclo[4.1.0]heptane. To 300 ml. of diethyl ether containing 0.1 mole of potassium hydroxide–dried diazomethane[16] was added 0.2 mole of dry barium oxide, and the mixture was swirled occasionally for 2 hr. at −5°. The yellow diazomethane solution was then added slowly to 0.1 mole of freshly prepared zinc iodide in anhydrous ether, prepared by refluxing the stoichiometric amounts of iodine and zinc in ether until the iodine color disappeared. An excess (0.2 mole) of cyclohexene was then added to the colorless solution, which was next heated at reflux for 24 hr. The organic phase was washed successively with 5% hydrochloric acid, water, and 5% sodium bicarbonate, and then was dried over calcium chloride. Distillation on a 4-ft. spinning-band column gave a 4 ml. fraction of bicyclo[4.1.0]heptane, b.p. 115–116°, whose infrared spectrum was identical with that of an authentic sample.[2] The yield was 27%, based upon the titer of diazomethane, analyzed by gas evolution from reaction with acetic acid. Unchanged cyclohexene, b.p. 83°, was recovered.

Careful drying of the diazomethane solution was necessary to prevent decomposition of the intermediate organozinc complex. A run with freshly fused commercial zinc iodide gave a 23% yield of bicyclo[4.1.0]heptane. No improvement in yield was obtained when the zinc iodide and cyclohexene were mixed before addition of diazomethane. A trace amount of zinc iodide rapidly decomposed a solution of diazomethane to give a quantitative yield of nitrogen and a nonvolatile oil, presumed to be polymethylene.[17]

Reaction of 2-diazopropane with acetic acid. To a freshly prepared solution of 0.055 mole of 2-diazopropane in ether still mixed with silver and silver oxide from the oxidation, was added an excess of glacial acetic acid. The mixture was washed with aqueous bicarbonate and fractionally distilled through a spinning-band column to obtain a fore-run, b.p. 37–83°, and a sample of pure isopropyl acetate, b.p. 84–87°, n_D^{26} 1.3743 (lit. b.p. 89–90°. n_D^{25} 1.3740[18]) whose infrared spectrum was identical with that of an authentic sample. The fore-run was analyzed by gas chromatography, and the results combined with the distillation data to determine that the yields, based upon dimethyldiazomethane, were 9.3% tetramethylethylene and 52% isopropyl acetate. Some acetone (42% yield) was also found in the fore-run, but its amount was not considered significant since it doubtlessly arose at least in part from azine or hydrazone present after the formation of the diazo compound. The extraction procedure used here probably reduced the observed yield of acetone.

Another run, in which the diazo compound had been filtered free of silver and silver oxide before acetolysis, gave 45.5% tetramethylethylene and 35% isopropyl acetate.

Decomposition of 2-diazopropane on silver. 2-Diazopropane in ether was allowed to warm up to −15° in contact with the silver metal and silver oxide which remained after the preparation from acetone hydrazone. The red color disappeared almost immediately at this temperature, whereas a filtered solution decomposed only slowly at −15°. The reaction mixture was filtered and distilled to give a nearly quantitative yield of acetone azine, b.p. 129–131°, n_D^{20} 1.4518 (lit. b p. 131°, $n_D^{24.5}$ 1.4510[9]), infrared spectrum identical to that of an authentic sample, and a fore-run which contained a component identified by its gas chromatographic

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(16) F. Arndt, *Org. Syntheses*, **Coll. Vol. II**, 165 (1943).

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(18) C. Friedel, *Ann.*, **124**, 324 (1862).

retention time as tetramethylethylene (0.65% yield). A similar run yielded no detectable tetramethylethylene.

Reactions of 2-diazopropane with zinc iodide. A. Trace of zinc iodide. A solution of 0.083 mole of 2-diazopropane in 400 ml. of dry ether at −25° was treated with a trace of zinc iodide, which decolorized the solution completely. The solution was washed with 1% hydrochloric acid, dried over solid potassium hydroxide, and distilled fractionally to remove excess ether. Analysis by gas chromatography showed (in addition to some acetone, most of which was lost in the earlier washing) a 36.2% yield of tetramethylethylene (based on diazo compound) and a 0.46% yield of a substance having the same retention time as 1,1,2-trimethylcyclopropane. A sample of tetramethylethylene was collected and found to have an infrared spectrum identical to that of the authentic sample prepared above, including the foreign band at 890 cm.$^{-1}$ The NMR spectrum in carbon tetrachloride showed only a single sharp signal at τ 8.4 and a few very small signals due to contaminants, which were not further investigated. It was not found possible to collect enough of the possible 1,1,2-trimethylcyclopropane for identification. No high-boiling materials were found.

Controls were run to show that neither tetramethylethylene nor 1,1,2-trimethylcyclopropane was affected by 2 hr. of refluxing in ether with equimolar amounts of zinc iodide.

B. *Excess of zinc iodide.* A solution of 0.19 mole of 2-diazopropane in 375 ml. of ether was added to 0.25 mole of zinc iodide at −35°. The immediately decolorized reaction mixture was allowed to warm to room temperature. The evolved gas (shown in four separate small runs to be about half the volume formed in the acetic acid decomposition) was shown not to contain appreciable amounts of propene by its failure to react with bromine in carbon tetrachloride (authentic propene did react) and by the absence of propene bands in the infrared spectrum. Analysis as in the preceding reaction showed the reaction mixture to contain an 11.2% yield of tetramethylethylene and a 69% yield of acetone.

C. *Excess of zinc iodide in the presence of added olefins.* An experiment essentially like the preceding except that the zinc iodide was in 100 ml. of ether saturated with propene at −60° gave a 24.4% yield of tetramethylethylene and a 1.36% yield of the substance having the retention time of 1,1,2-trimethylcyclopropane (yields based upon diazo compound). When propene was added to the reaction mixture after the reaction between zinc iodide and 2-diazopropane, the yields were 27.5% and 1.7%, respectively, of these substances.

Diphenyldiazomethane was prepared in 89–95% yields in cyclohexane by the procedure of Smith and Howard[19] from benzophenone hydrazone. The solutions of diazo compound were dried for 1 hr. over barium oxide before use.

A solution of the diazo compound in 1:1 cyclohexane-ether was decomposed with ethereal acetic acid to give a quantitative evolution of nitrogen. The reaction mixture was decolorized, washed with bicarbonate, dried, and concentrated to leave a pale yellow oil whose infrared spectrum was identical with that of an authentic sample of benzhydryl acetate.

Reaction of diphenyldiazomethane with zinc iodide. A. Trace of zinc iodide. To 0.075 mole of dry diphenyldiazomethane in 350 ml. of 1:1 cyclohexane–ether was added 0.001 mole of zinc iodide in 10 ml. of ether. A gas was evolved and the red solution turned yellow in a few minutes. The reaction mixture was partitioned between 1% hydrochloric acid and diethyl ether and the aqueous layer discarded. The ether layer was dried over solid potassium hydroxide and evaporated to dryness to leave 13.0 g. of a yellow solid, m.p. 160–163°. Sublimation at 180° (0.5 mm.) gave 12.5 g. (97.5% yield) of yellow crystals, m.p. 163.5–165°, which showed no depression of the mixture melting point with authentic benzophenone azine. The infrared spectrum was identical with that of an authentic sample.

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.67; H, 5.60. Found: C, 86.69; H, 5.48.

B. *Excess zinc iodide.* To a stirred suspension of 0.2 mole of zinc iodide in 100 ml. of cyclohexane was added 0.0895 mole of diphenyldiazomethane in 250 ml. of cyclohexane over a 12-hr. period. The solution turned yellow and 0.043 mole of gas was evolved. The mixture was extracted several times with 1% hydrochloric acid, dried over solid potassium hydroxide, and evaporated to dryness *in vacuo.* Recrystallization from cyclohexane gave first 1.5 g. (10.8%) of benzophenone azine and then 14.5 g. (88.5%) of benzophenone. (In some runs these were identified by melting points and comparison of infrared spectra with authentic spectra, but where oily or impure products were obtained, the yields were determined by quantitative precipitation of benzophenone 2,4-dinitrophenylhydrazone.[20] The remaining mother liquor contained an oil which was chromatographed on alumina to give 0.17 g. (1.1%) of tetraphenylethylene, m.p. 221–223° after sublimation, mixed m.p. undepressed (lit.[21] m.p. 223–224°).

Anal. Calcd. for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.72; H, 6.15.

Analysis of the reaction solvent by vapor chromatography showed only a single peak with the retention time of cyclohexane. As much as 0.4% yield of cyclohexene would have been detected.

C. *Excess of zinc iodide in the presence of added olefins.* In a reaction very similar to the preceding except that the reaction medium was approximately 55% ether, 35% cyclohexane, and 10% cyclohexene, the only isolated products were benzophenone azine (19.9%) and benzophenone (74.8%). In another run, azine (60%), benzophenone (27%), and tetraphenylethylene (2.2%) were obtained. No benzhydrol was ever observed, although it was shown that the isolation procedure used would have detected 10% benzhydrol in the benzophenone.

A reaction in 55% ether, 36% cyclohexane, and 9% bicyclo[2.2.1]heptadiene gave azine (42%), benzophenone (46%), and tetraphenylethylene (8%). No products corresponding to reactions with the diene could be found, nor could benzhydrol. A second run gave 3%, 76%, and 10% yields of the three products, respectively.

Acknowledgment. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We wish also to thank the National Science Foundation and the Sloan Foundation for partial support.

Noyes Chemical Laboratory
University of Illinois
Urbana, Ill.

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The Stereochemistry of Ethanolysis of 2-Butyl *p*-Bromobenzenesulfonate and 2-Octyl *p*-Toluenesulfonate[1]

A. Streitwieser, Jr., and A. C. Waiss, Jr.

Received August 16, 1961

Despite the ready availability of optically active secondary alcohols, surprisingly little study has been

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(1) Presented at the 7th Conference on Reaction Mechanisms, University of Chicago, Chicago, Ill., September, 1958.