

and sublimes at 200°, darkens 251°, sinters 255°, and melts 263°. ²¹

Anal. Calcd. for C₃H₉N·HI: C, 19.25; H, 5.35; N, 7.48. Found: C, 19.43; H, 5.74; N, 7.44.

Similar results were obtained on attempting the preparation of the methiodide of IIIId.

Deamination of IIIf.—Alkylation of I with isopropyl bromide and treatment of the product with ethylmagnesium bromide was carried out as described above. In order to remove any unreacted aminonitrile II from the product, the crude mixture was refluxed in hydrochloric acid solution for 16 hours. On working up in the usual manner, only a small amount of type IV amine was isolated and no type III amine, obtained in 58–69% yield in the general procedure described above. The neutral fraction was distilled to give 16.5 g. of liquid boiling at 67–73° at 4.0 mm. The infrared spectrum indicated the lack of either carbonyl or hydroxyl groups, but showed the presence of a double bond in conjugation with a phenyl group. The liquid decolorized bromine in carbon tetrachloride, slowly at first, but then rapidly, in agreement with the olefinic structures VI and VII.

Independent Synthesis of 1-Dimethylamino-1-phenylpentane.—Phenylbutylcarbinol (Eastman Kodak Co. white label) was converted to the chloride in 87% yield by a previously reported procedure. ²¹

A solution of 25 g. of the chloride in 150 ml. of dry methanol was saturated with anhydrous dimethylamine and allowed to stand, under a drying tube, for 16 hours. The solution was then refluxed for 1 hour to remove the excess dimethylamine and the methanol was then removed under reduced pressure. The remaining slurry was taken up in dilute hydrochloric acid and extracted with ether to remove the neutral layer which formed. The acidic solution was made basic with solid sodium hydroxide, cooled, and extracted with three 100-ml. portions of ether. After drying over anhydrous magnesium sulfate and filtering, the ether was removed. The residue was distilled to give 16.4 g. (63%) of 1-dimethylamino-1-phenylpentane, b.p. 98–100° at 5.5 mm., *n*_D²⁰ 1.4964. The infrared spectrum was identical with that of the product obtained from the aminonitrile and a mixed m.p. of methiodides showed no depression.

Independent Synthesis of 1-Dimethylamino-1-phenylpropane.—Five-hundredths of a mole (10.3 g.) of α-dimethylaminobenzyl butyl ether was treated with ethylmagnesium

bromide in accordance with the previous procedure¹⁴ to give 6.03 g. (73%) of 1-dimethylamino-1-phenylpropane, b.p. 81–82° at 9.3 mm., *n*_D²⁰ 1.5007. The reported b.p. is 105–106° at 25 mm., *n*_D²⁰ 1.5002.²² The picrate melted at 166.5–167.5°, reported²² 165.5–166. The infrared spectrum was identical with that of the product obtained from the aminonitrile and a mixed m.p. of the picrates showed no depression.

Independent Synthesis of 1-Dimethylamino-1-phenyl-2-methylpropane.—The previous procedure¹⁴ was repeated to give a 65% yield of the amine, b.p. 61–62° at 1.8 mm., 77–78° at 4.1 mm., *n*_D²⁰ 1.4998; picrate m.p. 156–157°; reported b.p. 80.5° at 1.0 mm., *n*_D²⁰ 1.4996, picrate m.p. 156–157°. Due to the discrepancy in the b.p. the product was analyzed. The infrared spectrum was identical with that of the product obtained from the aminonitrile and a mixed m.p. of the picrates showed no depression.

Anal. Calcd. for C₁₂H₁₉N: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.53; H, 10.83; N, 7.88.

Isolation of Olefin Derivatives from the Reaction of Grignard Reagents with Aminonitriles II.—The alkylation of α-dimethylaminophenylacetone nitrile (I) was carried out with isopropyl bromide as described above and the crude product was added to a solution of isopropylmagnesium bromide in the usual manner. A Dry Ice-acetone trap was placed following the reflux condenser for the latter reaction. After completion of the addition of the nitrile and stirring for the desired time, the cold trap was removed and the contents quickly transferred to a three-necked flask equipped with a dropping funnel, stirrer and Dry Ice-acetone condenser. A solution of bromine in carbon tetrachloride was added dropwise (in the dark) until the persistence of the bromine color. The contents of the flask were fractionated to give a good yield of 1,2-dibromopropane boiling at 75–77° (pressure not recorded). The infrared spectrum was identical with that of an authentic sample.

In a similar reaction α-dimethylaminophenylacetone nitrile (I) was alkylated with ethyl bromide and the crude product treated with 4-heptylmagnesium bromide. After decomposing the reaction mixture with hydrochloric acid, the neutral fraction was isolated and the heptane–heptene fraction boiling at 85–105° (mostly 94–100°) was collected. After treatment with bromine in carbon tetrachloride, the mixture was redistilled to give 4.9 g. (9.6%) of 3,4-dibromoheptane, b.p. 104–108° at 25 mm. The infrared spectrum was identical with that of an authentic specimen.

(20) L. Wagner, *Z. Kryst. Mineral.*, **43**, 170 (1907).

(21) M. Protiva, J. Pliml, M. Borovicka and R. Rericha, *Chem. Listy*, **46**, 346 (1952). An infrared spectrum of our chloride indicated the presence of a carbonyl-containing impurity which was presumably the ketone corresponding to phenylbutylcarbinol.

(22) J. F. Bunnett, J. L. Marks and H. Moe, *THIS JOURNAL*, **75**, 985 (1953).

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The Synthesis and Some Reactions of Diazocyclobutane¹

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Diazocyclobutane has been prepared by the reaction of N-cyclobutyl-N-nitrosourea with alkoxides. The diazo compound forms cyclobutanone azine on thermal decomposition, cyclobutyl phenyl ketone on reaction with benzaldehyde, and a mixture of ethyl spirohexane-1-carboxylate and ethyl β-cyclobutylacrylates on reaction with ethyl acrylate. The reactions of the diazo compound with carboxylic acids in ether give mixtures of products which suggest both carbonium and oxonium ion intermediates. Cyclobutyl ethyl ether and cyclopropylcarbinyl ethyl ether are found as byproducts in the preparation of diazocyclobutane in ether–ethanol, and have been shown not to arise from diazocyclobutane.

Diazocyclobutane (I) appeared to be an important synthetic objective not only because of the paucity of knowledge about saturated secondary diazo compounds³ and the lack of information

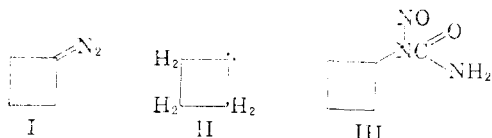
on highly strained diazo compounds, but more specifically because Compound I appeared a likely source of the unknown trimethylenecarbene (II) and, in view of the non-classical behavior of the

(1) Presented in part at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958, and in part at the Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June, 1959.

(2) Roger Adams Fellow, 1956–1957; Visking Corporation Fellow, 1957–1958.

(3) (a) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916); (b) M. Lipp, *ibid.*, **74**, 1 (1941); (c) K. Heyns and A. Heins, *Ann.*, **604**, 133 (1937); (d) F. W. Bollinger, F. N. Hayes and S. Siegel, Abstracts of the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951, p. 87-M; (e) G. Hesse and E. Reichold, *Ber.*, **90**, 2101 (1957).

cyclobutyl cation, might prove to be a useful diagnostic tool for the study of mechanisms of those reactions of diazo compounds which might proceed through carbonium ion intermediates.



Solutions of I have been prepared by the action of an alkoxide on N-cyclobutyl-N-nitrosourea (III) in ether-ethanol, toluene-ethanol, tetrahydrofuran-methanol and *trans*-2-butene-ethanol at -40° . The solutions that resulted were red in color, and this color was attributed to I on the basis that diazocyclohexane^{3c} and dimethyldiazomethane^{3a} are red. The red color slowly disappeared when the solution was warmed to 0° , and from such a decomposition in ether-ethanol, cyclobutanone azine (IV) was obtained in a 27% yield (based on III).

Additional confirmation that the red color was due to the presence of I was obtained from the reaction with benzaldehyde to give cyclobutyl phenyl ketone (19% yield based on III). That cyclopropylcarbinyl phenyl ketone was not also formed was demonstrated by the absence of n.m.r. signals in the region near 450 p.p. 10^8 from water in the n.m.r. spectrum of the product.⁴ The cyclobutyl phenyl ketone was identified by comparison with an authentic sample prepared by the acylation of benzene with cyclobutanecarbonyl chloride.

A certain amount of difficulty was found in the preparation of the N-cyclobutyl-N-nitrosourea (III) used in the preparation of I. Yields were not reproducible and varied from 0 to 60%. The major by-product formed appeared to be cyclobutyl isocyanate (V). This was indicated by the facts that the crude nitrosourea had a sharp irritating odor, had a strong band at 2265 cm^{-1} in its infrared spectrum and gave on reaction with lithium ethoxide cyclobutylurethan (VI).

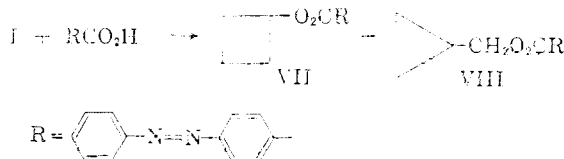


The urethan VI was tentatively identified from its analysis, infrared spectrum and n.m.r. spectrum (Fig. 3). The signals in the n.m.r. spectrum at 74 (quartet) and 361 (triplet) p.p. 10^8 from water were assigned to the hydrogens of the ethyl group, the signals at 280 p.p. 10^8 to the hydrogens of the cyclobutyl group and the broad signal at -88 p.p. 10^8 to the hydrogen on nitrogen.⁵ Heyns and Heins^{3c} also observed isocyanate formation in the preparation of N-cyclohexyl-N-nitrosourea.

Diazocyclobutane was allowed to react with *p*-phenylazobenzoic acid in toluene-ethanol, ether-

ethanol and tetrahydrofuran-methanol. The reaction in toluene-ethanol gave in 30% yield a mixture of esters which contained cyclobutyl *p*-phenylazobenzoate (VII) and cyclopropylcarbinyl *p*-phenylazobenzoate (VIII) in a ratio of 44:56. The esters were separated by chromatography on alumina and identified by comparison with authentic samples. The n.m.r. spectra of VII and VIII are given in Fig. 3. The signals at -300 p.p. 10^8 were assigned to the aromatic hydrogens. The signals at -10 and 300 p.p. 10^8 for VII were assigned to the tertiary and secondary hydrogens of the cyclobutyl group and those at 78 (doublet) and 445 p.p. 10^8 for VIII to the hydrogens of the methylene and the cyclopropyl group.^{4,5}

When diazocyclobutane was allowed to react with *p*-phenylazobenzoic acid in ether-ethanol there was formed in 30% yield (based on III) a mixture of esters which contained the cyclobutyl (VII), cyclopropylcarbinyl (VIII) and ethyl (IX) *p*-phenylazobenzoates in a ratio of 27:26:26. Similarly in the solvent tetrahydrofuran-methanol the ester product obtained in 8% yield (based on III) contained VII, VIII, the ω -cyclobutoxybutyl



(X) and ω -cyclopropylcarbinoxybutyl (XI) esters in the proportions 20:14:40:14, respectively.

In the majority of cases in which a diazo compound has been allowed to react with an acid in non-polar medium there has been no indication of a carbonium ion intermediate.⁶ Evidence for such an intermediate, however, was found in the reaction of 2-diazo-1,1,1-triphenylethane⁷ with benzoic acid in ether, which gave 1,1,2-triphenylethyl benzoate.

Huisgen⁸ has recently been able to show sufficient similarity between the reaction of diazo compounds with acids and the decomposition of acylnitrosoamines to propose a similar intermediate in the two reactions. In addition he has accumulated data which convincingly supports an ion-pair intermediate for these reactions. The products which one will obtain from a reaction of a diazo compound and an acid will thus depend on the ability of the solvent to separate the ion pair before combination of the ions occurs.

In the present case, the cation obtained from the reaction of I with acid is presumably non-classical⁹ and therefore yields both cyclobutyl and cyclopropylcarbinyl products regardless of the occurrence of solvent intervention in the ion pair. An alternative possibility, as far as the present data are concerned, is that a classical cyclobutyl cation is formed and either equilibrates with cyclopropylcarbinyl cation or rearranges to the latter at a rate comparable with the ion-pair collapse.

(6) D. Y. Curtin and S. M. Gerber, *THIS JOURNAL*, **74**, 4052 (1952).

(7) L. E. Hellerman and R. L. Garner, *ibid.*, **57**, 139 (1935).

(8) R. Huisgen and Ch. R  chardt, *Ann.*, **601**, 21 (1956), and earlier papers in this series.

(9) J. D. Roberts, 16th National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June, 1959.

(4) The signal for the hydrogens on the cyclopropyl group was observed at 460 p.p. 10^8 from water for cyclopropylcarbinol (see Experimental).

(5) (a) L. H. Meyer, A. Saika and H. S. Gutowsky, *THIS JOURNAL*, **75**, 4567 (1953); (b) B. P. Dailey and J. N. Shoolery, *ibid.*, **77**, 3977 (1955); (c) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

When the solvent used was an ether, products were observed which contained fragments from the solvent. The formation of these products indicates that at least a portion of the ion-pairs had become solvent separated. The tendency for an ion-pair to become solvent separated has been shown by Winstein to depend on both the stability of the ions and the ionizing power of the medium.¹⁰ The fact that the reactions of primary diazoalkanes with acids in ether¹¹ and other non-polar solvents¹² give little or no reaction with solvent or rearrangement would indicate that ion-pairs which contain primary carbonium ions are not readily solvent separated and are short lived in these solvents.

A possible mechanism for the formation of IX, X and XI as well as some of VII and VIII is given in Fig. 1. It might be expected that most of the VII and VIII would form directly from the intimate ion pair XII. The bicyclobutonium ion part of XII has been proposed by Roberts⁹ as an intermediate in the reaction of cyclobutylamine with nitrous acid.

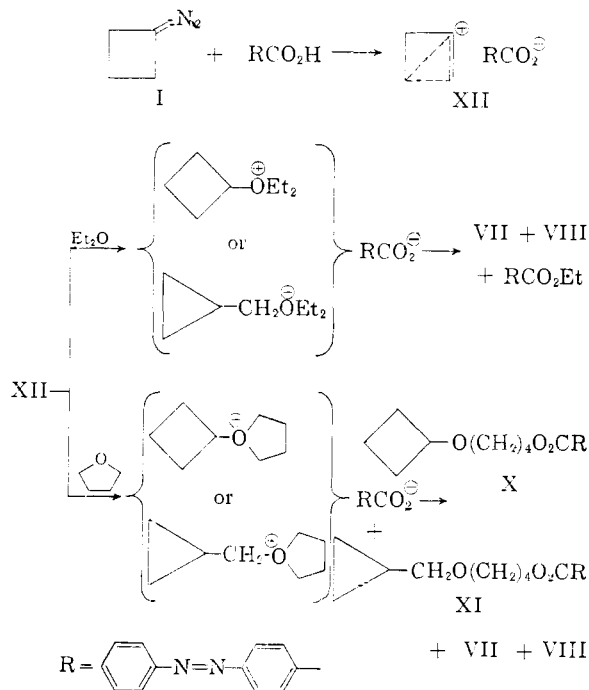


Fig. 1.—Reaction of diazocyclobutane with *p*-phenylazobenzoic acid in ether or tetrahydrofuran.

The ethyl ester IX was identified by comparison with an authentic sample. The structures assigned to the esters X and XI were based on their elemental analyses, infrared spectra and n.m.r. spectra (Fig. 3). The signals at -300 to -250 p.p. 10^8 from water were assigned to the aromatic hydrogens, those at 40 to 90 to the hydrogens on the carbons alpha to the ester oxygen, these at 120 to 150 to the hydrogens on the carbons alpha to the ether oxygen, those at 280 to 330 to the hydrogens on the methylenes beta to the oxygens and on the methylenes of the cyclobutyl ring, and those at

(10) S. Winstein and G. C. Robinson, *THIS JOURNAL*, **80**, 169 (1958).

(11) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935); A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan and J. F. Crooker, *Can. J. Research*, **28B**, 683 (1950).

(12) R. Huisgen and Ch. Ruchardt, *Ann.*, **601**, 1 (1956).

400 to 450 to the hydrogens on the cyclopropane ring.^{4,6}

Although allylcarbonyl *p*-phenylazobenzoate might also be expected as a product in the above reactions,⁹ it was not observed in these cases. Examination of the infrared spectra of mixtures of allylcarbonyl *p*-phenylazobenzoate with cyclopropylcarbonyl *p*-phenylazobenzoate indicated that mixtures up to 10% in the allyl ester would not be detectable.

In the reactions of diazocyclobutane with acids there was always an alcohol present. It is possible that the low yield of ester products is due to the side reaction of the bicyclobutonium ion with the alcohol. No effort was made to determine the amount of reaction by this path.

Diazocyclobutane has been used successfully to prepare ethyl spirohexane-1-carboxylate (XIII). Although no spirohexanes have been reported in the literature there have been at least two attempts¹³ to prepare compounds with this ring system.

In the present work pyrolysis of the pyrazoline from I and ethyl acrylate gave a liquid product which was shown by vapor chromatography to contain at least five components. Three of these were present in significant amounts and were isolated and identified by their elemental analyses and infrared and n.m.r. spectra (Fig. 3) to be ethyl *trans*- β -cyclobutylacrylate (XIV), ethyl *cis*- β -cyclobutylacrylate (XV) and ethyl spirohexane-1-carboxylate (XIII). Based on the areas under the peaks of the vapor chromatogram, these esters comprised 52, 13 and 30%, respectively, of the liquid product.

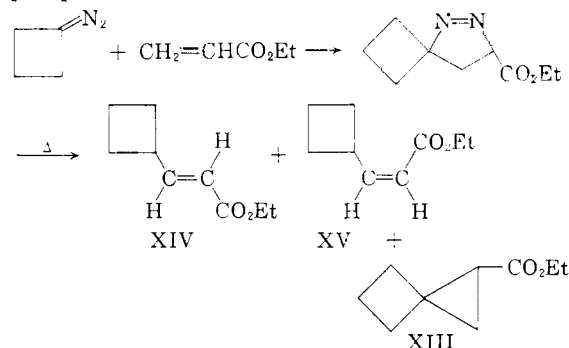


Fig. 2.—Synthesis of ethyl spirohexane-1-carboxylate.

The n.m.r. spectra of the esters are shown in Fig. 3. The signals at -200 to -50 p.p. 10^8 from water were assigned to the olefin hydrogens, those at 69 (quartet) and 359 (triplet) to the hydrogens of the ethyl group, those at 260–300 to the hydrogens of the cyclobutyl group and the signals mixed with the triplet at 359 for XIII were assigned to the hydrogens of the cyclopropane group. Signals from 380 to 408 have been observed for cyclopropanecarboxylic acid.¹⁴ The *trans* structure XIV has been assigned to the isomer with the larger vinyl hydrogen splitting constant.¹⁵ This

(13) (a) Ya. M. Slobodin and M. V. Blinova, *Zhur. Obshchei Khim.*, **23**, 1994 (1953); (b) H. M. Walborsky, *THIS JOURNAL*, **74**, 4962 (1952).

(14) A. H. Bottini, private communication.

(15) A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

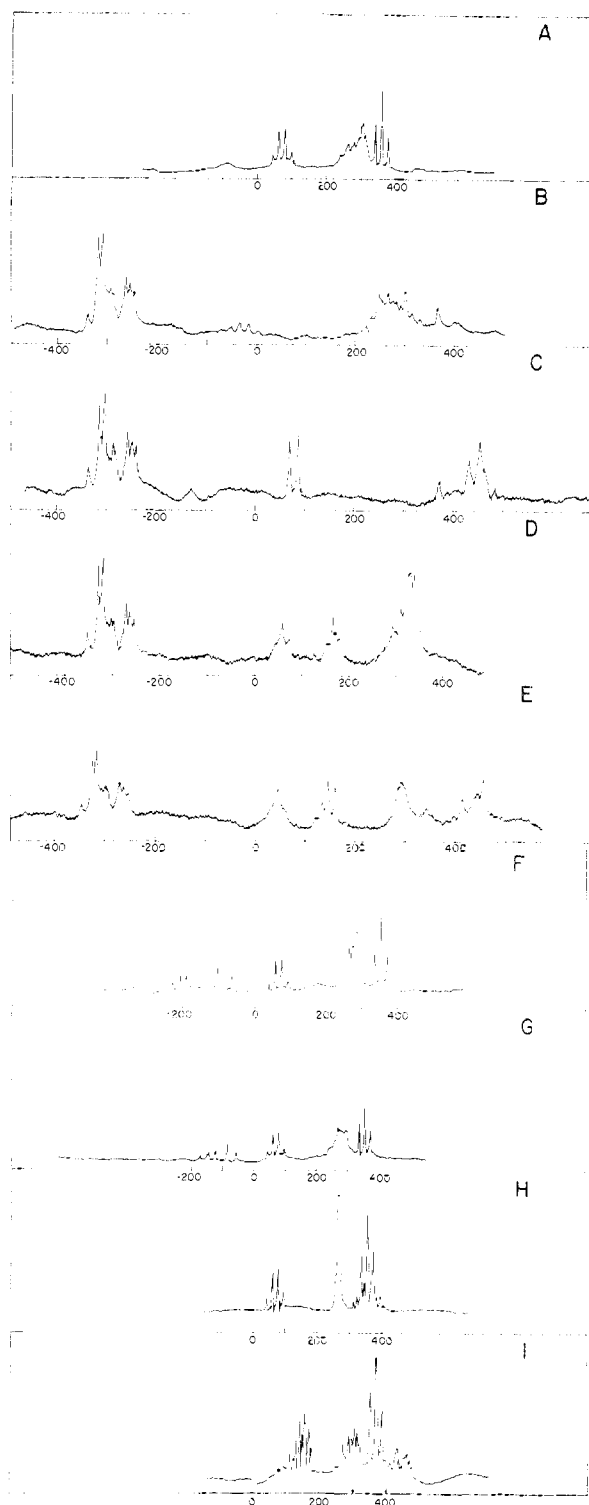


Fig. 3.—N.m.r. spectra: A, cyclobutylurethan (VI); B, cyclobutyl *p*-phenylazobenzoate (VII); C, cyclopropylcarbinyl *p*-phenylazobenzoate (VIII); D, ω -cyclobutoxybutyl *p*-phenylazobenzoate (IX); E, ω -cyclopropylcarbinoxybutyl *p*-phenylazobenzoate (XI); F, ethyl *trans*- β -cyclobutyl acrylate (XIV); G, ethyl *cis*- β -cyclobutyl acrylate (XV); H, ethyl spirohexane-1-carboxylate (XIII); I, mixture of cyclobutyl ethyl ether and cyclopropylcarbinylethyl ether (XVI). All spectra are in CCl_4 soln., 15–30%. External CH_2Cl_2 was used for calibration, and the scale is parts per 10^8 from water.

isomer also showed an absorption in the infrared at 982 cm.^{-1} characteristic of a *trans*-olefin¹⁶ which was absent in the spectra of XV and XIII.

During the investigation of the photochemical decomposition of I¹⁷ a liquid fraction (XVI) was obtained which gave an elemental analysis which corresponded to $\text{C}_6\text{H}_{12}\text{O}$. Vapor chromatography of this fraction showed that it was probably a mixture of two components in about equal quantities. The n.m.r. spectrum of the liquid fraction (XVI) (Fig. 3) indicated that the mixture contained cyclobutyl ethyl ether and cyclopropylcarbinyl ethyl ether. The signals at 120 to 150 pp 10^8 from water were assigned to hydrogens on carbons alpha to the ether oxygen, those at 260 to 300 to hydrogens on the cyclobutyl group, those at 350 to 375 to hydrogens of the methyl of the ethyl groups and those at 420 to 460 to hydrogens of the cyclopropyl group.^{4,5}

In the thermal decomposition of I a product which was identified to be the same as XVI by its retention time in a vapor chromatogram was observed. In order to test whether these ethers were formed by the reaction of I with ethanol or by an alternate path during the formation of I, a solution of I was prepared in ether and half was decomposed thermally and the other half was allowed to react with benzaldehyde. In the thermal reaction, the diazocyclobutane was in the presence of ethanol at least three times as long as in the benzaldehyde reaction and yet both reactions gave the same yield of the ether mixture.

This suggests that diazocyclobutane does not react with ethanol under these reaction conditions. It is evident from the products that a carbonium ion intermediate is formed. This intermediate might be expected to arise from the solvolysis of a particularly reactive species in solution. The nitroso compound III is not solvolyzed under the reaction conditions. We would like to suggest the reaction scheme shown in Fig. 4 for the formation of the carbonium ion intermediate. Evidence has been reported for diazoate anions like XVII in the reactions of nitroso compounds with base.¹⁸

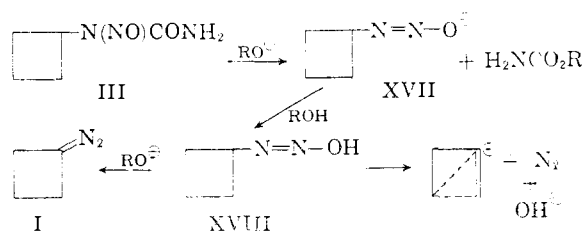


Fig. 4.—Synthesis and side reactions in the preparation of diazocyclobutane.

The foregoing experiments serve to clarify some observations made by Heyns and Heins^{8c} in their studies on diazocyclohexane. It was observed that among the products from reaction of diazocyclohexane with cyclohexanone in anhydrous ether-ethanol were roughly equal amounts of cy-

(16) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 40.

(17) Results of this investigation will be reported after completion of further work.

(18) (a) A. Hantzsch and M. Lehmann, *Ber.*, **35**, 897 (1902); (b) R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952).

clohexanol and cyclohexyl methyl ether. It was proposed that the latter arose from diazocyclohexane by way of the cyclohexyl cation. It now seems more probable that these products were formed competitively with diazocyclohexane by some mechanism like that in Fig. 4, and the relatively high yield of cyclohexanol is then explicable in terms of collapse of the ion pair before the cation can diffuse away to attack methanol or methoxide.

The possibility of a reaction path from the diazoate XVII other than to the diazo compound I might also explain the low yields obtained in the preparation of diazocyclobutane (maximum of about 50%) compared to that of diazomethane (nearly quantitative). Solvolysis of methane diazohydroxide would be expected to be much more difficult than that of cyclobutane diazohydroxide (XVIII).

Acknowledgment.—The authors wish to thank the Research Corp. and the Sloan Foundation for support during the summers of 1957 and 1958, respectively. We are indebted to Mr. J. Nemeth and his staff for the microanalytical results, to Mr. B. Shoulders for the n.m.r. spectral determinations, and to Mr. P. McMahon and his associates for the infrared spectra.

Experimental¹⁹

Cyclobutylurea.—Cyclobutylamine prepared by the method of Heisig²⁰ was used to prepare cyclobutylurea by the procedure of Boivin.²¹ The crude urea, m.p. 167–169°, obtained in 66% yield was crystallized from ethyl acetate to give an analytical sample, m.p. 170.5–171°.

Anal. Calcd. for C₆H₁₀ON₂: C, 52.61; H, 8.83; N, 24.54. Found: C, 52.70; H, 8.53; N, 24.25.

N-Cyclobutyl-N-nitrosoarea (III).—A solution of 11.4 g. (0.1 mole) of cyclobutylurea in 250 ml. of water, 3.2 ml. (0.12 mole) of concentrated sulfuric acid and 100 ml. of ether was cooled in an ice-water-bath to 5°, and a solution of 7.6 g. (0.11 mole) of sodium nitrite in 25 ml. of water was added dropwise over a period of 20 minutes. The mixture was stirred an additional 10 minutes. The two phases were separated. The water layer was extracted with ether and then made neutral with potassium carbonate and evaporated to dryness. The residue was extracted with acetone to give, on evaporation, 2.1 g. of recovered cyclobutylurea, m.p. 160–164°.

The combined ether extracts were washed with 50 ml. of 5% potassium bicarbonate solution and 3 small portions of ice water, dried over Drierite and filtered. Fifty ml. of pentane was added to the ether solution and the solution was evaporated at 15° under reduced pressure in a Rinco evaporator. When III began to crystallize (caution is necessary since further evaporation induces decomposition) it was cooled in a Dry Ice-isopropyl alcohol-bath (to complete crystallization) and filtered. The yellow solid was washed with cold pentane to remove all traces of isocyanate (sharp odor). The yield of N-cyclobutyl-N-nitrosoarea was 60% based on recovered starting material. This was a maximum yield and was not readily reproduced. Yields from 0 to 60% were obtained with the average yield about 45%. For purification the product was dissolved in a small amount of chloroform, pentane was added and the mixture was cooled to –50° to give N-cyclobutyl-N-nitrosoarea as yellow needles, m.p. 67–69° dec.

(19) All melting points and boiling points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer model 21 spectrometer with sodium chloride optics and the n.m.r. spectra were measured at 20° on a Varian nuclear magnetic spectrometer, model V-4300B with super stabilizer at a frequency of 40 megacycles. The vapor fractometer used throughout was a Perkin-Elmer model 154B with helium carrier gas.

(20) G. B. Heisig, *THIS JOURNAL*, **63**, 1698 (1941).

(21) J. L. Boivin and P. A. Boivin, *Can. J. Chem.*, **29**, 478 (1951).

Anal. Calcd. for C₆H₉O₂N₃: C, 41.95; H, 6.34. Found: C, 41.94; H, 6.13.

A sample of III decomposed at room temperature in one week.

Diazocyclobutane (I).—In a 100-ml. 3-necked flask fitted with a pressure-equalized dropping funnel, a mercury stirrer and a 100-ml. gas buret filled with mercury was placed 25 ml. of ether, 0.5 g. of anhydrous magnesium sulfate and 0.488 g. (0.0034 mole) of N-cyclobutyl-N-nitrosoarea. The system was flushed with nitrogen and cooled to –50°. After equilibrium had been reached, 5 ml. of a 4% solution of sodium methoxide (0.004 mole) in methanol was added dropwise. After a period of 20 min. at –50°, 55 cc. of gas had been collected and the solution had developed a deep red color. If it is assumed that all of the nitroso compound III had reacted and that the portion which had not been transformed to I liberated its nitrogen quantitatively, then the yield of I was 45%.

Cyclobutanone Azine.—To a solution of 4 g. (0.028 mole) of N-cyclobutyl-N-nitrosoarea in 100 ml. of ether at –40° were added a solution of lithium ethoxide (from 0.6 g. (0.086 g. atom) of lithium) in 25 ml. of ethanol and 25 ml. of ether. The resulting red solution was warmed slowly to room temperature and the red color disappeared. The mixture, which contained an insoluble lithium salt, was filtered and the filtrate evaporated to give 0.5 g. (27% based on III) of cyclobutanone azine, m.p. 66–68°. Recrystallization from ether-pentane at –40° raised the melting point to 69–70° (lit.²² m.p. 68.4–69.1°).

Anal. Calcd. for C₈H₁₂N₂: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.23; H, 9.18; N, 20.88.

The n.m.r. spectrum (270 mg./ml. in deuteriochloroform) showed signals at 171 pp 10⁸ from water (triplet) and 261 (multiplet) due to the hydrogens on the α - and β -carbons from the nitrogen-carbon double bond, respectively.

Cyclobutanecarbonyl Chloride.—To 10 g. (0.1 mole) of cyclobutanecarboxylic acid was added 20 g. (0.17 mole) of thionyl chloride, and the mixture was refluxed for 1.5 hours. The product was distilled to give 6 g. of forerun and 9.5 g. (70%), b.p. 130–140° (lit.²³ b.p. 137–139°), of cyclobutanecarbonyl chloride.

Cyclobutyl Phenyl Ketone.—A solution of 9.5 g. (0.07 mole) of cyclobutanecarbonyl chloride in 25 ml. of benzene was added dropwise to a solution of 13 g. (0.1 mole) of aluminum chloride in 30 ml. of benzene. The solution became brown and hydrochloric acid fumes were evolved. After the addition was complete, the mixture was stirred for 15 minutes at room temperature and then 30 minutes at reflux. The solution was cooled and poured into 200 ml. of water and 5 ml. of concentrated hydrochloric acid. The benzene was separated and washed with water, 5% potassium carbonate solution, and water; dried over Drierite, filtered and distilled to give 0.64 g. of cyclobutyl phenyl ketone, b.p. 124–127° (9 mm.), n_D^{25} 1.5453, 1.71 g., b.p. 127° (9 mm.), n_D^{25} 1.5453, and 1.47 g., b.p. 127–130° (9 mm.), n_D^{25} 1.5460 (lit.²⁴ b.p. 114.4° (7 mm.), n_D^{25} 1.5452).

The n.m.r. spectrum (550 mg./ml. in carbon tetrachloride) showed phenyl hydrogen signals from –306 to –239 p.p. 10⁸ from water and cyclobutyl hydrogen signals from 94 to 135 and from 239 to 287 p.p. 10⁸.

The 2,4-dinitrophenylhydrazone was prepared in the usual way from 0.5 g. of ketone. Since the melting point of this product, m.p. 182–183°, differed from the literature value,²⁴ m.p. 172–173°, an analysis was obtained.

Anal. Calcd. for C₁₇H₁₆O₄N₄: C, 59.99; H, 4.74. Found: C, 60.21; H, 4.61.

Reaction of Diazocyclobutane with Benzaldehyde.—To a solution of 2.5 g. (0.018 mole) of N-cyclobutyl-N-nitrosoarea in 100 ml. of ether at –40° was added a slurry of 1 g. (0.02 mole) of lithium ethoxide in 50 ml. of ether. The mixture was stirred at –35° until it was deep red (1 hour) and 1 g. (0.01 mole) of benzaldehyde was then added. The red color of the solution disappeared over a period of 3 minutes. The solution was warmed to room temperature, washed

(22) C. G. Overberger, H. Bilech, A. B. Finestone, J. Lilker and J. Herbert, *THIS JOURNAL*, **75**, 2078 (1953).

(23) N. Ya. Demyanov and Z. I. Shukina, *Zhur. Obshchei Khim.*, **5**, 1213 (1935).

(24) R. P. Mariella and R. R. Raube, *THIS JOURNAL*, **74**, 518 (1952).

with water, dried over Drierite, filtered, and evaporated to give 1.2 g. of an oil. The oil was shaken with 3 ml. of 40% sodium bisulfite solution in water-ethanol and the benzaldehyde bisulfite addition compound filtered and washed with ether. The filtrate was extracted with ether, and the extract was washed with water, dried over Drierite, filtered and distilled to give 0.5 g. (16%) of crude cyclobutyl phenyl ketone.

The infrared spectrum (carbon tetrachloride) was identical with that of an authentic sample except for a band at 1495 cm^{-1} which was not in the authentic sample.

The 2,4-dinitrophenylhydrazone, m.p. 181-182°, when mixed with an authentic sample melted at 181-182°.

Cyclobutylurethan (VI).—The ether solution obtained from the reaction of 11.4 g. (0.1 mole) of cyclobutylurea with nitrous acid by the procedure used to prepare III was used, after it had been dried over Drierite, for the preparation of diazocyclobutane to be used for reaction with ethyl acrylate.

To the ether solution at -40° was added a solution of lithium ethoxide (from 0.45 g. (0.06 g. atom) of lithium) in 25 ml. of ether and 2 ml. of ethanol. The diazo compound I formed but only in poor yield as indicated by the color. A solution of 0.8 g. (0.008 mole) of ethyl acrylate was added and the red color disappeared. The solution was warmed and combined with a second similar run, washed with water, dried over Drierite, filtered and evaporated to give 5.4 g. of an oil. This oil was heated to pyrolyze any pyrazoline, and then distilled to give 0.42 g., b.p. 90-105°; 0.56 g., b.p. 105-115°; and 0.72 g., b.p. 115-140°. The pot residue was 1.8 g.

The two high boiling fractions had similar infrared spectra so were combined and distilled in a sublimation apparatus to give 0.82 g. of a solid which readily melted but resolidified when it was cooled.

The n.m.r. spectrum (200 mg./ml. in carbon tetrachloride, A in Fig. 3) showed a triplet at 343, 361 and 378 p.p. 10⁸ from water a quartet at 47, 65, 83 and 100, cyclobutyl hydrogen signals from 262 to 300 and a broad band at -88 p.p. 10⁸.

The sample was sublimed three times to give pure cyclobutylurethan, m.p. 35-6°.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{O}_2\text{N}$: C, 58.72; H, 9.15. Found: C, 58.88; H, 9.06.

The infrared spectrum (chloroform) showed absorption at 3440, 1700 and 1501 cm^{-1} .

The fraction b.p. 90-105° (9 mm.) was a mixture of ethyl *cis*- and *trans*- β -cyclobutylacrylate and ethyl spirohexane-1-carboxylate as described below.

Allylcarbinol.—Reduction of 3-butyne-1-ol (Farchan) by the procedure of Roberts²⁵ gave allylcarbinol, b.p. 110-115°, n_{D}^{20} 1.4156 (lit.²⁵ b.p. 115°, n_{D}^{20} 1.4182).

Allylcarbinyl *p*-Phenylazobenzoate.—To 0.24 g. (0.0033 mole) of allylcarbinol in 10 ml. of pyridine was added 1 g. (0.004 mole) of *p*-phenylazobenzoyl chloride. The solution was boiled 1 min. and then poured onto 5 g. of ice and let stand until the ice melted. The red precipitate was filtered, washed with 5% sodium bicarbonate and water, and dried. Crystallization from methanol gave allylcarbinyl *p*-phenylazobenzoate, m.p. 58-59°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$: C, 72.84; H, 5.75. Found: C, 72.84; H, 5.81.

Cyclopropylcarbinol.—Reduction of cyclopropanecarboxylic acid (Aldrich) with lithium aluminum hydride by the procedure of Nystrom and Brown²⁶ gave cyclopropylcarbinol (43%), b.p. 120-130°, n_{D}^{20} 1.4294 (lit.²⁶ b.p. 123°, n_{D}^{20} 1.4300).

The n.m.r. spectrum (262 mg./ml. in carbon tetrachloride) showed signals due to the tertiary and secondary hydrogens of the cyclopropyl group at 393 (multiplet) and 460 (multiplet) p.p. 10⁸ from water, respectively, due to the methylene hydrogens at 151 (doublet) and due to the hydroxyl hydrogen at 23 pp 10⁸.

Cyclopropylcarbinyl *p*-Phenylazobenzoate (VIII).—A solution of 1 g. (0.014 mole) of cyclopropylcarbinol in 10 ml. of pyridine was treated with 2 g. (0.008 mole) of *p*-phenylazobenzoyl chloride by the procedure used for the preparation of allylcarbinol ester. The red solid thus obtained was crystallized from pentane at -40° to give cyclopropylcarbinyl *p*-phenylazobenzoate, m.p. 82.5-83.5°.

(25) J. D. Roberts and R. H. Mazur, *THIS JOURNAL*, **73**, 2509 (1951).

(26) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2543 (1947).

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.65; H, 5.77; N, 9.74.

The n.m.r. spectrum (328 mg./ml. in carbon tetrachloride, C in Fig. 3) showed signals due to cyclopropyl hydrogens from 363 to 475 p.p. 10⁸, methylene hydrogens at 69 and 87 p.p. 10⁸ (doublet) and aromatic hydrogens from -345 to -250 p.p. 10⁸.

Cyclobutyl *p*-Phenylazobenzoate (VII).—Reaction of cyclobutylamine with nitrous acid by the procedure of Roberts and Mazur²⁵ yielded a mixture of cyclobutanol, cyclopropylcarbinol and allylcarbinol (70%), b.p. 110-125°.

A solution of 2 g. (0.027 mole) of the mixed alcohols in 10 ml. of pyridine was treated with 2 g. (0.008 mole) of *p*-phenylazobenzoyl chloride by the procedure used in the preparation of allylcarbinyl ester. The red solid (1.5 g., 0.0058 mole, 72%) thus obtained was chromatographed on a column packed with acid-washed alumina (Merck) with Skelly B as the eluant. The first four fractions (0.031 g., m.p. 71-72°; 0.076 g., m.p. 72.5-73°; 0.099 g., m.p. 73-73.5°; and 0.162 g., m.p. 73-73.5) were combined and rechromatographed. The first 200 mg. collected (m.p. 70-72°) was crystallized from pentane at -40° to give cyclobutyl *p*-phenylazobenzoate, m.p. 72-72.5°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.87; H, 5.53; N, 9.99.

The n.m.r. spectrum (332 mg./ml. in carbon tetrachloride, B in Fig. 3) showed signals due to the tertiary cyclobutyl hydrogen from -50 to 4 p.p. 10⁸, the secondary cyclobutyl hydrogens from 233 to 312 p.p. 10⁸ and the aromatic hydrogens from -339 to -245 p.p. 10⁸. There was an unassigned peak at 368 p.p. 10⁸.

Reaction of Diazocyclobutane with *p*-Phenylazobenzoic Acid in Toluene-Ethanol.—To a solution of 0.5 g. (0.0035 mole) of *N*-cyclobutyl-*N*-nitrosourea in 100 ml. of toluene at -40° was added a solution of lithium ethoxide (from 0.05 g. (0.007 g. atom) of lithium) in 25 ml. of toluene and 2 ml. of ethanol. After 30 min., the dark pink color of I had developed and 0.8 g. (0.0035 mole) of *p*-phenylazobenzoic acid was added. The solution was warmed to room temperature; then washed with water, 5% potassium carbonate solution until all the acid was removed, and finally with water; dried over anhydrous magnesium sulfate; filtered; and evaporated to give 0.172 g. (20%) of a red oil. Chromatography of 75 mg. of this material on a column packed with acid-washed alumina with 5% benzene in Skelly B gave two fractions (31 and 39 mg.). Elution with ether gave a third fraction (3 mg. of yellow solid) which was not identified.

The first two fractions were identified by their infrared spectra to be the cyclobutyl and cyclopropylcarbinyl esters, respectively. The relative proportions of the two esters based on the weights of the fractions was 44:56. This ratio holds a certain degree of uncertainty due to the presence of an impurity in both fractions as shown by their infrared spectra (absorptions at 2920, 1460 and 1375 cm^{-1}), possibly due to incomplete removal of the solvent from the samples.

Ethyl *p*-Phenylazobenzoate (IX).—A solution of 0.5 g. of *p*-phenylazobenzoyl chloride in 2 ml. of ethanol was treated by the procedure used in the preparation of allylcarbinyl ester. The precipitate thus obtained was crystallized from ethanol-water to give ethyl *p*-phenylazobenzoate, m.p. 88-89° (lit.²⁷ 85-86°).

Reaction of Diazocyclobutane with *p*-Phenylazobenzoic Acid in Ether-Ethanol.—To a stirred solution of 2.5 g. (0.017 mole) of *N*-cyclobutyl-*N*-nitrosourea in 100 ml. of ether at -40° was added a slurry of 2.5 g. of lithium ethoxide in 50 ml. of ether. The lithium ethoxide was prepared from 0.25 g. (0.036 g. atom) of lithium and ethanol which corresponds to 1.8 g. of lithium ethoxide. There was therefore 0.7 g. of ethanol in the lithium ethoxide.

The pink color of the diazo compound I developed slowly under these conditions and appeared to have reached a maximum after 1 hour. To one-third of the ether solution was added 1.6 g. (0.07 mole) of *p*-phenylazobenzoic acid. This mixture was warmed to room temperature and 100 ml. of chloroform was added to dissolve the precipitated solid. The solution was washed with water, 5% potassium carbonate and water, dried over Drierite, filtered and evaporated to give 0.5 g. of an oil.

(27) E. O. Woolfolk, F. E. Beach and S. P. McPherson, *J. Org. Chem.*, **20**, 391 (1955).

Partial separation of this oil by chromatography on acid-washed alumina gave three equal fractions which were analyzed by infrared analysis by the base line method of Heigl,²⁸ to contain cyclobutyl, cyclopropylcarbonyl and ethyl *p*-phenylazobenzoates. The relative proportions of the three esters found by this method were 27:26:26, respectively. Infrared analysis of the oil without partial chromatographic separation gave the relative proportions of 28:29:27 for the three esters, respectively.

The Reaction of Diazocyclobutane with *p*-Phenylazobenzoic Acid in Tetrahydrofuran-Methanol.—To 2 g. (0.014 mole) of *N*-cyclobutyl-*N*-nitroso-urea in 75 ml. of tetrahydrofuran and 25 ml. of methanol at -40° was added dropwise a solution of 0.8 g. (0.015 mole) of sodium methoxide in 25 ml. of methanol. The red color of diazocyclobutane developed immediately but started to fade soon after the addition was complete. Immediately 2.4 g. (0.01 mole) of *p*-phenylazobenzoic acid was added. The mixture was warmed to room temperature, filtered, and the filtrate evaporated to 10 ml. Ether (100 ml.) was added and the solution was washed with water, 5% potassium carbonate solution, water, 5% ferrous sulfate solution and water; dried over Drierite; filtered and evaporated to give 0.5 g. of a red oil.

The oil (0.442 g.) was separated by chromatography on a column packed with acid-washed alumina (Merck). Elution with 5% benzene in Skelly B yielded two fractions (70 mg., m.p. 66–67.5°; and 43 mg. m.p. 73.5–77°). Elution with a 50:50 solution of benzene in Skelly B which contained 0.5% of ether gave two fractions (166 mg. of a red oil and 61 mg. of a red oil). Elution with 1% ether in benzene gave two fractions (29 mg. of red oil and 6 mg. of red oil). Elution with 5% ether in benzene gave one fraction (6 mg. of red oil), with 10% ether in benzene gave one fraction (17 mg. of a yellow oil) and with chloroform gave one fraction (7 mg. of a yellow oil). The total recovery was 0.405 g. or 92%.

A total of three runs were carried out and the corresponding fractions from the three chromatograms were combined. The first fraction (70 mg., m.p. 66–67.5°) had an infrared spectrum identical to that of cyclobutyl *p*-phenylazobenzoate.

The second fraction (43 mg. m.p. 73.5–77°) had an infrared spectrum which showed absorption at 2920 and 1375 cm^{-1} in addition to the absorptions due to cyclopropylcarbonyl *p*-phenylazobenzoate. These absorptions have been noted in previous reactions but could not be identified.

The third fraction (166 mg. of red oil) with the corresponding fractions from two other runs (total of 495 mg.) was chromatographed through a column packed with acid-washed alumina (Merck). Elution with benzene gave a fast moving band (24 mg. red oil) and a broad band which was divided into two fractions. The first of these (278 mg., m.p. 47–50°) was crystallized from pentane at -40° to give ω -cyclobutoxybutyl *p*-phenylazobenzoate, m.p. 52–53°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_3\text{N}_2$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.46; H, 6.90; N, 7.85.

The n.m.r. spectrum (356 mg./ml., in carbon tetrachloride, D in Fig. 3) showed signals due to aromatic hydrogens from -357 to -258 p.p. 10^8 , methylene and cyclobutyl hydrogens from 288 to 332 p.p. 10^8 , and methylenoxy from 46 to 93 p.p. 10^8 for the methylene α to the ester oxygen and from 152 to 180 p.p. 10^8 for the methylene α to the ether oxygen.

The fourth fraction (61 mg. of red oil) with the corresponding fractions from two other runs (total of 150 mg.) was chromatographed through a column packed with acid-washed alumina (Merck). Elution with benzene gave a single broad band which was divided into three fractions. The center fraction (80 mg. of red oil) was crystallized from pentane at -40° to give 21 mg. of ω -cyclopropylcarbonylbutyl *p*-phenylazobenzoate, m.p. 46–47°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_3\text{N}_2$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.77; H, 6.96; N, 8.07.

A further 51 mg., m.p. 41–43°, was recovered from the mother liquors and the other two fractions from the chromatogram.

The infrared spectra of both the ω -cyclobutoxybutyl and ω -cyclopropylcarbonylbutyl esters showed absorptions at 1710 and 1604 cm^{-1} , typical of *p*-phenylazobenzoates.

The n.m.r. spectrum (255 mg./ml., in carbon tetrachloride, E in Fig. 3) showed signals due to aromatic hydrogens from -335 to -244 p.p. 10^8 , methylene hydrogens from 303 to 318 p.p. 10^8 , cyclopropyl hydrogens at 363 and from 435 to 477 p.p. 10^8 , and methylenoxy hydrogens from 48 to 64 p.p. 10^8 for the methylene α to the ester oxygen and from 140 to 171 p.p. 10^8 for the methylenes α to the ether oxygen.

Based on two chromatograms the molar percentages of the components formed in this reaction were: cyclobutyl (20%), cyclopropylcarbonyl (14%), ω -cyclobutoxybutyl (40%) and ω -cyclopropylcarbonylbutyl (14%) *p*-phenylazobenzoates and unidentified products (12%). The molecular weight of the unidentified products was assumed to be the same as the ω -cyclobutoxybutyl *p*-phenylazobenzoate. The yield in this reaction of ester product was 8% based on the *N*-cyclobutyl-*N*-nitroso-urea used as starting material. There is a fair degree of uncertainty in the percentage of the cyclopropylcarbonyl ester due to the component which gives infrared absorption at 2920 and 1375 cm^{-1} .

Reaction of Diazocyclobutane with Ethyl Acrylate.—To a solution of 5.5 g. (0.038 mole) of *N*-cyclobutyl-*N*-nitroso-urea in 100 ml. of ether at -40° was added a solution of lithium ethoxide (made from 0.45 g. (0.06 mole) of lithium) in 2 ml. of ethanol and 20 ml. of ether. The red color of the diazo compound developed slowly over a period of 5 minutes. After 15 minutes a 5% solution of ethyl acrylate in ether was added dropwise until the red color had disappeared. A total of 2 g. (0.020 mole) of ethyl acrylate was thus added. The solution was warmed to room temperature, washed with water, dried over Drierite, filtered and evaporated to give 4.2 g. of an oil. The oil was heated in a 500-ml. round-bottom flask fitted with a reflux condenser to induce pyrolysis. The flask was heated until the evolution of nitrogen was apparently complete. The residue was distilled through a modified Holzman column²⁹ to give 1.4 g., b.p. 75–110° (15 mm.).

A vapor chromatogram of this sample through two didecyl phthalate columns at 175° with a helium flow rate of 40 cc per min. showed 5 peaks at 36, 46, 52, 57.5 and 74 minutes. The relative areas of these peaks, determined as the average of two runs by planimeter measurements and by determination of the weight of the curves cut out of paper, were, respectively 1, 30, 13, 4 and 52% and 1, 29, 12, 4 and 54%.

Two more runs were made of this reaction in which 6 g. and 4.5 g. of *N*-cyclobutyl-*N*-nitroso-urea were used. The product from the pyrolysis was distilled through a modified Holzman column²⁹ to give 0.94 g., b.p. 77–83° (11 mm.); 0.75 g., b.p. 83–85° (11 mm.); and 0.75 g., b.p. 93–96° (11 mm.).

Vapor chromatography of 100- λ portions of these fractions gave sufficient quantities of the 46-, 52- and 74-min. components for identification.

The 74-min. component was ethyl *trans*- β -cyclobutylacrylate (XIV), n_D^{20} 1.4618. The infrared spectrum (chloroform) had absorption at 1700, 1645 and 982 cm^{-1} characteristic of a *trans*- α,β -unsaturated ester.¹⁶ The n.m.r. spectrum (200 mg./ml. in carbon tetrachloride, F in Fig. 3) showed cyclobutyl hydrogen signals from 266 to 297 p.p. 10^8 , ethoxy hydrogen signals at 69 (quartet) and 355 (triplet) p.p. 10^8 and olefin hydrogen signals at -244 , -228 , -205 and -190 (quartet) and -103 and -64 (doublet) p.p. 10^8 .

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 69.95; H, 9.09.

The 46-min. component was ethyl spirohexane-1-carboxylate (XIII), n_D^{20} 1.4494. The infrared spectrum (chloroform) showed an ester band at 1705 cm^{-1} but no absorption in the 1640 cm^{-1} region. The n.m.r. spectrum (200 mg./ml. in carbon tetrachloride, H in Fig. 3) showed an unresolved peak for cyclobutyl hydrogens at 267 p.p. 10^8 , ethoxy hydrogen signals at 70 (quartet) and 357 (triplet) p.p. 10^8 . Among the signals for the triplet there were a number of peaks at 314, 326, 349, 370, 380, 387, 398 and 408 p.p. 10^8 .

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 70.11; H, 9.40.

(28) J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

(29) C. W. Gould, Jr., G. Holzman and C. Niemann, *ibid.*, **20**, 361 (1948).

The 52-min. component was ethyl *cis*- β -cyclobutylacrylate (XV), n_D^{20} 1.4578. The infrared spectrum (chloroform) had absorption characteristic of an α,β -unsaturated ester at 1700 and 1635 cm^{-1} .¹⁶ The n.m.r. spectrum (135 mg./ml. in carbon tetrachloride, G in Fig. 3) showed cyclobutyl hydrogen signals from 239 to 293 p.p. 10⁸ ethoxy hydrogen signals at 68 (quartet) and 357 (triplet) p.p. 10⁸ and olefin hydrogen signals at -174, -152, -145, and -125 (quartet) and -88 and -58 (doublet) p.p. 10⁸.

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{O}_2$: C, 70.10; H, 9.15. Found: C, 70.49; H, 8.86.

Isolation of a Mixture of Cyclobutyl Ethyl Ether and Cyclopropylcarbinyl Ethyl Ether from a Photochemical Reaction of Diazocyclobutane.—In the workup of reaction mixtures from the irradiation of solutions of diazocyclobutane in *trans*-2-butene-ethanol,¹⁷ a number of volatile fractions were obtained. One of these, b.p. 80° (130 mm.) to b.p. 110° (25 mm.), when it was further purified by vapor chromatography through a didecyl phthalate column (retention time 16.5 min. at 70° with a helium flow rate of 60 cc./min.) was found to have the properties of a mixture of cyclobutyl ethyl ether and cyclopropylcarbinyl ethyl ether, n_D^{20} 1.4042 (lit.³⁰ n_D^{20} 1.4050, b.p. 99.5–100.8° for cyclopropylcarbinyl ethyl ether). The infrared spectrum (chloroform) showed no absorption between 1500 and 2700 cm^{-1} or above 3150 cm^{-1} . There was absorption at 3080, 2970, 2860 and 1115 cm^{-1} .

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}$: C, 71.95; H, 12.08. Found: C, 71.74; H, 12.05.

The n.m.r. spectrum (215 mg./ml. in carbon tetrachloride, I in Fig. 3) showed a triplet at 353, 371 and 387 p.p. 10⁸ and groups of signals from 114 to 181 p.p. 10⁸, 273 to 314 p.p. 10⁸ and 431 to 461 p.p. 10⁸.

A sample of this ether mixture when fractionated through two didecyl phthalate columns at 70° with a flow rate of 50 cc./min. showed two peaks of about equal heights at 45.8 and 49 min.

Formation of Cyclobutyl Ethyl Ether and Cyclopropylcarbinyl Ethyl Ether in the Preparation of Diazocyclobutane.—

(30) C. G. Bergstrom and S. Siegel, *THIS JOURNAL*, **74**, 145 (1952).

To a solution of 4.5 g. (0.031 mole) of *N*-cyclobutyl-*N*-nitrosourea in 100 ml. of ether at -45° was added a solution of lithium ethoxide (from 0.5 g. (0.07 g. atom) of lithium) in 25 ml. of ethanol and 25 ml. of ether. The diazo compound formed immediately to give a cherry-red solution. The solution was turbid but homogeneous. Seventy-five ml. of the solution was transferred to another flask at -45°. A solution of 1.5 g. (0.015 mole) of benzaldehyde in 15 ml. of ether was added to this solution, and the color disappeared in 3 min. The remaining solution of diazo compound was allowed to warm to room temperature, by which time the color of the diazo compound had disappeared. The color was still present but faint at 0°.

Both reactions were washed with 4 portions of 25 ml. of water, dried over anhydrous calcium chloride and filtered. Twenty ml. of freshly distilled decalin was added to each of the solutions and they were distilled through a semi-micro spinning band column to give, in addition to an ether fraction (b.p. 34°), a fraction b.p. 42 to 160°. The weight of the latter fraction was 0.833 g. for the reaction which included benzaldehyde and 0.727 g. for the reaction which did not.

Vapor chromatography of the foreruns through two didecyl phthalate columns at 80° showed only ether, at 6.6 minutes. Chromatography of the other fractions at 90° gave the following results. The yields are based on areas of the peaks.

Component	Benzaldehyde reacn., min.	%	Thermal reacn., min.	%
Ether	6.1	17	6.0	23
Ethanol	7.4	47	7.3	36
Mixed ethers	28.4, 29.2	11	28.0, 28.9	13
Decalin	120	25	120	28

The retention times of cyclobutyl and cyclopropylcarbinyl ethyl ethers from the photochemical reaction above at 90° were 27.8 and 28.8 min. The estimated yields of these ethers for the benzaldehyde and thermal reactions were 92 mg. (6%) and 94 mg. (6%), respectively.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF TEXAS AND THE UNIVERSITY OF LONDON, QUEEN MARY COLLEGE]

The Synthesis and Properties of the Perinaphthenylium Cation

BY R. PETTIT

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The synthesis of perinaphthenylium perchlorate is described. This salt is thermodynamically stable; although very reactive, it can be stored under nitrogen. The salt is insoluble in non-polar solvents though it readily dissolves in nitromethane and 60% perchloric acid. The perinaphthenylium cation reacts with water to produce perinaphthene and perinaphthenone; it reacts with zinc dust to form porphyrane.

Simple L.C.A.O. molecular orbital calculations^{1a} predict that the perinaphthenyl cation (Ia), anion (Ib) and radical (Ic) should all possess the same value of the π -electron delocalization energy, namely, 5.83 β ($\beta = 20$ kcal.). This follows from the fact that like the allyl and triphenylmethyl systems, the perinaphthenyl system is an odd alternant hydrocarbon and the extra one and two electrons possessed by the radical and anion, respectively, occupy a molecular orbital of energy zero (with reference to the energy of an electron in the p_z -orbital of an isolated sp^2 -hybridized carbon atom). Furthermore, similar calculations show

(1) (a) M. J. S. Dewar and R. Pettit, unpublished results. Other independent calculations have been reported by V. Gold and F. I. Tye, *J. Chem. Soc.*, 2184 (1956); (b) based upon a value of 4.13 β for the π -electron delocalization energy of 1-vinylnaphthalene as given by C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Vol. III, p. 68.

that the gain in π -electronic energy in deriving each of the above species following loss of a hydride ion, hydrogen atom or proton from perinaphthene (II) should be 1.7 β or 34 kcal.^{1b} These two facts together then predict that the perinaphthenyl cation, radical and anion might display unusual stability and, in a suitable environment, each may be capable of more than a transient existence.

The successful preparations of a salt of the perinaphthenylium cation and of the perinaphthenyl radical have recently been reported^{2,3} and solutions containing the corresponding anion⁴ have been made. Even prior to these reports there was considerable evidence supporting the

(2) R. Pettit, *Chemistry & Industry*, 1306 (1956).

(3) D. H. Reid, *ibid.*, 1504 (1956).

(4) V. Boekelheide and C. E. Larrabee, *THIS JOURNAL*, **72**, 1245 (1950).