added. The mixture was stirred for 0.5 hr., allowed to stand 3 hr., and filtered. The precipitate was washed three to four times with water and the filtrate was evaporated to dryness *in vacuo*. Yield 34.8 g. of crude product, used as such for the subsequent step.

Anal. Calcd. for $C_{16}H_{21}NO_3$: C, 69.78; H, 7.68; N, 5.08. Found: C, 69.94; H, 7.65; N, 4.92. The product gave a positive reaction with ferric chloride.

The hydrochloride had m.p. 172–173°. *Anal.* Calcd. N, 4.49. Found: N, 4.48.

1-Methyl-2-benzyl-4-piperidone (VI).—A mixture of 30.8 g. of V and 125 ml. of 1:1 hydrochloric acid was refluxed 2.5 hr. to a negative ferric chloride reaction. The mixture was filtered hot with charcoal, and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in water and the solution made alkaline with 50% potassium hydroxide, saturated with potassium carbonate and then extracted with ethyl ether. The extract was dried over sodium sulfate then over potassium carbonate and evaporated to dryness *in vacuo*. The residue was distilled *in vacuo;* yield 13 g., b.p. 135–140°/0.2–0.3 mm. The product, when exposed to air, turned brown-red very rapidly.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.81; H, 8.42; N, 6.88. Found: C, 77.10; H, 8.30; N, 6.65.

1-Methyl-2-benzyl-4-piperidol (VII).—Two grams of VI was dissolved in 40 ml. of methanol and 2 ml. of water. The solution was cooled on ice and 0.375 g. of sodium borohydride was added in 15 min. The reaction was exothermic. The solution was allowed to stand 3 hr. at 25° and then methanol was removed by distillation. The residue was extracted with a large amount of ethyl ether and the extract was dried over potassium hydroxide and concentrated to a small volume. On cooling 1.4 g. of VII melting at 115–116° separated.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.32; N, 6.81. Found: C, 76.28; H, 9.15; N, 6.92.

Condensed Cyclobutane Aromatic Compounds. XX. Photolysis of the Isomeric 3,3-Diphenyldiazoindanones

M. P. CAVA, D. G. MCCONNELL, K. MUTH, AND M. J. MITCHELL

Evans Chemical Laboratory, The Ohio State University, Columbus 10, Ohio

Received November 27, 1961

The photolysis of α-diazoindanones has proven to be a method of general applicability in the synthesis of benzocyclobutene derivatives.[1,2] In an attempt to prepare 2,2-diphenylbenzocyclobutene-1-carboxylic acid (I) by this method, we have studied the photolysis of 3,3-diphenyl-1-diazo-2-indanone (II).[2] Ultraviolet irradiation of diazo ketone II was carried out in a two-phase solvent system of ether and aqueous sodium bicarbonate, using a Pyrex glass vessel; however, acidification of the aqueous phase gave, not the expected benzocyclobutene acid (I), but rather a lactone (IV) of the same composition, $C_{21}H_{16}O_2$. Similarly, photolysis of the isomeric diazo ketone (III) gave only lactone IV.

Hydrogenolysis of IV in ethanol with palladium-on-charcoal catalyst gave *o*-(diphenylmethyl)phenylacetic acid (V). The identity of this acid was confirmed by an independent synthesis, starting from α,α-diphenyl-*o*-toluic acid (VI),[3] and proceeding *via* the acid chloride (VII) and the diazo ketone (VIII) to acid V.

In the formation of lactone IV, it seems likely that the initial process is a ring contraction of the diazo ketone (II or III) to give the benzocyclobutene acid (I). The acid, in the form of its sodium salt (Ia), might reasonably be expected to undergo cleavage of the four-membered ring to give an intermediate (IX) of the *o*-quinodimethane type, since such cleavage would be greatly facilitated by the resulting conjugation of the carboxyl and the phenyl substituents with the quinodimethane system.[4] Re-aromatization of the six-membered ring could then be accomplished by a simple 1,4-addition of water to IX, which would result in the formation of the sodium salt (X) of a hydroxy acid. Finally, acidification would cause ring closure to give the observed lactone IV. These proposals are supported by the fact that lactone IV, once it is formed, is not saponified by (nor is it soluble in) aqueous sodium bicarbonate solution. Hence, the material which is found dissolved in the bicarbonate phase of the reaction mixture and which gives the lactone on acidification, must be the sodium salt of the benzocyclobutene acid (Ia) or, what is more likely, of the hydroxy acid (X).

In preparing diazo ketone II, only a few modifications were made in the sequence of reactions reported in the literature.[5] Thus, 3,3-diphenyl-2-oximino-1-indanone was prepared from 3,3-diphenyl-1-indanone[6] by treatment with *n*-butyl nitrite and potassium *t*-butoxide in *t*-butyl alcohol in yields (80–85%) which are superior to those (40–50%) obtained by the literature method (*n*-butyl nitrite and sodium ethoxide in ethanol).[7] Diazo ketone II was found to be more easily purified by chromatography on Woelm Grade II neutral alumina with 1:1 methylene chloride–petroleum ether than by recrystallization from cyclohexane as described previously.[2]

Experimental[8]

3,3-Diphenyl-2-oximino-1-indanone.—3,3-Diphenyl-1-indanone[6] (25.0 g., 0.088 mole) was added with stirring and under nitrogen to a solution of potassium *t*-butoxide in *t*-butyl alcohol [prepared from 7.4 g. (0.189 mole) of potassium and 320 ml. of *t*-butyl alcohol]. When the indanone had

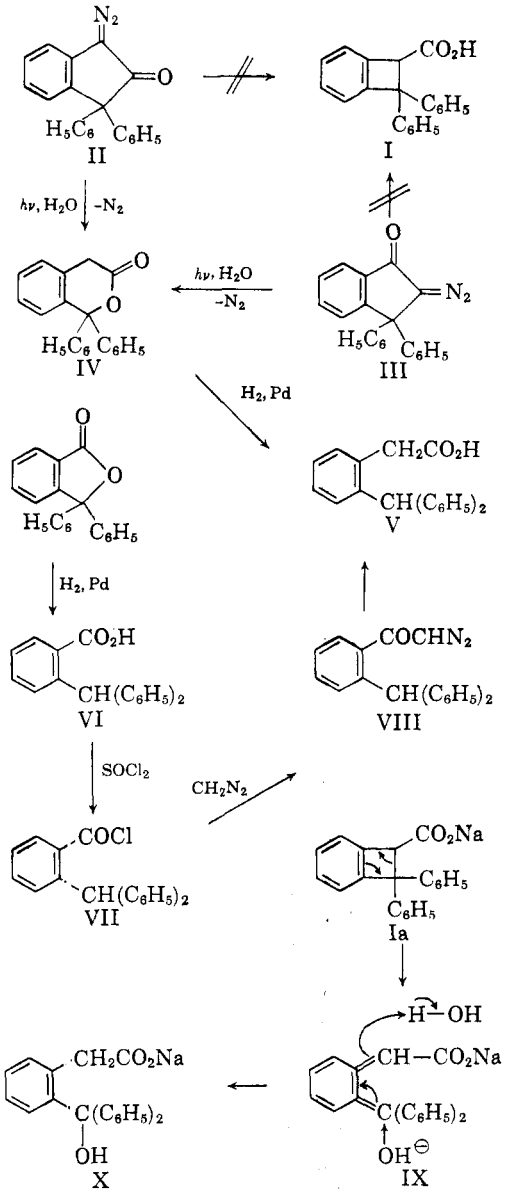
(1) L. Horner, W. Kirmse, and K. Muth, *Chem. Ber.*, **91**, 430 (1957).

(2) M. P. Cava, R. L. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

(3) R. Brisson, *Ann. chim.*, [12] **7**, 311 (1952).

(4) A precedent for this proposal is found in the chemistry of 1,2-diphenylbenzocyclobutene: The compound readily undergoes ring cleavage under mild conditions to give the highly reactive species, α,α′-diphenyl-*o*-quinodimethane. *Cf.* F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.*, **80**, 6149 (1958); M. P. Cava, M. J. Mitchell, and A. A. Deana, *J. Org. Chem.*, **25**, 1481 (1960).

(5) For a description of the latter stages of the sequence, see ref. 2.



dissolved completely (30 min.), 25 ml. of *n*-butyl nitrite was added. The reaction mixture was stirred for 12 hr. at room temperature and was then poured into a mixture of 500 ml. of ether and 2 kg. of crushed ice. The ether layer was extracted repeatedly with 0.05 *N* aqueous sodium hydroxide solution until the last few extracts were almost colorless. Acidification of the combined aqueous extracts with acetic acid gave crude 3,3-diphenyl-2-oxime-1-indanone, which was recrystallized from acetic acid to give 23.4 g. (85%) of product, m.p. 198–207°; reported,[7] m.p. 206–209°.

Photolysis of 3,3-Diphenyl-1-diazo-2-indanone (II).—A solution of 500 mg. of 3,3-diphenyl-1-diazo-2-indanone (II) in 200 ml. of ether was mixed with 200 ml. of 1% aqueous sodium bicarbonate solution in a 1-l. Pyrex flask. The resulting suspension was stirred under nitrogen and irradiated for 12 hr. with a Westinghouse 100-w. mercury spotlight, without filter. The two phases of the reaction mixture were separated and subjected to several counter-extractions with ether and aqueous sodium bicarbonate solution. The aqueous extracts were combined and acidified with dilute hydrochloric acid; the resulting suspension was extracted several times with ether, the ether extracts were evaporated to dryness, the residue was dissolved in methylene chloride and chromatographed with the same solvent on Woelm Grade II acid alumina to give 234 mg. (48%) of lactone IV, m.p. 163–164°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.86; H, 5.25.

Photolysis of 3,3-Diphenyl-1-diazo-2-indanone (III).—Under the same conditions which were used in the photolysis of diazoketone II (see above), 500 mg. of 3,3-diphenyl-1-diazo-2-indanone gave 142 mg. (29%) of lactone IV.

α,α-Diphenyl-*o*-toluic Acid (VI).—3,3-Diphenylphthalide[9] (147.3 mg., 0.515 mmole) was dissolved in 10 ml. of absolute methanol and hydrogenolyzed at room temperature and atmospheric pressure and in the presence of 43.2 mg. of 5% palladium-on-charcoal catalyst. The compound absorbed 11.9 ml. (STP) of hydrogen during 2 hr. [11.5 ml. (STP) is equivalent to 0.515 mmole of hydrogen] and gave 145 mg. (98%) of α,α-diphenyl-*o*-toluic acid, m.p. 159–160° (reported,[10] m.p. 160–162°), which was used without purification.

β-Benzhydryl-α-diazoacetophenone (VIII).—A solution of α,α-diphenyl-*o*-toluyl chloride[11] in 25 ml. of benzene [prepared by refluxing 0.973 g. (3.38 mmoles) of the toluic acid (VI) with 0.413 g. (3.5 mmoles) of thionyl chloride in 25 ml. of 1:1 benzene–methylene chloride for 2.5 hr., removing the solvent and the excess thionyl chloride *in vacuo*, and adding benzene to the residue] was added dropwise to a chilled solution of excess diazomethane in dry ether. Evaporation of the solvent *in vacuo* gave an oil which was extracted with a minimal amount of warm benzene. Petroleum ether (b.p. 30–60°) was added dropwise to the extract until a brief cloudiness was observed. On standing, the extract deposited 0.821 g. (78%, based on acid VI) of pure product, *o*-benzhydryl-α-diazoacetophenone (VIII), obtained as pale yellow crystals, m.p. 114–116°. The analytical sample was recrystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 80.95; H, 5.52; N, 9.33.

Conversion of Diazoketone VIII into Acid V.—A solution of 100 mg. (0.32 mmole) of *o*-benzhydryl-α-diazoacetophenone (VIII) was irradiated in the usual way in a quartz vessel which was cooled by an air jet. After 12 hr., the reaction mixture was evaporated to an oil and the oil was extracted several times with hot 5% aqueous sodium bicarbonate solution. The extracts were combined and acidified with dilute hydrochloric acid to give 13 mg. of crystalline *o*-(diphenylmethyl)phenylacetic acid (V), m.p. 207–209°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.40; H, 6.01. Found: C, 83.44; H, 6.24.

Hydrogenolysis of Lactone IV.—Lactone IV (11.4 mg., 0.0375 mmole), obtained by the photolysis of 3,3-diphenyl-1-diazo-2-indanone (II), was dissolved in 5.0 ml. of methanol and was hydrogenolyzed in a microhydrogenation apparatus in the presence of 9.5 mg. of 5% palladium-on-charcoal (prereduced with hydrogen). The compound absorbed 0.847 ml. (STP) of hydrogen during 4 hr. [0.729 ml. (STP) is equivalent to 0.0374 mmole of hydrogen]. The product, *o*-(diphenylmethyl)phenylacetic acid (V), m.p. 206–208°, was identical in its infrared spectrum with an authentic sample prepared from diazo ketone VIII (see above).

Acknowledgment.—The partial support of this work by the National Science Foundation is gratefully acknowledged.

(6) Prepared from triphenylpropionic acid [P. Gagnon, *Ann. chim.*, [10] **12**, 296 (1929)]. The propionic acid was prepared from triphenylcarbinol and malonic acid [L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1735 (1927)].

(7) C. F. Koelsch and C. D. Le Claire, *J. Org. Chem.*, **6**, 531 (1941).

(8) Melting points are corrected. The analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(9) H. Bauer, *Chem. Ber.*, **38**, 240 (1905).

(10) R. C. Fuson and D. E. Brasure, *J. Am. Chem. Soc.*, **77**, 3131 (1955).

(11) L. W. Jones and F. B. Root, *J. Am. Chem. Soc.*, **48**, 191 (1926).