

Intramolecular Reactions of Olefinic Diazo Ketones¹

MAGED M. FAWZI AND C. DAVID GUTSCHE

Department of Chemistry, Washington University, St. Louis, Missouri

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The copper-catalyzed decomposition of a series of unsaturated diazo ketones has been studied to assess the usefulness of the method for the synthesis of compounds containing a bicyclo[*x*.1.0]moleity. On the basis of the results it appears that the proximity of the olefinic center and the diazoalkyl center is an important factor in determining the success of the reaction, while the nature or degree of substitution at the olefinic center has relatively little effect.

A number of years ago an investigation was initiated in this laboratory which was directed to the intramolecular reaction of olefinic diazo ketones. During the course of this work, several reports of similar and in some cases identical reactions have appeared.²⁻⁸ The

present communication records several examples which, with one exception, have escaped the published attention of others and which, it is hoped, will serve to round out some aspects of the scope and limitations of this synthesis.

To study the effect of the distance between the diazoalkyl group and the olefinic group and to study the effect of changing the steric and electronic environment around the olefinic group, a series of olefinic diazo ketones of structure I was synthesized (Scheme I). The yields of bicyclic ketones, II obtained upon copper-

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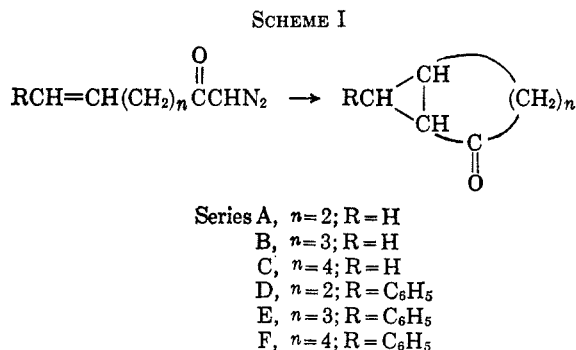
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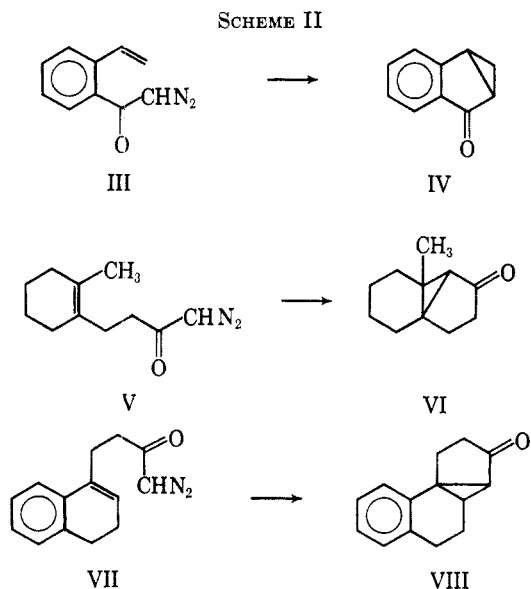
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catalyzed decomposition of these diazo ketones, I, were as follows: series A (59%); series B (37%); series C (ca. 3%); series D (59%); series E (30%); series F (very low). Thus, it is apparent that the proximity of the olefin to the diazoalkyl group is an important factor in determining the success of the cyclization, while the nature of the substitution at the double bond appears to have little effect.

The possibility of achieving cyclization in three other cases where phenyl substitution or severe hindrance is present at the olefinic bond is demonstrated by the conversions III to IV, V to VI, and VII to VIII (Scheme II), in 41.5, 29, and 22% yield, respectively.



On the basis of the present study, on the basis of the systematic study by Doering, Fossel, and Kaye,^{3b} and on the basis of the several other reports of intramolecular olefin-diazo ketone reactions, it appears that the method has considerable utility in the preparation of polycyclic compounds containing interesting structural features.

Experimental Section⁹

Preparation and Decomposition of 1-Diazo-5-hexen-2-one (I-A).—A 6.0-g sample (0.05 mole) of 4-pentenoyl chloride,

(9) All melting points are corrected; all boiling points are uncorrected. The infrared spectra were measured with a Perkin-Elmer Infracord spectrometer; the nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer. The vapor phase chromatographic analyses were performed on (a) a Perkin-Elmer Model 154 B instrument containing a 0.25 in. \times 8 ft column packed with 20% Dow-Corning 710 silicone oil on firebrick and (b) a homemade instrument containing a 0.25 in. \times 16 ft

prepared by the action of oxalyl chloride¹⁰ on the sodium salt of 4-pentenoyl chloride,¹¹ was converted with 0.3 mole of ethereal diazomethane to 5.7 g (92%) of 1-diazo-5-hexen-2-one, obtained as a yellow oil which was used without further purification (ν_{\max}^{liq} cm⁻¹ 2100, 1645 characteristic of α -diazo ketones^{12,13}). The diazo ketone was dissolved in ca. 550 ml of cyclohexane, treated with 1 g of anhydrous copper sulfate, and refluxed for 18 hr. The solvent was then largely removed by fractionation through a 2-ft Vigreux column, the copper sulfate was removed by filtration, the infrared spectrum of the residue was checked for the disappearance of the bands characteristic of the diazo ketone, and the residue was distilled in a short-path apparatus to yield 2.6 g (59%) of product 110° (30 mm). Analytical vpc analysis of this material indicated that only one component was present, identified as bicyclo[3.1.0]hexan-2-one (II-A) by comparison of its infrared spectrum and vpc characteristics with an authentic sample.¹⁴ A 2,4-dinitrophenylhydrazone was obtained, after one recrystallization from ethanol, as fine, orange needles, mp 175–177° (lit.¹⁴ mp 175.5–176°). Admixture with the 2,4-dinitrophenylhydrazone prepared from authentic material showed no depression in melting point.

Preparation and Decomposition of 1-Diazo-6-hepten-2-one (I-B).—A 17.5-g sample (0.13 mole) of 5-hexenoyl chloride, prepared by the action of oxalyl chloride on the sodium salt of 4-hexenoic acid,¹⁵ was converted to the diazo ketone, dissolved in 1700 ml of cyclohexane, and decomposed in the manner described above. The volatile product consisted of 6.8 g (50%) of material boiling up to 130° (25 mm) which was shown by vpc analysis to consist of three components, present in the ratio of 1:1.6:7.2. The identity of the major component as bicyclo[4.1.0]heptan-2-one (II-B) was established by comparison of the infrared spectrum and the vpc characteristics with an authentic sample.¹⁶ A 2,4-dinitrophenylhydrazone was obtained, after one recrystallization from ethanol, as fine, orange needles, mp 155–157.5° (lit.¹⁶ mp 159.5–161.5°). Admixture with the 2,4-dinitrophenylhydrazone prepared from authentic material showed no depression in melting point.

Preparation and Decomposition of 1-Diazo-7-octen-2-one (I-C).—A 15.6-g sample (0.107 mole) of 6-heptenoyl chloride, prepared by the action of oxalyl chloride on the sodium salt of heptenoic acid,¹⁷ was converted to the diazo ketone with ethereal diazomethane, and the diazo ketone was dissolved in 1500 ml of cyclohexane and decomposed in the manner described above. The volatile product (distilling up to 115° at 8 mm) consisted of 1.37 g (10.5%) of a liquid which was shown by vpc analysis to consist of four materials present in the ratio of 1.8:1.8:1.8:1. The probable identity of the third peak as bicyclo[5.1.0]octan-2-one was established by enriching the product mixture with an authentic sample of this compound,¹⁸ prepared by the reaction of 4-hydroxycycloheptene with iodomethylzinc iodide (57% yield) followed by chromium trioxide oxidation (54% yield).

Preparation and Decomposition of 1-Diazo-6-phenyl-5-hexen-2-one (I-D).—A 10.7-g sample (0.055 mole) of 5-phenyl-4-pentenoyl chloride, prepared by the action of oxalyl chloride on the sodium salt of 5-phenyl-4-pentenoyl chloride,¹⁹ was converted to the diazo ketone with ethereal diazomethane. The diazo ketone was dissolved in 1100 ml of cyclohexane and decomposed in the manner described above to give 5.6 g (59%) of a volatile fraction (distilling up to 150° at 0.3 mm) which solidified upon standing, mp 64–66°, and which was indicated by vpc analysis to be an essentially pure sample of 6-phenylbicyclo[3.1.0]hexan-2-one

column packed with 15% A3 neopentyl glycol sebacate on 40–50 mesh type ABS Anakrom (both are products of the Analytical Engineering Laboratories, Inc., Hamden, Conn.). The ratios stated for the components in the mixtures analyzed by vpc were calculated from area measurements and are uncorrected for relative heat capacities. The microanalyses were performed by Mikroanalytisches Laboratorium, Vienna, Austria.

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(II-D). Recrystallization from an ether-petroleum ether (bp 63–69°) mixture gave white needles, mp 75–77°. *Anal.* Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.63; H, 6.93.

The semicarbazone of II-D was obtained, after two recrystallizations from ethanol, as white needles, mp 204–206°. *Anal.* Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59. Found: C, 67.88; H, 6.50.

Authentic Synthesis of 5-Phenylbicyclo[3.1.0]hexan-2-one (II-D).—A mixture of 40 g (0.21 mole) of methyl 5-phenyl-4-pentenoate and 40 g (0.35 mole) of ethyl diazoacetate was added, over a period of 4 hr, to a well-stirred suspension of 1 g of anhydrous copper sulfate in 60 g (0.32 mole) of methyl 5-phenyl-5-pentenoate maintained at 100–120°. Distillation of the resulting product gave 38 g (75% yield based on the recovery of 65 g of unreacted ester) of ethyl 2-phenyl-3-(2-carbomethoxyethyl)cyclopropane carboxylate, bp 148–149° (1 mm). *Anal.* Calcd for $C_{15}H_{16}O_4$: C, 69.54; H, 7.30. Found: C, 69.16; H, 7.29. A solution of 13.8 g (0.05 mole) of this product in 50 ml of benzene was added, in an atmosphere of nitrogen and over a period of 15 min, to a stirred suspension of 3.0 g (0.056 mole) of sodium methoxide in 50 ml of benzene. After 2 hr of stirring and refluxing, the reaction mixture was worked up to give 1.0 g (9%) of base-soluble fraction believed to be 3-carbomethoxy-6-phenylbicyclo[3.1.0]hexan-2-one. Treatment of this material with 10 ml of 1 *N* sodium hydroxide at room temperature for 4 hr followed by acidification and heating the steam bath for 10 min yielded a product which, after three recrystallizations from petroleum ether (bp 63–69°), melted at 75–78°. Admixture with 6-phenylbicyclo[3.1.0]hexan-2-one obtained by the decomposition of I-D showed no depression in melting point.

Preparation and Decomposition of 1-Diazo-7-phenyl-6-hepten-2-one (I-E).—A 117-g sample (0.5 mole) of ethyl 5-benzoylpentanoate²⁰ in 500 ml of methanol was cooled to 18–25° and treated, over a period of 15–30 min, with a solution of 10 g (0.186 mole) of potassium borohydride in 10 ml of 2 *N* sodium hydroxide and 80 ml of water. The product consisted of 107 g (90%) of ethyl 6-hydroxy-6-phenylhexanoate. A mixture of 80 g (0.34 mole) of this material and 2 g of β -naphthalenesulfonic acid was heated to *ca.* 180° under reduced pressure (*ca.* 1 mm) until no more distillate was collected (*ca.* 1.5 hr). Both the distillate and the residue were dissolved in ether, the ether solution was washed with sodium bicarbonate, the ether was removed under vacuum, and the residue was fractionated through a short Vigreux column to yield 30 g (41%) of ethyl 6-phenyl-5-hexenoate, bp 110–115° (0.3–0.5 mm). Hydrolysis of 30 g of this material yielded 22 g (84%) of 6-phenyl-5-hexenoic acid, bp 145–146° (0.5 mm). *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 76.00; H, 7.36; neut equiv, 190. Found: C, 75.69; H, 7.55; neut equiv, 190. An 8.4-g sample (0.044 mole) of the acid was converted to the acid chloride by the action of oxalyl chloride on the sodium salt of the acid, the acid chloride was treated with ethereal diazomethane to yield the diazo ketone, and the diazo ketone was dissolved in 950 ml of cyclohexane and decomposed by the method described above. The volatile product (distilling up to 155° at 0.3 mm) consisted of 3.6 g (43%) of an oil which was shown by vpc analysis to consist of three compounds present in the ratio of 1:1.04:4.85. The identity of the major component as 7-phenylbicyclo[4.1.0]heptan-2-one (II-E) was inferred from its infrared carbonyl stretching frequency (ν_{max}^{liq} 1695 cm^{-1}) and its nmr spectrum which, in addition to multiplets for the phenyl protons and the methylene protons, showed a band at τ 8.9 corresponding to one proton in a position β to the phenyl ring and β to the carbonyl group; the vinyl proton resonances of the starting compound were absent in this product.

Preparation and Decomposition of 1-Diazo-8-phenyl-7-octen-2-one (I-F).—6-Benzoylhexanoic acid,²¹ prepared by oxidation of 1-phenylcycloheptene or by base-catalyzed hydrolysis of benzoylcyclohexanone, was converted to the ethyl ester and reduced with potassium borohydride to ethyl 7-hydroxy-7-phenylheptanoate (88% yield). A 66-g sample of the hydroxy ester was treated with β -naphthalenesulfonic acid as described above for the dehydration of ethyl 6-hydroxy-6-phenylhexanoate to give 30 g (49.5%) of ethyl 7-phenyl-6-heptenoate, bp 140–142° (1.2 mm). Hydrolysis of the ester yielded the acid which, after two recrystallizations from petroleum ether (bp 63–69°), was ob-

tained as colorless prisms with mp 62–64°. *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; neut equiv, 204. Found: C, 76.59; H, 7.97; neut equiv, 204.

The acid was converted to the acid chloride by the action of oxalyl chloride on the sodium salt, the acid chloride was treated with ethereal diazomethane to yield the diazo ketone, and the diazo ketone was decomposed in the manner described above to give 1.8 g (15%) of volatile product (distilling up to 205° at 0.3 mm). Analysis of the product by vpc showed at least seven compounds to be present with no one compound predominating to any extent. No separations or identifications were attempted.

Preparation and Decomposition of *o*-Vinyl diazoacetophenone (III).—A 46.0-g sample (0.21 mole) of *o*-bromobenzoyl chloride, prepared by the action of thionyl chloride on *o*-bromobenzoic acid, in 200 ml of ether was slowly added to an ice-cold solution of 0.7 mole of diazomethane in 1500 ml of ether. The resulting diazo ketone was dissolved in 330 ml of methanol and treated, according to the directions of Newman and Beal,²² with silver benzoate and triethylamine. The product consisted, after distillation through a 6-in. Vigreux column, of 37.5 g (78%) of methyl *o*-bromophenylacetate. Reduction with lithium aluminum hydride followed by passage of the alcohol over alumina at 420–445° gave *o*-bromostyrene in 53% yield. Following published directions²³ this was converted to *o*-vinylbenzoic acid in 85% yield, mp 93–95° (lit.²³ mp 94–95°), which was taken to the acid chloride by the action of oxalyl chloride on the sodium salt. Addition of 2.15 g (0.013 mole) of *o*-vinylbenzoyl chloride to an ethereal solution containing 0.1 mole of diazomethane gave 2.10 g (93.5%) of *o*-vinyl diazoacetophenone. This was dissolved in 200 ml of benzene, treated with 1 g of copper sulfate, and the solution refluxed for 10 hr. Removal of the benzene and copper sulfate followed by distillation produced 0.50 g (28%) of volatile product (distilling up to 110° at 0.3 mm) which was shown by vpc analysis to consist of only one compound. The identity of this material as 3,4-benzobicyclo[3.1.0]hexan-2-one (IV) was shown by a comparison of the infrared and vpc characteristics with those of an authentic sample.²⁴

The 2,4-dinitrophenylhydrazone of IV was obtained as orange-red needles after recrystallization from ethanol, mp 220–222° (lit.²⁴ 208–209). *Anal.* Calcd for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.73. Found: C, 59.43; H, 3.79.

The semicarbazone of IV was obtained as colorless needles after recrystallization from aqueous ethanol, mp 204–206°. *Anal.* Calcd for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.47. Found: C, 65.60; H, 5.56.

An alternate synthesis of 3,4-benzobicyclo[3.1.0]hexan-2-one was carried out according to published procedures.²⁴ The aluminum chloride-catalyzed cyclization of 2-phenylcyclopropanecarbonyl chloride gave a 15% yield of a colorless oil, bp 80° (0.4 mm) [lit.²⁴ bp 105° (0.5 mm)]. The 2,4-dinitrophenylhydrazone prepared from this material, mp 220–222°, showed no depression in melting point when admixed with the 2,4-dinitrophenylhydrazone obtained from the decomposition of III.

Preparation and Decomposition of 1-Diazo-5-(2-methyl-1-cyclohexene)-2-butanone (V).—Following published procedures, 2-methylcyclohexanone was converted to 2-methyl-1-cyclohexene-1-acetic acid²⁵ which was submitted to an Arndt-Eistert synthesis to give in *ca.* 15% over-all yield 2-methyl-1-cyclohexene-1-propionic acid as a liquid, bp 120–125° (25 mm) lit.²⁶ 112–113° (14 mm). A 16.0-g sample of the acid was converted to the sodium salt, treated with oxalyl chloride, and the resulting acid chloride treated with ethereal diazomethane to yield 18.0 g of the diazo ketone. This was dissolved in 1800 ml of cyclohexane, treated with 1 g of copper powder, and refluxed for 18 hr. The volatile product obtained upon work-up consisted of 8.9 g (58%) of material boiling up to 165° (25 mm) and was shown by vpc analysis to consist of two compounds present in the ratio of 2.5:1. The major component, obtained in a pure form by preparative vpc, is identified as 5,6-cyclohexano-6-methylbicyclo[3.1.0]hexan-2-one (VI): ν_{max}^{liq} 1740 cm^{-1} (cyclopentanone carbonyl); nmr: no vinyl protons, singlet at τ 8.85 (accounting

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for 3 protons (methyl group).²⁷ *Anal.* Calcd for C₁₁H₁₆O: C, 80.44; H, 9.83. Found: C, 80.17; H, 9.86.

Preparation and Decomposition of 1-Diazo-4-(3,4-dihydro-1-naphthyl)-butan-2-one (VII).— β -(3,4-Dihydro-1-naphthyl)propionic acid, mp 105–108° (lit.²⁸ 105–107°), was converted to the acid chloride *via* the action of oxalyl chloride on the sodium salt, and the acid chloride was taken to the diazo ketone with ethereal diazomethane. An 18.0-g sample of the diazo ketone was dissolved in 1800 ml of cyclohexane, treated with copper powder, and refluxed for 18 hr. The solvent and catalyst were removed to

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leave a light brown oil containing some crystalline material. Filtration to remove the oily portion and one recrystallization of the solid residue yielded 3.5 g (22%) of colorless crystals, mp 94–96°. Additional crystallizations from petroleum ether (bp 63–69°) gave 5,5-benzotricyclo[5.3.0.0^{8,10}]decan-1-one (VIII) as colorless needles: mp 99–101°; $\nu_{\text{max}}^{\text{CCl}_4}$ 1740 cm⁻¹ (cyclopentanone carbonyl); $\lambda_{\text{max}}^{\text{EtOH}}$ (ϵ) 235 m μ (8700). *Anal.* Calcd for C₁₄H₁₄O: C, 85.00; H, 7.08. Found: C, 84.84; H, 7.05.

A 0.75-g sample of VIII was treated with phenylmagnesium bromide, and the resulting alcohol was dissolved in xylene and treated with iodine to effect dehydration. The product from this treatment was mixed with 0.21 g of sulfur and heated for 2 hr at 380–400° to effect dehydrogenation. From the reaction mixture there was obtained 0.15 g of 2-phenylphenanthrene, mp 192–194° (lit.²⁹ mp 195–196°), which formed a 2,4,6-trinitrofluorenone derivative, mp 164–166° (lit.²⁹ mp 168.8–169.4°).

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Structural Features Facilitating the Photodecarbonylation of Cyclic Ketones^{1,2}

J. EDWARD STARR AND RICHARD H. EASTMAN

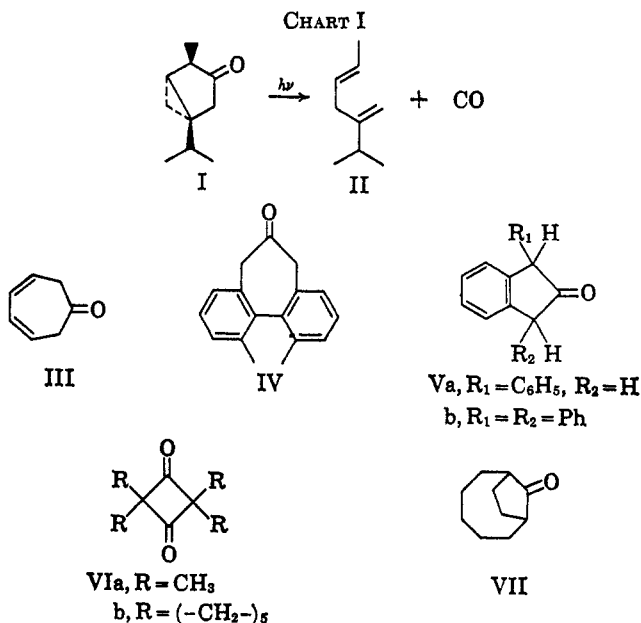
Department of Chemistry of Stanford University, Stanford, California

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A number of cyclic ketones have been synthesized and found to undergo facile photodecarbonylation in solution, a process which has been reported for only a relatively small number of ketones. It has been found that incorporation of certain structural features into a cyclic ketone, including β,γ -unsaturation, a cyclopropylcarbinyl system, and α -alkyl substitution, enables such a molecule to decarbonylate readily. An explanation for the influence of these structural features on photodecarbonylation has been advanced.

Of the various types of photochemical reactions exhibited by nonconjugated ketones in solution,^{3,4} photodecarbonylation, a process which is well known in the gas phase,^{5,6} has only recently been observed as an important pathway in solution. Among those ketones which do decarbonylate readily in the liquid phase are included *l*-thujone⁷ (I), 3,5-cycloheptadienone⁸ (III), ketone⁹ IV, derivatives of 2-indanone¹⁰ (V), derivatives of 1,3-cyclobutanedione¹¹ (VI), and bicyclo[5.2.1]decan-10-one¹² (VII) (Chart I).

The structural features facilitating decarbonylation suggested by these examples include a double cyclopropylcarbinyl system, β,γ -unsaturation, and α -alkyl substitution. In order to generalize the influence of the cyclopropane ring, as exhibited by *l*-thujone (I), and to determine whether the reaction can be extended to related systems, ketones XIV and XVI (Scheme I) and ketone XXIV (Scheme II) were prepared. In order to study the influence of α -alkyl substitution and a doubly



β,γ -double bond on liquid phase photodecarbonylation, ketones XXV, XXVI, and XXIX (Scheme III) and the readily available 2,2,6,6-tetramethylcyclohexanone (XXXVIII) were also prepared and photolyzed.

Results

I. Synthesis.—In order to prepare ketones XIV and XVI (Scheme I) containing, respectively, a cyclopropane and oxacyclopropane ring, it was considered that the unsaturated alcohol XII would be a convenient intermediate. The method of Horan and Schiessler¹³

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