borosilicate 1.6 × 1.8 mm collection tubes are easily converted into direct insertion sample containers. After fraction collection, one end of the collection tube is sealed and the resin containing the sorbed sample is pushed to the sealed end. The unsealed end is then cut off, leaving an 18–20 mm long sample container which is identical with those supplied by Du Pont. Using this technique high-quality mass spectra were obtained for samples as volatile as toluene as well as for benzaldehyde, o-xylene, benzyl chloride, 1-methylnaphthalene, acenaphthylene, α-methylstyrene, 2-ethyl-1-hexanol, acetophenone, and methyl octanoate, with quantities as low as 10^{-8} g. The background spectra caused by the XAD-4 resin as it is received is significantly reduced by vacuum degassing the resin used in preparing the collection tubes at 10^{-6} Torr and ~200° for 1 hr.

Bisdiazo Insertion in Cycloheptanone

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In connection with an investigation into steric effects on the McLafferty rearrangement,[2] we were interested in obtaining a sample of bicyclo[6.2.1]undecan-11-one (**1**). This compound has not previously been prepared, but both bicyclo[5.2.1]decan-10-one (**2**) and bicyclo[4.2.1]nonan-9-one (**3**) have been obtained by reaction of 1,4-bisdiazobutane (**4**) with cyclopentanone and cyclohexanone respectively,[3] and also by intramolecular diazoinsertion of the side chain diazoalkyl ketones **6** and **7**, respectively.[4] In the original report describing the reactions of **4**, it was stated that reaction with cycloheptanone (**8**), which would have been expected to yield the desired ketone **1**, yielded complex mixtures, and it was inferred from a study of the vapor phase chromatographic behavior of these mixtures that the bridged ring ketones could be no more than minor constituents.[3] No information was available on the alternate route to **1** via the side chain diazoalkyl ketone

1, n = 3
2, n = 2
3, n = 1

5, n = 3
6, n = 2
7, n = 1

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(1) Author to whom inquiries should be directed: Virginia Polytechnic Institute and State University.

(2) J. D. Henion and D. G. I. Kingston, unpublished work.

(3) C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).

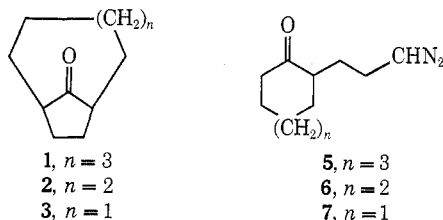(4) C. D. Gutsche and D. M. Bailey, *J. Org. Chem.*, **28**, 607 (1963).

5, but a recent paper by Wiseman and Chan showed that the structures of the two major product ketones produced by reaction of 1,3-bisdiazopropane with cyclohexanone differed from those previously assigned on the assumption of double expansion of the six-membered ring.[5] It thus seemed likely that the reaction of **4** with cycloheptanone would not prove to be a good synthetic route to the ketone **1**.

In spite of this discouraging situation, we decided to investigate the reaction of **4** with **8** in order to determine whether any of the desired product at all was produced. Since our need was for only a small quantity of **1**, it was believed that sufficient material could be obtained even from a low-yield reaction. Reaction of bis-*N*,*N*′-dinitroso-1,4-butanediamine with cycloheptanone by the method of Gutsche and Smith yielded a mixture of six major products, as detected by vapor phase chromatography (vpc). In contradistinction to the findings of Gutsche and Smith, however, one of these products (and only one), representing about 20% of the total product mixture, had a vpc retention time in the region expected for the desired ketone **1**. Examination of this product by high-resolution mass spectrometry showed that it had the composition $C_{11}H_{18}O$. The presence of a cyclopentanone ring was confirmed by its infrared absorption maximum of 1731 cm^{-1}, and the bicyclic nature of the material was shown by the absence of low-field resonances in the nmr spectrum due to vinyl protons.

In spite of the similarity of the isolated product to the ketone **1**, there were some features in its mass spectrum which were not consistent with its formulation as **1**; in particular, the compound showed a moderately intense ion at m/e 148 $[M - H_2O] \cdot ^+$ which was absent in the spectra of compounds **2** and **3**. The location of the carbonyl group in the compound was deduced by deuteration followed by mass spectral analysis of deuterium incorporation. This showed clearly that it possessed three exchangeable hydrogens, and it must, therefore, have the bicyclic structure of bicyclo[6.3.0]undecan-2-one (**13**). Other structures are incompatible with the requirement of a cyclopentanone ring in the product, the nature of the starting materials, and the absence of olefinic protons in the nmr spectrum.

A plausible rationalization for the formation of **13** from the reagents used is given in Scheme I.

Monodiazo insertion into cycloheptanone would yield the intermediate **9**, which could react to form the intermediate **10**. Rearrangement of **10** by the pinacol route (pathway A) would yield the cyclononanone **11**, while rearrangement via the epoxide **12** (pathway B) would yield the observed product **13**. The structure **11** is, of course, excluded for the product by the observed infrared adsorption of the latter; presumably, the angular strain in the transition state leading to a cyclobutane is sufficient to make pathway A energetically unfavorable as compared with pathway B. The latter pathway must also be favored over the bis insertion to give **1**, presumably also because of conformational restrictions when forming a medium-ring ketone by ring expansion.[6] It is well known that the formation of medium-ring alicyclic ketones by ring expansion of the lower homologs with diazomethane is
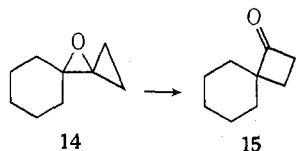
(5) J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).

(6) C. D. Gutsche, *Org. React.*, **8**, 364 (1954).

SCHEME I
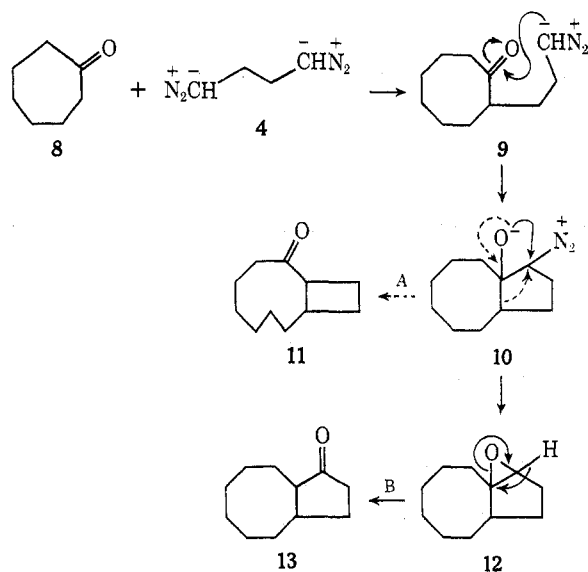
difficult unless Lewis acid catalysts are used.[7] Formation of the epoxide is an important side reaction of diazomethane ring expansions,[6] and collapse of the epoxide to give **13** is analogous to the formation of spiro[3.5]nonan-1-one (**15**) from 10-oxadispiro[2.0.5.1]-

decane (**14**).[5] In this connection, it should be noted that the ketone **13** may be an artifact of the work-up procedure, with the epoxide **12** being the initial product rather than a reaction intermediate. Wiseman and Chan showed that the epoxide **14** was, indeed, the initial product of the reaction of cyclohexanone and 1,3-bisdiazopropane and that rearrangement of **15** occurred on injection into the vpc.[5] It did not prove practicable to separate our crude reaction mixture without recourse to vpc, however; so it was not possible to confirm this point.

Many attempts under a variety of conditions were made to prepare the desired ketone **1** by the bisdiazo insertion route, but all such attempts were uniformly unsuccessful. Similarly, attempts to prepare **1** by the alternate route of Gutsche and Bailey[4] were also unsuccessful. Base-catalyzed decomposition of *N*-nitroso-*N*-acetyl-3-(2'-ketocyclooctyl) propylamine (**16**)
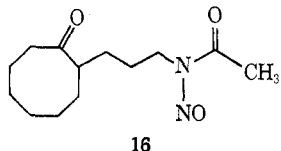
yielded a similar mixture to that obtained from **4** and **8**, and the ketone **13** was again isolated as the only product having a retention time close to that expected for **1**. This formation of **13** from the diazo ketone **9**

generated from **16** lends support to the mechanistic pathway outlined in the scheme.

Bicyclo[6.3.0]undecan-2-one (13). Method A.—A 25-ml three necked round-bottomed flask equipped with a magnetic stirrer, thermometer, addition funnel, and gas bubbler was flame dried in a stream of dry nitrogen and charged with a solution of cycloheptanone (1 g, 8.9 mol), anhydrous (3A molecular sieve) methanol (3.2 ml), and anhydrous pulverized potassium carbonate (1.2 g, 8.9 mol).[9] This mixture was cooled to 5° in an ice bath and a solution of bis-*N*,*N*'-dicarbethoxy-*N*,*N*'-dinitroso-1,4-butanediamine[10] (2.6 g, 8.9 mol) in 6.4 ml of reagent chloroform added dropwise with stirring at a rate slow enough to keep the temperature below 10°. The resulting yellow reaction mixture was stirred for an additional hour at 5° and then allowed to warm to room temperature. The crude product was diluted with 20 ml of chloroform, filtered, and concentrated *in vacuo*. Preparative gas chromatography (inlet temperature 250°; column temperature 175°) yielded **13** (20% yield estimated from peak area): mp 49–50°; ν_{max} 1731 cm^{-1}; nmr 1.17–2.26 ppm (multiplet); parent ion at *m/e* 166.1357 (calcd for $C_{11}H_{18}O$: 166.1358); mass spectrum major peaks observed at *m/e* (rel intensity) 166 (80), 148 (12), 139 (11), 123 (22), 112 (36), 109 (40), 97 (80), 84 (100), 67 (60), 55 (64), 41 (62).

Method B.—A 10-ml, one-necked flask fitted with an addition funnel and magnetic stirrer was charged with anhydrous methanol and cooled to 5° in an ice bath. A solution of *N*-nitroso-*N*-acetyl-3-(2'-ketocyclooctyl)propylamine[4] (0.5 g, 2.1 mmol) in methylene chloride was added dropwise over a 45-min period to produce a yellow reaction mixture which was stirred for 1 hr at 5° and then allowed to warm to room temperature.

The crude product was steam distilled to give an aqueous distillate which was extracted with ether, dried over anhydrous magnesium sulfate, and concentrated by careful fractionation. The pleasant-smelling yellow pot residue on purification by preparative gas chromatography yielded a product identical in all respects with that obtained by method A.

Deuterium Exchange.—Deuterium exchange of **13** was carried out most efficiently by a modification of the on-column exchange procedure of Burlingame.[11] An 8 ft × 0.25 in. stainless steel column was packed with 5% phosphoric acid and 10% Apiezon L on 60–80 mesh Chromosorb W. Immediately prior to use, the column was equilibrated by injection of several hundred microliters of 99.7% deuterium oxide, followed by injection of the sample to be exchanged. The exchanged sample was collected, the column was reequilibrated with deuterium oxide, and the cycle was repeated twice. It was found that these conditions gave good deuterium incorporations even in some cases where base-catalyzed exchange in solution gave poor results. Application of this procedure to **13** yielded a compound having parent ion peak *m/e* 169.

(7) H. O. House, E. J. Grubbs, and G. F. Gannon, *J. Amer. Chem. Soc.*, **82**, 4099 (1960); E. Muller, B. Zeeh, R. Heischkeil, F. Fricke, and H. Suhr, *Justus Liebigs Ann. Chem.*, **662**, 38 (1963).

(9) The second insertion step appears to be quite slow, and in the presence of traces of water the intermediate diazo ketone **9** appears to be intercepted to form a keto alcohol such as **17**.
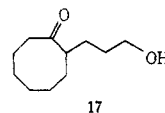
(10) C. M. Samour and J. P. Mason, *J. Amer. Chem. Soc.*, **76**, 441 (1954).

(11) M. Senn, W. J. Richter, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **87**, 680 (1965).