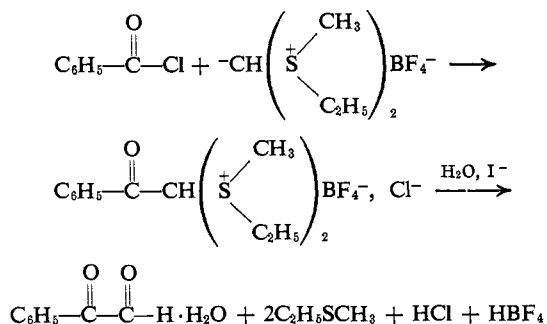


ylide followed by an iodide-catalyzed hydrolysis of the resulting substituted bissulfonium salt.<sup>1</sup>



The preparation of bis(dimethylsulfonium)methylide tetraphenylboronate ( $4\text{-B}(\text{C}_6\text{H}_5)_4^-$ ), a typical case, is described below. Dry methanol (10 ml), 1.35 g of methylenebis(dimethylsulfonium) fluoroborate,<sup>1</sup> and 0.27 g of potassium hydroxide were stirred together for 10 min. The mixture was filtered to remove suspended potassium fluoroborate, and the filtrate was concentrated under reduced pressure. The concentrate was taken up in 10 ml of deionized water and treated with 1.51 g of sodium tetraphenylboronate in 20 ml of deionized water to precipitate  $4\text{-B}(\text{C}_6\text{H}_5)_4^-$ . Three crystallizations from hot acetone-deionized water yielded glistening white crystals, mp 159–159.5° (yield 79%). *Anal.* Calcd: C, 76.30; H, 7.29; S, 14.05. Found: C, 76.30; H, 6.86; S, 14.40.

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### The Acid-Catalyzed Decomposition of 3-Diazonorcamphor. A Novel Rearrangement

Sir:

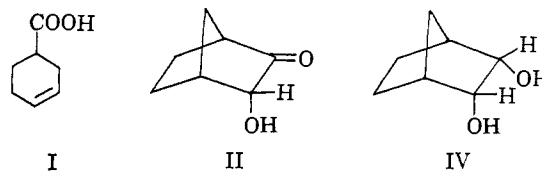
3-Diazonorcamphor<sup>1</sup> in aqueous tetrahydrofuran at pH 5 has been found to undergo decomposition at room temperature to give 3-cyclohexenecarboxylic acid (I, 17%), *endo*-3-hydroxybicyclo[2.2.1]heptan-2-one (II, 33%), and 2 $\beta$ -hydroxybicyclo[3.1.1]heptan-6-one (III, 29%).

The acid I was identified by spectral comparison with an authentic sample prepared by oxidation of 3-cyclohexenecarboxaldehyde with silver oxide<sup>2</sup> and by comparison of the corresponding amides.<sup>3</sup>

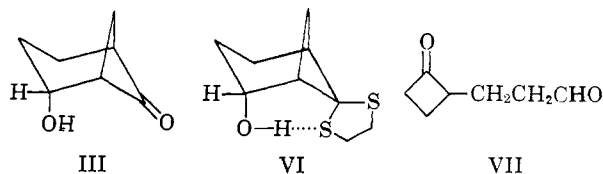
The hydroxy ketone II, mp 143–151°<sup>4</sup> (*Anal.* Found: C, 66.57; H, 8.07), had  $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) 2.78, 2.88 (br), and 5.70  $\mu$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.3–2.2 (6 H), 2.72 (2 H), 3.32 (1 H, absent after treatment with  $\text{D}_2\text{O}$ ), and 3.93 ppm (1 H, doublet of doublets,  $J = 5$  and 1.5 cps). Reduction with  $\text{LiAlH}_4$  gave *cis-endo*-2,3-dihydroxybicyclo[2.2.1]heptane (IV), mp 207–208°, identified by spectral comparison with an authentic sample,<sup>5</sup> pre-

pared by reduction of bicyclo[2.2.1]heptane-2,3-dione (V) with  $\text{LiAlH}_4$ . Reduction of V with zinc and acetic acid gave II (56%).

The hydroxy ketone III, mp 113.5–115.5° (*Anal.* Found: C, 66.03; H, 8.11),  $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) 2.76, 2.90 (br), and 5.62  $\mu$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.3–2.5 (6 H), 2.80 (1 H, absent



after treatment with  $\text{D}_2\text{O}$ ), 3.15 (2 H), and 4.55 ppm (1 H, triplet of doublets,  $J = 6$  and 3 cps), formed a 2,4-dinitrophenylhydrazone, mp 170.5–171° (*Anal.* Found: C, 50.88; H, 4.94; N, 18.46), and an ethylene dithioketal (VI), mp 83–84° (*Anal.* Found: C, 53.44; H, 6.84; S, 31.90),  $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) 2.82  $\mu$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.13 (1 H, doublet,  $J = 9$  cps), 1.5–2.9 (7 H), 2.94 (1 H, absent after treatment with  $\text{D}_2\text{O}$ ), 3.23 (4 H), and 4.15 (1 H) ppm. Attempted vpc of III on a Carbowax 20M column at 175° gave a product,  $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) 5.61 and 5.78  $\mu$ ,  $\delta$  ( $\text{CDCl}_3$ ) 1.4–3.5 (9 H) and 9.70 ppm (1 H, triplet,  $J = 1$  cps), considered to be the keto aldehyde VII. Oxidation of III with dichromate and acid gave 4-oxocyclohexanecarboxylic acid, mp 68–69.5°, identified by comparison with an authentic sample<sup>6</sup> and comparison of the corresponding semicarbazones.<sup>7</sup> The gross structure of III follows from these data; its stereochemistry is assigned on the following basis. The position of the signal due to the hydroxyl proton in the nmr spectrum of VI is concentration independent and no nonbonded hydroxyl stretching band appears in the infrared spectrum of this compound. These observations demonstrate the presence of a strong intramolecular hydrogen bond in the dithioketal, which is only possible if the hydroxyl group is  $\beta$  as in III and VI.<sup>8,9</sup>



The formation of II and III can be interpreted in terms of *exo* protonation of 3-diazonorcamphor to give the diazonium ion VIII, loss of nitrogen to give IX, and *endo* attack by water at C-3 or C-4, respectively; the acid I may arise *via* fission of the C-2–C-3 bond in IX or its hydrated form. Alternatively, formation of II from VIII may involve displacement of nitrogen by *exo* attack of water and epimerization of the resulting *exo*-hydroxy ketone to II;<sup>10</sup> attack of water concerted

(5) K. Alder, H. Wirtz, and H. Koppelberg, *Ann.*, **601**, 138 (1956).

(6) W. H. Perkin, Jr., *J. Chem. Soc.*, 416 (1904).

(7) D. E. Applequist and J. P. Klieman, *J. Org. Chem.*, **26**, 2178 (1961).

(8) The designation of III as the  $\beta$  isomer is based on arbitrary convention: *cf.* J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857, 5445 (1960); G. Fodor and K. Nádor, *J. Chem. Soc.*, 721 (1953).

(9) The conformation of III is tentatively assigned on the basis of the nmr data.

(10) This possibility must be entertained since it is unknown whether the formation of the *endo* product results from kinetic or thermodynamic control.

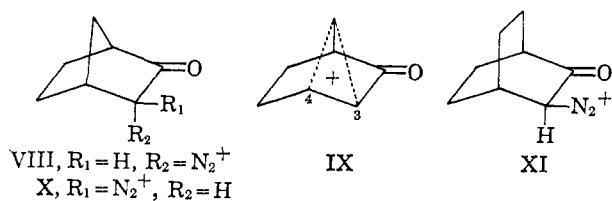
(1) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).

(2) We thank Mr. L. Kilmurry for this sample.

(3) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

(4) The broad melting range for this  $\alpha$ -ketol may result from partial conversion to a dimer; *cf.* W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).

with bond migration and loss of nitrogen could also account for the formation of III from VIII. It seems unlikely that the *exo*-diazonium ion X is formed to any



appreciable extent since no significant amounts of nortricyclanone or *exo*-2-hydroxy-7-norbornanone could be detected among the products.<sup>11</sup> Although rearrangement of the bicyclo[2.2.1]heptane system to the bicyclo[3.1.1]heptane system has been postulated previously as an intermediate step in certain cationic processes,<sup>13</sup> the isolation of III represents the first example of the isolation of such a rearrangement product. The well-known reverse process is normally favored because of relief of strain in the bicyclo[3.1.1]heptane system.<sup>14</sup> In the present case the increase in strain energy resulting from the delocalization of the electrons of the C-4-C-7 bond as in IX is compensated by reduction of unfavorable electrostatic interaction.

Similar acid-catalyzed decomposition of 3-diazobicyclo[2.2.2]octan-2-one<sup>15</sup> has been shown to give 4-cycloheptenecarboxylic acid (31%),<sup>16</sup> tricyclo[2.2.2.0<sup>2,6</sup>]octan-3-one (16%),<sup>17, 18</sup> *exo*-2-hydroxybicyclo[3.2.1]octan-8-one (34%),<sup>18a, 19</sup> and bicyclo[3.2.1]oct-2-en-8-one.<sup>20, 21</sup> These are considered to be formed *via* XI, the sole diazonium ion derivable from this diazo ketone by protonation on carbon.<sup>22</sup>

**Acknowledgment.** Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National

(11) Products analogous to these have been obtained by the acid-catalyzed decomposition of 3-diazocamphor, together with products derived by cleavage of the C-4-C-7 bond;<sup>12</sup> this difference can be interpreted in terms of steric and electronic effects engendered by the C-7 methyl groups.

(12) O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963); J. C. Crano, W. P. Wetter, and R. L. Little, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 30.

(13) W. Hüchel and U. Ströle, *Ann.*, **585**, 182 (1954); W. Hüchel and H. Wolowski, *Ber.*, **80**, 39 (1947); D. S. Noyce, *J. Am. Chem. Soc.*, **72**, 924 (1950); S. G. Levine, *ibid.*, **82**, 2556 (1960); R. P. Lutz and J. D. Roberts, *ibid.*, **84**, 3715 (1962).

(14) P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964).

(15) P. Yates and R. J. Crawford, *ibid.*, **88**, 1562 (1966).

(16) G. Stork and H. Landesman, *ibid.*, **78**, 5129 (1956).

(17) (a) N. A. LeBel and J. E. Huber, *ibid.*, **85**, 3193 (1963); (b) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

(18) (a) We thank Professor N. A. LeBel, Wayne State University, for providing us with the infrared spectrum of this compound. (b) We thank Mr. L. Kilmurry for providing a sample, prepared by the method of ref 17b.

(19) N. A. LeBel and L. A. Spurlock, *J. Org. Chem.*, **29**, 1337 (1964).

(20) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964); N. A. LeBel and L. A. Spurlock, *ibid.*, **20**, 215 (1964).

(21) This product was isolated only by vpc of the product mixture; it constituted 6% of the total eluate.

(22) NOTE ADDED IN PROOF. Since the submission of this paper, another report on the acid-catalyzed decomposition of 3-diazonorcamphor has appeared: M. Hanack and J. Dolde, *Tetrahedron Letters*, 321 (1966). The conditions used were different from those in the present work, and although the formation of I and II together with other products is reported, the formation of III was not observed.

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Received December 23, 1965

## Decomposition of 3-Diazobicyclo[2.2.2]octan-2-one. A Copper-Catalyzed Wolff Rearrangement

Sir:

Yates and Fugger<sup>1</sup> have reported that cuprous iodide in methanol-acetonitrile catalyzes the Wolff rearrangement of 2-diazoacetophenone. As has been emphasized recently,<sup>2</sup> this observation is highly unusual in that copper catalysts, unlike silver and platinum catalysts, normally convert  $\alpha$ -diazo ketones to unrearranged products.<sup>3</sup> We report now a Wolff rearrangement which is catalyzed by copper metal.

3-Diazobicyclo[2.2.2]octan-2-one (I), mp 71–72° (*Anal.* Found: C, 63.85; H, 6.69; N, 18.89),  $\lambda_{\text{max}}$  (CCl<sub>4</sub>) 4.79, 6.02, and 7.31  $\mu$ ,  $\delta$  (CCl<sub>4</sub>) 1.80 (8 H), 2.37 (1 H), and 3.02 (1 H) ppm, was prepared<sup>5</sup> by the action of aqueous NaOH on bicyclo[2.2.2]octane-2,3-dione monotosylhydrazone, mp 133–134° (*Anal.* Found: C, 58.83; H, 6.06; N, 9.24; S, 10.43), itself obtained from bicyclo[2.2.2]octane-2,3-dione (II).<sup>6</sup> A solution of the diazo ketone (0.51 g) in anhydrous benzene (1 l.) was stirred with copper powder<sup>7</sup> (11 g) under nitrogen at reflux for 21 hr, by which time all of the diazo ketone had been consumed. The products obtained were the azine III (28%), the tricyclic ketone IV (5%), and the ketene dimer V (46%).

The azine III, mp 247–248° dec, was identified by comparison with an authentic sample, prepared by treatment of II with hydrazine:  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 5.81, 6.19, and 6.26 (sh)  $\mu$ ,  $\delta$  (CDCl<sub>3</sub>) 1.87 (16 H), 2.62 (2 H), and 3.00 (2 H) ppm (*Anal.* Found: C, 70.55; H, 7.46; N, 10.05). The ketone IV<sup>2,8</sup> was identified by spectral and  $R_f$  comparison with an authentic sample.<sup>9</sup>

Compound V, mp 225.5–226.5° (*Anal.* Found: C, 78.63; H, 8.50), had  $\lambda_{\text{max}}$  (CCl<sub>4</sub>) 5.78, 5.80 (sh), and 5.86 (w)  $\mu$ ,  $\lambda_{\text{max}}$  (EtOH) 232 ( $\epsilon$  336), 287 ( $\epsilon$  39), 301 ( $\epsilon$  66), 309 ( $\epsilon$  32), and 345 ( $\epsilon$  20) m $\mu$ ,  $\delta$  (CDCl<sub>3</sub>) 1.1–2.3 (16 H) and 2.68 (4 H) ppm. These data may be compared with those for the ketene dimer VI:<sup>10</sup>  $\lambda_{\text{max}}$  (CCl<sub>4</sub>) 5.76 and 5.89 (w)  $\mu$ ,  $\lambda_{\text{max}}$  (EtOH) 233 ( $\epsilon$  194), 288 ( $\epsilon$  25), 301 ( $\epsilon$  39), 311 ( $\epsilon$  32), and 341 ( $\epsilon$  20) m $\mu$ . The mass spectrum of V included peaks with  $m/e$

(1) P. Yates and J. Fugger, *Chem. Ind. (London)*, 1511 (1957).

(2) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

(3) Subsequent investigation<sup>4</sup> has shown that the Wolff rearrangement of  $\alpha$ -diazo ketones of type RCOCHN<sub>2</sub> by cuprous iodide in methanol-acetonitrile is general.

(4) P. Yates and F. X. Garneau, unpublished results.

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

(6) K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

(7) Fisher electrolytic copper dust, washed with ether and pentane and vacuum dried, was used.

(8) N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).

(9) We thank Professor N. A. LeBel, Wayne State University, for providing us with the infrared spectrum of this compound, and Mr. L. Kilmurry for providing a sample, prepared by the method in ref 2.

(10) H. M. Walborsky and E. R. Buchman, *J. Am. Chem. Soc.*, **75**, 6339 (1953); we thank Mr. A. G. Fallis for providing a sample of this compound.