

close to 109° . If the contribution of each oxygen atom to the ligand field is approximately proportional to the reciprocal of its distance from the metal ion, the metal ion should then experience a ligand field approximately tetrahedral in shape, in accord with the implications of the magnetic and spectroscopic results.

In $[\text{Cr}(\text{O}_2)_4]^{3-}$, where the short O-O distances are only 1.41 Å.⁶ (as compared to ~ 2.1 Å. in NO_3^-), the structure is more regular, all Cr-O distances being within a range of 0.1 Å., and the centers of the four O_2^{2-} ions form a moderately flattened tetrahedron. In $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$, where there are only six oxygen atoms bonded to Co, both O atoms of each nitrate are about equidistant⁴ from Co. Finally, in $\text{Mg}_3\text{Ce}_2(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, each cerous ion is surrounded by six nitrate ions, each presenting two of its oxygen atoms to the cation. The actual coordination number is 12 and the coordination polyhedron is a distorted icosahedron, but the midpoints of the pairs of coordinated oxygen atoms lie approximately at the vertices of an octahedron.⁷

(6) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

(7) A. Zalkin, J. D. Forrester, and D. H. Templeton, *ibid.*, **39**, 2881 (1963).

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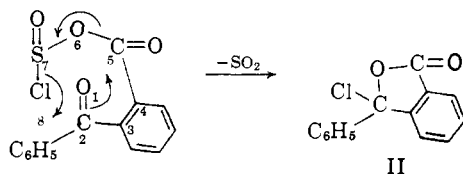
RECEIVED MAY 23, 1964

The 3,2,1-Bicyclic Reaction Path

Sir:

Three-, four-, five-, and six-centered reaction paths have been used to describe the course of many reactions in organic chemistry. Herein is described a 3,2,1-bicyclic path which may prove to be of general importance because in three instances of competition the 3,2,1-bicyclic path wins out over four- and six-centered paths.

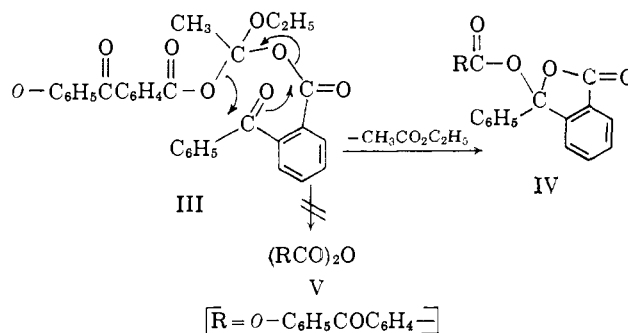
When *o*-benzoylbenzoic acid (I) is treated with thionyl chloride, the cyclic acid chloride II is produced.¹ We picture this reaction as proceeding through the 3,2,1-bicyclic path as shown below.



Carbon atoms 2 and 5 are the bridgehead atoms in this example and the three connecting links in the 3,2,1-bicyclic transition state are, respectively, the carbonyl oxygen (1), the aromatic carbons (3 and 4), and the oxygen-sulfur-chlorine grouping (6, 7, and 8). In competition with the formation of II is the usual four-centered path involved in forming acid chlorides from acids such as benzoic. The latter path wins out when *o*-mesitylbenzoic acid is treated with thionyl chloride as infrared analysis shows that the normal acid chloride is formed.

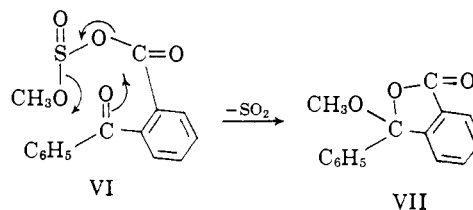
(1) McRenson, *Bull. soc. chim. Belges*, **70**, 77 (1961) shows that *o*-phthalaldehydic, *o*-acetylbenzoic, and *o*-benzoylbenzoic acid chlorides exist mainly, if not entirely, in the cyclic structure, but no mechanism to account for their formation has been proposed.

Another case, wherein the competition lies between a six-atom cyclic mechanism and the 3,2,1-bicyclic path, is that of the treatment of *o*-benzoylbenzoic acid with ethoxyacetylene. The normal-pseudo anhydride IV is produced from the postulated intermediate III which would be expected to yield the normal-normal anhydride V if the six-atom mechanism² obtained.



We have shown that the anhydride, m.p. 140° , produced has structure IV contrary to other conclusions.³ The absorption spectrum of an equimolar mixture of normal and pseudo methyl *o*-benzoylbenzoates proved to be almost identical through the range 260–340 $m\mu$ to that of 1 equiv. of the anhydride (IV).

The third example of the involvement of the 3,2,1-bicyclic path is supplied by the fact that when sodium *o*-benzoylbenzoate is treated with methyl chlorosulfite, an intermediate VI is formed which decomposes to yield the pseudo methyl ester VII⁴ almost exclusively, as shown below.



This example provides convincing evidence for the 3,2,1-bicyclic path since the normal methyl ester of *o*-benzoylbenzoic acid is the stable isomer. As far as the mechanism of formation of ester from a simple acid by this procedure is concerned, either a four- or six-atom cyclic path can be pictured, depending on whether oxygen A or B of intermediate $\text{RCOOSOOR}'$ is retained in the ester formed.⁴

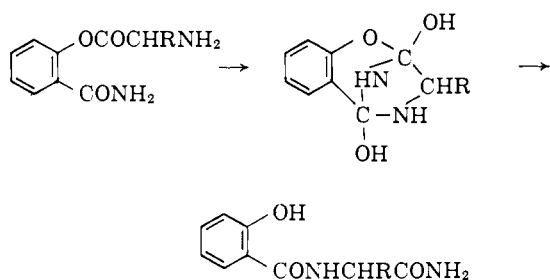
In the three cases cited as evidence for a 3,2,1-bicyclic path, the reactions involve compounds which have two carbonyl groups in the 1,4-position. Since α -acylamino and α -acetoxy acids each have this feature, further exploration of the generality of this path seems desirable. It has already been claimed that a 3,2,1-bicyclic compound is involved in the "amino-

(2) H. H. Wasserman and P. S. Wharton, *J. Am. Chem. Soc.*, **82**, 3457 (1960), and references therein.

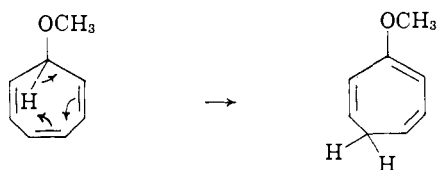
(3) H. Schmid, M. Hochweber, and H. V. Halben, *Helv. Chim. Acta.*, **31**, 354 (1948), reported that since the ultraviolet absorption spectra of the anhydride and normal methyl *o*-benzoylbenzoate were fairly close in the 260–290 $m\mu$ region, the anhydride had normal-normal structure, V. If the anhydride really had structure V the intensity of this absorption should have been about double.

(4) M. S. Newman and W. S. Fones, *J. Am. Chem. Soc.*, **69**, 1046 (1947), have shown that sodium salts of a variety of acids are converted into intermediates, $\text{RCO}_2\text{SO}_2\text{C}_4\text{H}_9$, by treatment with *n*-butyl chlorosulfite. On warming, these intermediates evolve sulfur dioxide and yield butyl esters.

acyl insertion" reaction of aminoacylated salicylamide and related compounds.⁵ As shown below the postulated⁵ mechanism involves initially a 1,5-dicarbonyl compound.



The thermal isomerization of 7-methoxycycloheptatriene to 3-methoxycycloheptatriene and related isomerizations⁶ may also be postulated to proceed *via* the 3,2,1-bicyclic path in which the two carbons forming the leaving and arriving sites for the migrating hydrogen are the bridgehead atoms.



We are carrying out other studies to test the generality of this path.⁷

(5) M. Brenner and J. P. Zimmermann, *Helv. Chim. Acta*, **40**, 1933 (1957); **41**, 467 (1958); M. Brenner and J. Wehrmüller, *ibid.*, **40**, 2374 (1957); H. Dahn, R. Menasse, J. Rosenthaler, and M. Brenner, *ibid.*, **42**, 2249 (1959). We thank Dr. F. Kagan of the Upjohn Company for bringing this reaction to our attention.

(6) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964). We thank Dr. N. Nelson of the Upjohn Company for bringing this reaction to our attention.

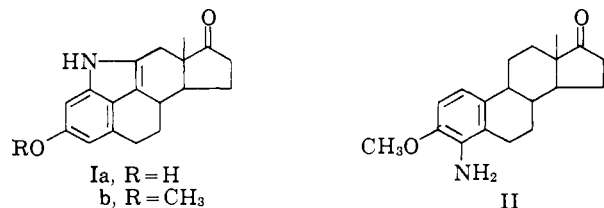
(7) This work has been supported by a grant from the National Science Foundation.

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RECEIVED MAY 2, 1964

The Synthesis of a Novel Steroid Heterocyclic System *Sir*:

We wish to report the synthesis of a novel heterocyclic steroid, 3-hydroxy-1,11-iminoestra-1,3,5(10),9-(11)-tetraen-17-one (Ia) by a pathway whose key feature was the generation of a nitrene intermediate appropriately situated for ring formation.



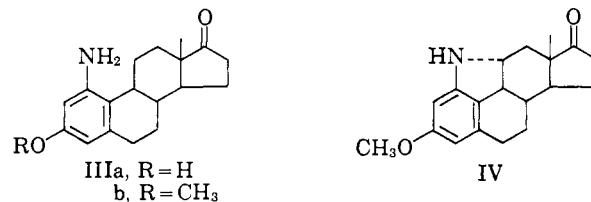
4-Amino-3-methoxyestra-1,3,5(10)-trien-17-one (II)¹ in acetic acid was coupled with *p*-nitrophenyldiazonium chloride to give directly the 4-amino-3-methoxy-1-*p*-nitrophenylazo compound (87% yield),² m.p. 243–244°

(1) S. Kraychy, *J. Am. Chem. Soc.*, **81**, 1702 (1959).

(2) The yields reported are for material after initial purification.

dec., λ_{\max} 280 (ϵ 10,100) and 406 $m\mu$ (24,750); $[\alpha]_{6907 \text{ \AA}}$ -468° .³ Diazotization of the latter followed by the reduction of the diazonium salt with 50% aqueous hypophosphorous acid gave the 3-methoxy-1-*p*-nitrophenylazo compound (89% yield), m.p. 223–224°; λ_{\max} 279 (ϵ 9500) and 350 $m\mu$ (16,200); $[\alpha]_{6907 \text{ \AA}}$ -348° . Reductive cleavage of the azo compound with zinc dust and glacial acetic acid provided 1-amino-3-methoxyestra-1,3,5(10)-trien-17-one (IIIb, 73% yield), m.p. 213–214°; λ_{\max} 245 (sh, ϵ 6720) and 291 $m\mu$ (3000); $[\alpha]_{\text{D}} +301^\circ$.⁴ The free 1-amino-3-hydroxy-17-one IIIa was obtained by demethylation of IIIb with pyridine hydrochloride (66% yield), m.p. 280–288° dec., λ_{\max} 212 (ϵ 40,000), 240 (sh, 7850), and 292 $m\mu$ (3080); ν_{\max}^{KBr} 3412, 3380, 1725, and 828 cm^{-1} ; $[\alpha]_{\text{D}}^{25} +264^\circ$ (pyridine).

The 1-amino-3-methoxy compound IIIb on diazotization at -25° (sodium nitrite, glacial acetic acid, and 1 *N* sulfuric acid) followed by the addition of sodium azide in water at -25° was converted into the 1-azide (85% yield), m.p. 147–149°; λ_{\max} 218 (ϵ 23,000), 255 (6500), 293 (3620), and 303 $m\mu$ (sh 3000); ν_{\max}^{KBr} 2100 and 831 cm^{-1} . The latter, on being heated in *n*-hexadecane for 5 min. at 200°, gave the indoline, 1,11 α -



imino-3-methoxyestra-1,3,5(10)-trien-17-one (IV, 65% yield),⁵ m.p. 199–201°; λ_{\max} 212 (ϵ 28,000), 235 (sh, 5800), and 293 $m\mu$ (3550); ν_{\max}^{KBr} 3300, 824, and 728 cm^{-1} ; $[\alpha]_{\text{D}} +164^\circ$. Dehydrogenation of IV with palladium-charcoal in xylene (1 hr. reflux) gave the indole, 1,11-imino-3-methoxyestra-1,3,5(10),9(11)-tetraen-17-one (Ib, 90% yield), m.p. 203–205°; λ_{\max} 229

(3) The ultraviolet absorption spectra are for a methanol solution. The optical rotations are for a chloroform solution at 25° unless noted otherwise. All new compounds reported here gave satisfactory elemental analyses. The n.m.r. spectra were taken in deuteriochloroform, and the chemical shifts were measured with respect to TMS. (Varian A60 spectrometer).

(4) The n.m.r. spectrum of the 1-amino-3-methyl ether IIIb showed two aryl protons barely separated from one another at 366 and 367 c.p.s. In contrast the C-1 and C-4 protons of the corresponding 2-amino-3-methyl ether¹ were seen as singlets at 388 and 397 c.p.s., and the 4-amino-3-methyl ether II showed a single sharp line at 400 c.p.s. which had an integrated value of two protons.

(5) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960), has shown that aryl azides on thermal or photolytic decomposition yield nitrenes which, either by a direct insertion (singlet process) or by abstraction of hydrogen and subsequent closure of the resulting diradical (triplet process), yield cyclic products.

An examination of molecular models indicates that, in the formation of IV, insertion could occur either 11 α or 11 β , with the former being slightly favored when ring B assumes a normal half-chair conformation. However if the biradical two-step process pertains then C-11 α -N bond formation would be favored since the C-18 methyl group would be expected to exert a stronger orienting effect than in the singlet process. The n.m.r. spectrum of IV does not indicate whether the C-9 and -11 hydrogens have a *cis* or *trans* relationship, which feature was not resolved by an initial attempt with spin-spin decoupling [S. L. Manatt and D. D. Elleman, *ibid.*, **83**, 4095 (1961)]. However, it is known that an 11 β -hydroxyl group^{6,7} shifts the C-18 methyl absorption *ca.* 15 c.p.s. downfield from its normal position while an 11 α -hydroxyl group⁶ produces a similar shift of only 2 c.p.s. The position of the C-18 methyl group of IV (59 c.p.s.) is shifted only 2 c.p.s. downfield from that of the unbridged precursor IIIb (57 c.p.s.) which supports the α assignment of the C-11-N bond.

(6) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, and K. Tsuda, *Chem. Pharm. Bull.*, **10**, 338 (1962).

(7) E. Capsi, T. A. Wittstruck, and P. K. Grover, *Chem. Ind. (London)*, 1716 (1962).