

mixture was heated at 45–50° with stirring in a nitrogen atmosphere for 70 hr. After filtration, the precipitate was dissolved in water and acidified with hydrochloric acid to give 0.1 g. of benzoic acid. The filtrate was submitted to chromatographic analysis on alumina to give 0.7 g. of triphenylmethyl isocyanide, 25 mg. of triphenyl carbinol, m.p. 160–163°, and finally an unidentified oily product, which, however, was not diphenylacetylene.

When tetrahydrofuran was used as solvent instead of benzene, a part of the isocyanide was isomerized to cyanide. The mixture had m.p. 128–132° and the infrared spectrum had peaks at 2130 and 2250  $\text{cm}^{-1}$ .

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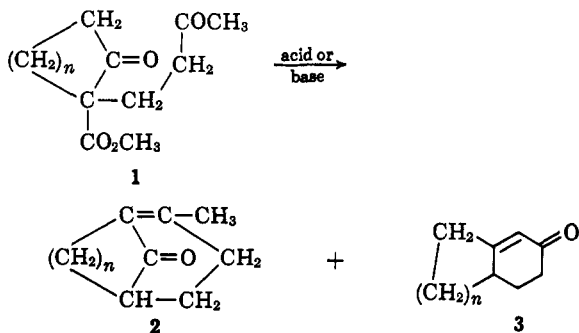
### The Application of Bredt's Rule to Bicyclo[3.3.1]nonanes

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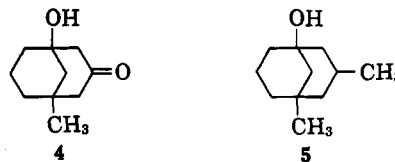
Bredt's rule<sup>1</sup> is an empirical formulation which, when applied to bridged ring systems, defines the minimum geometrical requirements necessary to accommodate a double bond at a bridgehead position. In an attempt to determine the lower limit of  $n$  in the bicyclo[ $n$ .3.1] series compatible with unsaturation at the bridgehead, Prelog<sup>2</sup> studied the aldol condensation of **1** and found that the ratio of products **2** and **3** was a sensitive function of  $n$ . When  $n$  was 6, 5, or 4, the yields of **2** and **3** were 76 and 0, 14 and 36, and 0 and 65%, respectively.



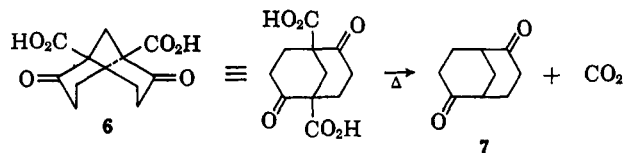
Although these data clearly show that when  $n = 5$  there is sufficient flexibility in **2** to tolerate an olefinic linkage at the bridgehead, they cannot be used to place a lower limit on the value of  $n$  since the reaction studied is subject to thermodynamic control and the ratio of products observed reflects only the relative stabilities of these compounds.

During a study of the bicyclo[3.3.1]nonanes, Rabe<sup>3</sup> observed that **4** was extremely resistant to dehydration

and recognized that this was probably a consequence of the strain associated with the hypothetical product. In a subsequent study Rabe<sup>4</sup> found that 3,5-dimethylbicyclo[3.3.1]nonan-1-ol (**5**) could not be dehydrated even under drastic conditions.



In contrast to these results, Meerwein<sup>5</sup> later found that **6** was decarboxylated rapidly in water at relatively mild conditions (*ca.* 180°) for a compound of this structure. Since this reaction is believed to proceed through formation of the enol, it would appear that at least a transient double bond can exist at a bridgehead of the bicyclo[3.3.1]nonane system. To investigate this pos-



sibility further we have studied the base-catalyzed deuterium exchange of bicyclo[3.3.1]nonan-2-one (**8**) in detail.

When **8** was heated at 95° in deuterium oxide (*ca.* 0.1 *M* NaOD) up to three atoms of deuterium per molecule were incorporated. Table I summarizes the

TABLE I  
BASE-CATALYZED DEUTERIUM EXCHANGE OF  
BICYCLO[3.3.1]NONAN-2-ONE

Sample	Ex-change time, days	D <sub>0</sub> , %	D <sub>1</sub> , %	D <sub>2</sub> , %	D <sub>3</sub> , %	Average number of D per molecule
1	6	1.5	8.1	32.0	58.4	2.46
2	26	0.8	3.2	35.1	60.9	2.56
3	40	1.1	2.45	19.3	77.2	2.72

results of three separate, but similar, experiments. Under no conditions were more than three deuterium atoms per mole incorporated. In **8** the three hydrogens adjacent to the carbonyl group appear at  $\tau$  7.6 units in the n.m.r. spectrum. Since this absorption disappears after deuterium exchange and the remainder of the spectrum is unchanged, it is apparent that only the hydrogens adjacent to the carbonyl group are acidic enough to undergo exchange. Furthermore, since Bartlett and Woods<sup>6</sup> have shown that the cumulative inductive effect of two adjacent carbonyl groups is insufficient to increase the acidity of the bridgehead hydrogen in bicyclo[2.2.2]octane-2,6-dione significantly, it must be concluded that there is sufficient orbital overlap in the enolate ion **9** to confer substantial acidity upon the bridgehead hydrogen, or, in terms of valence bond

(1) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

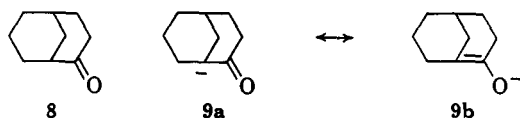
(2) V. Prelog, *J. Chem. Soc.*, 420 (1950); V. Prelog, P. Barman, and M. Zimmerman, *Helv. Chim. Acta*, **32**, 1284 (1949); V. Prelog, L. Ruzicka, P. Barman, and L. Frenkiel, *ibid.*, **31**, 92 (1948).

(3) P. Rabe, R. Ehrenstein, and M. Jahr, *Ann.*, **360**, 265 (1908).

(4) P. Rabe and K. Appuhn, *Ber.*, **76B**, 982 (1943).

(5) H. Meerwein and W. Schürmann, *Ann.*, **398**, 196 (1913).

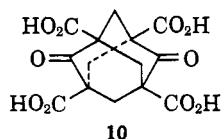
(6) P. D. Bartlett and G. F. Woods, *J. Am. Chem. Soc.*, **62**, 2933 (1940).



pictures, structure **9b** must be an important resonance form.

A difficulty which arises when enolization data is used to evaluate the limits of Bredt's rule is that the degree of resonance stabilization of the enolate ion (and therefore, the acidity of the bridgehead hydrogen) is a function of the cosine of the projected angles between the interacting orbitals in the ion. Since it has not been ascertained how much orbital overlap is necessary to allow enolate formation, these data only require the conclusion that significant double-bond character can exist between C-1 and C-2 in the bicyclo[3.3.1]nonane series and not that a stable double bond can be formed between these carbon atoms.

Although there is ample evidence that the preferred conformation of bicyclo[3.3.1]nonanes is the chair-chair modification,<sup>7</sup> an examination of Dreiding models of **8** immediately shows that formation of a true enolate is not possible in this conformation since the C-1-H bond is orthogonal to the p-orbitals of the carbonyl group. However, if the ring containing the carbonyl group is in the boat form, the projected angle between the interacting orbitals decreases to 30° ( $\cos 30^\circ = 0.866$ ) and resonance interactions in the transition state for removal of the proton and in the subsequent enolate ion can result in significant delocalization energies. The importance of the conformational factor on enol formation is dramatically illustrated by the stability of **10** toward decarboxylation<sup>8</sup> since all rings are locked in the chair conformation, in contrast to **6** where the rings are mobile.



#### Experimental

In a test tube was placed 200 mg. (1.45 mmoles) of bicyclo[3.3.1]nonan-2-one,<sup>9</sup> 5 ml. of freshly distilled dioxane, 5 ml. of deuterium oxide, and ca. 20 mg. of sodium. The tube was sealed, placed in a constant-temperature bath at 95°, and after several days (see Table I) was removed and cooled and the contents were poured into 100 ml. of pentane. The pentane solution was washed with five 50-ml. portions of ice-water to remove the dioxane and dried over magnesium sulfate. After removal of the pentane the ketone was sublimed and analyzed on the mass spectrometer.

**Acknowledgment.**—The authors wish to express their gratitude to the Petroleum Research Foundation (Grant PRF-789) for their generous support of the initial phases of this work.

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## Reduction of Sulfoxides by Triphenylphosphine and Carbon Tetrachloride

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While the reduction of sulfoxides by triphenylphosphine is acid catalyzed<sup>2</sup> and thus the reduction does not take place in an inert solvent such as benzene, it was found<sup>3</sup> that di-*p*-bromophenyl sulfoxide was reduced to the corresponding sulfide when heated with triphenylphosphine in the presence of carbon tetrachloride.

The purpose of this Note is to report this new reaction in view of its potential usefulness since, generally speaking, it produces good yields of sulfides even in the presence of nitro groups.

#### Experimental

The reductions of most diaryl sulfoxides were performed by refluxing, during 2 hr., a mixture of 0.01 and 0.02 moles of the sulfoxide and triphenylphosphine, respectively, in 100 ml. of carbon tetrachloride. The reaction mixture was then evaporated on a steam bath and the residue was worked up depending upon the solubility of the sulfide. Sulfides which crystallize readily from ethanol (di-*p*-bromophenyl and di-*p*-nitrophenyl sulfides) were obtained by dissolving the residue in ethanol in which triphenylphosphine oxide is readily soluble, while the lower melting sulfides were obtained by extraction of the residue with petroleum ether (b.p. 35–47°) and by evaporation of this extract.

In the case of di-*p*-hydroxyphenyl sulfoxide which is highly insoluble in carbon tetrachloride, the dry, finely ground powder was suspended in a mixture of 100 ml. each of carbon tetrachloride and benzene and the reflux period was extended to 18 hr. The reaction mixture was concentrated as described above and the oily residue was then extracted with aqueous sodium hydroxide. This left behind most of the triphenylphosphine oxide, and the sulfide was isolated by acidification of the alkaline extract, extraction with ether, crystallization from water, and recrystallization from benzene.

The reaction of dimethyl sulfoxide is highly exothermic and thus a solution of 0.01 mole of this sulfoxide in 50 ml. of carbon tetrachloride was added slowly to the solution of the phosphine in 100 ml. of carbon tetrachloride. The volatile dimethyl sulfide was swept by means of a stream of nitrogen into a 2.5% solution of mercuric chloride in water in order to precipitate the sulfide in the form of the metallic complex.<sup>4</sup>

The experimental results are summarized in Table I. The yields and melting points of the sulfides are those of the crude products. In all cases these were further purified and found to give satisfactory mixture melting points with samples of the authentic sulfides. The purity of the crude products was also examined by thin layer chromatography. Owing to the high solubility of triphenylphosphine oxide in ethyl alcohol the crudes obtained by crystallization from this solvent (*p*-bromo and *p*-nitro) were free from the oxide; conversely all the crudes obtained by petroleum ether extraction contained a trace of it. The crude of di-*p*-hydroxyphenyl sulfide contained a larger amount of the oxide but crystallization from water brought about a satisfactory purification of the sulfide.

The reaction between di-*p*-bromophenyl sulfoxide and triphenylphosphine in carbon tetrachloride was also carried out using equimolar quantities of the first-mentioned reagents, and the expected sulfide was isolated in 91% yield.

(1) To whom all inquiries should be addressed.

(2) H. H. Szmant and O. Cox, manuscript in preparation.

(3) O. Cox, M.S. Thesis, University of Puerto Rico, 1964.

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