the reaction. The mixture was cooled to −10° for the remainder of the addition. Stirring was continued for 50 min. at 0–5° before the addition of 4.27 g. (0.041 mole) of 1.[12] The stirring was stopped 3.5 hr. later (0–5°), and the mixture was forced onto a large excess of powdered Dry Ice. Until this point, the reaction mixture had been maintained in an atmosphere of nitrogen. The carboxylate salts were dissolved in water and extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid and again extracted with ether. Titration of an aliquot of this ether solution indicated that acidic groups were obtained in 49% yield, based on the amount of butyl chloride used. Evaporation of the ether solution gave 1.80 g. of a residue which was digested in petroleum ether (b.p. 30–60°). The soluble portion was judged to be mainly aliphatic acids by virtue of its odor and infrared spectrum. The insoluble residue provided crystals of **2**, m.p. 187–190°, from an aqueous ethanolic solution which had been cooled in an ice box. This material weighed 0.11 g. and represents approximately a 3% yield based on the available organometallic reagent.[13]

A sample of **2** was purified for analysis by sublimation (120°, 0.1 mm.): m.p. 188–191° (sealed capillary); ν_{max}^{KBr} 3300–2300, 1675, 926, 779, and 749 cm.$^{-1}$.

Anal. Calcd. for $C_9H_8O_2$: C, 72.95; H, 5.44; O, 21.60; neut. equiv., 148. Found: C, 72.80; H, 5.37; O, 22.53; neut. equiv., 148.

In another experiment, 5.51 g. (0.053 mole) of 1[12] was allowed to react in a sealed bottle with 0.06 mole of amylsodium suspended in 150 ml. of pentane for 1 week at room temperature. The amylsodium had been prepared from sodium sand and amyl chloride in a manner analogous to that described above for butylpotassium. Carbonation and similar work-up provided, after purification by sublimation, 0.45 g. of **2**, m.p. 188–191° (sealed capillary) (6% yield, based on the amount of 1 used).[15]

Methyl Benzocyclobutene-3-carboxylate (2a).—A sample of **2** was treated with ethereal diazomethane to give the ester **2a**, which, after two recrystallizations from Skellysolve B, had m.p. 50.5–51°[16]; ν_{max}^{KBr} 1727, 776, and 729 cm.$^{-1}$; $\lambda_{max}^{95\%\ ethanol}$ 241 and 290 mμ (ϵ 8130 and 2560).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22; O, 19.73. Found: C, 74.13; H, 5.97; O, 19.90.

The isomeric methyl dimethylbenzoates were similarly prepared by diazomethylation of the commercially available acids.

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[12] This sample was kindly supplied by Drs. M. P. Cava and M. J. Mitchell.

[13] This low yield is no doubt owing in part to the fact that insufficient substrate was available to be used as the suspending medium, as in the recommended procedure for the metalation of alkyl aromatic hydrocarbons. Furthermore, subsequent observations[14a] have revealed inadequacies in the method used here for the preparation of butylpotassium as well as the surprisingly rapid decomposition of the alkyl potassium reagent, once formed.[14b,c] These results[14a-c] underscore the recommendation for having the substrate present in excess during the preparation of the potassium reagent, provided, of course, that it is inert to the metal itself.

[14] (a) R. A. Finnegan, *Tetrahedron Letters*, 1303 (1962); (b) *ibid.*, 429 (1963); (c) *ibid.*, 851 (1963).

[15] The assistance of Mr. A. W. Hagen in carrying out this experiment is acknowledged.

A Study of the Mechanism of the Reaction of the Silver Salt of Phenylnitroacetonitrile with Triphenylmethyl Chloride

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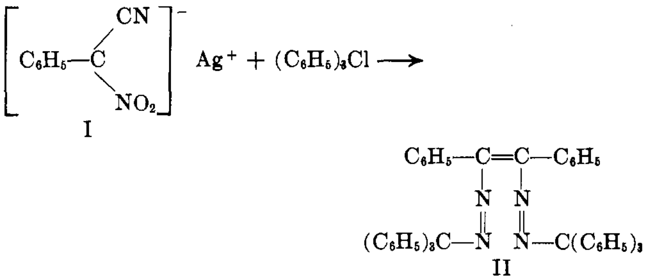
The main product of the reaction of the silver salt of phenylnitroacetonitrile (I) with triphenylmethyl chloride has been found to be one of the stereoisomeric α,α'-bis(triphenylmethaneazo)stilbenes (II).[2]



In this reaction benzonitrile oxide (III) was also formed as shown by its interception with phenylacetylene to give 3,5-diphenylisoxazole.[2] The benzonitrile oxide and the triphenylmethyl isocyanate (IV), which had previously been isolated by Wieland and Höchtlen,[3] were proposed as possible intermediates

$$\underset{\text{III}}{C_6H_5{-}C{\equiv}\overset{+}{N}{-}\overset{-}{O}} \qquad \underset{\text{IV}}{(C_6H_5)_3CNCO}$$

leading to the formation of the product, II. The reaction of compounds III and IV was expected to give carbon dioxide and the nitrilimine V, which might then dimerize to the bisazoethylene derivative II.[2,4]

$$\underset{\text{V}}{C_6H_5{-}\overset{-}{C}{=}\overset{+}{N}{=}N{-}C(C_6H_5)_3}$$

However, the benzonitrile oxide has been found not to react with the triphenylmethyl isocyanate to give compound II. The isocyanate IV was prepared according to Jones and Hurd.[5] Its infrared spectrum in carbon tetrachloride showed peaks at 2260, 1590, and 700 cm.$^{-1}$ and the n.m.r. spectrum of a 12% solution in carbon disulfide had a singlet at τ 2.80. The infrared spectrum of benzonitrile oxide, immediately after its preparation, in carbon tetrachloride was similar to that which has previously been reported,[6] with peaks at 2290, 1710, 1365, 1095, and 1025 cm.$^{-1}$.

The n.m.r. spectrum of a sample after the reaction of the triphenylmethyl isocyanate with the benzonitrile oxide, in carbon disulfide, had peaks at τ 2.80 and 2.60. It was a mixture of isocyanate IV and 3,4-diphenylfuroxan (peak at τ 2.60) produced from dimerization of the benzonitrile oxide.

In order to establish whether the benzonitrile oxide takes any part in the formation of the bisazoethylene II, experiments with labeled benzonitrile oxide ($C_6H_5C^{14}NO$) were carried out. This radioactive compound was prepared according to the method of Quilico and Speroni,[7] by using labeled benzaldehyde ($C_6H_5C^{14}HO$).

When to a mixture of the silver salt I and triphenylmethyl chloride at −20° a solution of labeled benzonitrile oxide was added, 5.6% of bisazoethylene II, in the form of red crystals, was obtained with m.p. 143° dec. The specific activity of the benzonitrile oxide was 0.693 μc./mmole, measured in the form of 3,4-diphenylfuroxan. Before the addition of the benzonitrile oxide to the reaction mixture its infrared spectrum was obtained; it did not show the presence of

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[1] Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece.

[2] D. Y. Curtin, R. J. Crawford, and D. K. Wedegaertner, *J. Org. Chem.*, **27**, 4300 (1962).

[3] H. Wieland and A. Höchtlen, *Ann.*, **505**, 237 (1933).

[4] D. K. Wedegaertner, Ph.D. Thesis, University of Illinois, 1962.

[5] C. Jones and C. Hurd, *J. Am. Chem. Soc.*, **43**, 2422 (1921).

[6] R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960).

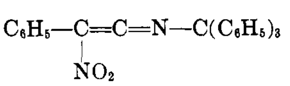
[7] A. Quilico and G. Speroni, *Gazz. chim. ital.*, **76**, 148 (1946).

3,4-diphenylfuroxan. The specific activity of the product II was 0.0148 μc./mmole by combustion and measurement of the radioactivity of the produced carbon dioxide. In this reaction the total amount of the benzonitrile oxide was 17.32 mmoles (added 2.32 mmoles, produced from the reaction 15 mmoles). By assuming that 2 moles of benzonitrile oxide participate in the formation of the bisazoethylene II, its radioactivity should be 0.1856 μc./mmole. Therefore, 8% of the used labeled benzonitrile oxide seems to be incorporated in this reaction. (In another experiment the incorporated amount was 5%.)

However, when the isolated radioactive product (II) was decomposed[2,3] by heating in benzene, the specific activity of the formed diphenylacetylene was found to be only 3.58×10^{-5} μc./mmoles. The ultraviolet spectrum of this sample in ethanol was identical with that of an authentic sample of diphenylacetylene. Therefore, the almost inactive diphenylacetylene obtained from this reaction is evidence that the benzonitrile oxide does not participate in the formation of the compound II, but is probably an intermediate of a side reaction. In any other case, the obtained diphenylacetylene should have the same activity as the compound II. The radioactivity of compound II is probably due to radioactive impurities. The bisazoethylene II is insoluble in all common solvents[2,3] and for this reason its purification by crystallization was impossible.

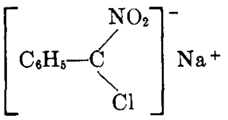
The above conclusion, that the benzonitrile oxide is not an intermediate in the formation of bisazoethylene II, is in agreement with the fact that the reaction of silver salt I with triphenylmethyl chloride in presence of *p*-chlorobenzonitrile oxide gave a product which was identical with the bisazoethylene II.

Another reasonable hypothesis for the mechanism of the reaction of I with triphenylmethyl chloride is that these two compounds form the nitroketimine VI, which further gives the bisazoethylene II. Attempts to prepare compound VI from the sodium salt of phenylchloronitromethane (VII) and triphenylmethyl isocyanide (VIII) were unsuccessful.



$C_6H_5-C(NO_2)=C=N-C(C_6H_5)_3$

VI



VII

$(C_6H_5)_3CNC$

VIII

It is apparent that further work is required, in order to elucidate the mechanism of this unusual reaction.

Experimental[8]

Reaction of Triphenylmethyl Isocyanate (IV) with Benzonitrile Oxide (III).—To 0.2 g. of IV[5] (m.p. 91–93°) in 5 ml. of ether, a solution of 0.18 g. of III[7] in 18 ml. of ether, dried over calcium chloride for 10 min. at 0°, was added and the solution was allowed to stand at 0° for 2 days. After evaporation of the solvent a yellowish solid was obtained, m.p. 80–110°, the infrared spectrum (in chloroform) of which showed that it is a mixture of IV and 3,4-diphenylfuroxan. The n.m.r. spectrum of a 12% solution in carbon disulfide gave two singlets at τ 2.80 and 2.60 and was identical with that of a mixture of IV and 3,4-diphenylfuroxan. The ultraviolet spectrum in ethanol of the solid, after heating on a water bath for 1 hr., did not show the presence of diphenylacetylene.

The same results were also obtained by changing the solvent, the amount of benzonitrile oxide, the time, and the temperature.

Reaction of the Silver Salt I with Triphenylmethyl Chloride in the Presence of Labeled Benzonitrile Oxide.—A typical experiment is described. To 4 g. (15 mmoles) of I in 15 ml. of dry toluene, 4.2 g. of triphenylmethyl chloride in 30 ml. of toluene (kept over potassium carbonate for 10 min.) was added at −20° with stirring, under a nitrogen atmosphere, in a period of 30 min. After 1 hr., 0.276 g. (2.32 mmoles) of labeled benzonitrile oxide[7] (freshly prepared) in 18 ml. of ether was added. The ratio of $C_6H_5C^{14}NO$:Ag salt I was equal to 0.155. When this ratio was greater than 0.2, no product II was formed. The mixture was stirred for 1 hr. at −20° and then filtered cold. The filtrate was allowed to stand overnight at 0° to give 0.3 g. (5.6%) of red crystals (II), m.p. 143° dec. The specific activity of the benzonitrile oxide, measured in form of 3,4-diphenylfuroxan by using a liquid scintillation counter, found was 0.693 μc./mmole. (The specific activity of the benzaldoxime used was 0.698 μc./mmole.) If the entire amount of labeled benzonitrile oxide were incorporated in the reaction, the specific activity of the bisazoethylene II should be $(2 \times 2.32 \times 0.693)/17.32 = 0.1856$ μc./mmole. The specific activity of the isolated bisazoethylene II was found to be 0.0148 μc./mmole; it was determined by combustion and measurement of the radioactivity of the carbon dioxide, by using an ion chamber in conjunction with a vibrating-reed electrometer (Drift method). The sample before measurement was washed with benzene, ether, and then dried under vacuum.

Anal. Calcd. for $C_{52}H_{40}N_4$: C, 86.6. Found: C, 87.1.

When compound II was decomposed[2,3] by heating in benzene on a water bath for 30 min., it gave an oily product which was submitted to vapor-phase chromatographic analysis through a 4-ft. SE-30 column on Chromosorb W at 180°. The product which had the same retention time (4.4 min.) as an authentic sample of diphenylacetylene was collected. Its specific activity was measured by using a liquid scintillation counter and found to be 3.58×10^{-5} μc./mmoles. The ultraviolet spectrum of this product in ethanol was identical with that of diphenylacetylene.

In a similar manner the reaction was carried out in presence of *p*-chlorobenzonitrile oxide. The isolated red crystals had m.p. 143° dec. and the Beilstein test for chlorine was negative.

Preparation of Phenylchloronitromethane.—This compound was prepared by treatment of phenylchloronitroacetamide with a solution of potassium hydroxide.[9] The oily product had peaks in the infrared spectrum (in carbon disulfide) at 1560, 1350, 715, and 690 cm.$^{-1}$. The n.m.r. spectrum in carbon tetrachloride showed peaks at τ 3.30 (singlet, area 0.95) and 2.50 (multiplet, area 5.05).

Preparation of Triphenylmethyl Isocyanide (VIII).—Compound VIII was prepared by a method analogous to that of Hertler and Corey[10] by treatment of 20 g. of N-triphenylmethylformamide,[11] m.p. 199–201°, with 17.5 g. of *p*-toluenesulfonyl chloride in 80 ml. of pyridine. The resulting solution was allowed to stand at room temperature for 8 hr.; then cold water was added, the mixture was filtered, and the filtrate was extracted with ether. The ether layer was washed with water and then dried over anhydrous sodium sulfate. After chromatography on alumina (eluent carbon tetrachloride), 5.7 g. of VIII were obtained, m.p. 130–133°, after crystallization from benzene. The infrared spectrum in chloroform showed peaks at 2130 and 1590 cm.$^{-1}$ and the n.m.r. spectrum of a 10% solution in deuteriochloroform gave an unresolved singlet at τ 2.70. The infrared spectrum of triphenylmethyl cyanide,[12] m.p. 127–128°, showed a strong absorption at 2230 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{15}N$: C, 89.2; H, 5.6; N, 5.2. Found: C, 89.0; H, 5.7; N, 5.2.

Reaction of the Sodium Salt of Phenylchloronitromethane (VII) with Triphenylmethyl Isocyanide (VIII).—To 0.5 g. of phenylchloronitromethane in 4 ml. of ether a solution 0.17 g. of sodium hydroxide in 10 ml. of absolute ethanol was added in portions with stirring. The resulting precipitate was filtered in the absence of air and washed with ether. It was placed in a flask containing 10 ml. of dry benzene and to this suspension 1 g. of triphenylmethyl isocyanide in 10 ml. of benzene was added. The

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[8] All melting points are corrected. N.m.r. spectra were obtained with a Varian Associates A-60 spectrometer at 60 Mc. The author is indebted to Mr. O. Norton, Mr. D. Johnson, and their associates for these spectra. Infrared were measured with a Perkin-Elmer Model 21 spectrophotometer. Microanalyses were obtained in the Microanalytical Laboratory at the University of Illinois under the direction of Mr. J. Nemeth.

[9] A. van Peski, *Rec. trav. chim.*, **41**, 687 (1922).

[10] W. Hertler and E. Corey, *J. Org. Chem.*, **23**, 1221 (1958).

[11] H. Bredereck, R. Gompper, and G. Theilig, *Chem. Ber.*, **87**, 537 (1954).

[12] C. Schimelpfenig, *J. Org. Chem.*, **26**, 4156 (1961).

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 cm.$^{-1}$.

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

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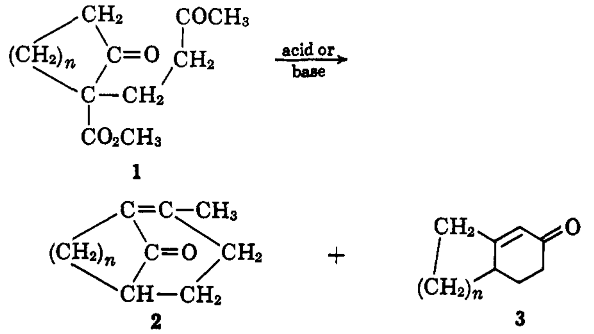
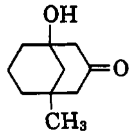
Bredt's rule[1] is an empirical formulation which, when applied to bridged ring systems, defines the minimum geometrical requirements necessary to accommodate a double bond at a bridgehead position. In an attempt to determine the lower limit of n in the bicyclo[n.3.1] series compatible with unsaturation at the bridgehead, Prelog[2] 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[3] 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[4] found that 3,5-dimethylbicyclo[3.3.1]nonan-1-ol (**5**) could not be dehydrated even under drastic conditions.



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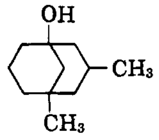
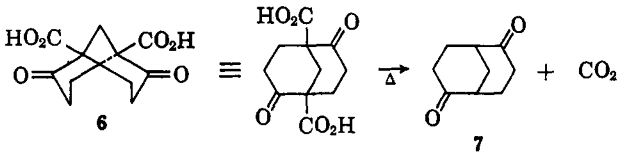


5

In contrast to these results, Meerwein[5] 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 possibility 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 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 τ 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[6] 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

Table I

Base-Catalyzed Deuterium Exchange of Bicyclo[3.3.1]nonan-2-one

Sample	Exchange time, days	D_0, %	D_1, %	D_2, %	D_3, %	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

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[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).

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[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).