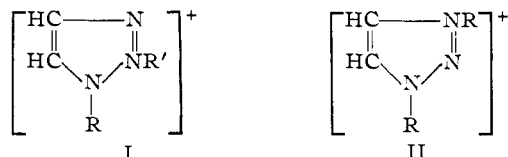


structure of quaternary salts obtained by alkylation of 1-alkyl-1,2,3-triazoles. This quaternization can result in two structural possibilities—the 1,2-dialkyl I and 1,3-dialkyl II types. The formation



of quaternary salts of known structure from triazoles which may be of either the 1- or 2-alkyl type can be coupled with other information and alternative routes of synthesis to establish or exclude structural possibilities. The only previous study of the alkylation of a 1-alkyl-1,2,3-triazole is that of Wolff² who treated methyl iodide with 1,5-dimethyl-1,2,3-triazole and obtained a quaternary salt but offered no evidence as to its structure. We wish to record data which eliminate the formation of the 1,2-structure in the quaternization of 1-alkyl-1,2,3-triazoles.

1-Benzyl-1,2,3-triazole³ has been methylated with methyl iodide in 70% yield, and 1-methyl-1,2,3-triazole has been benzylated with benzyl iodide in 83% yield. The 1-methyl-1,2,3-triazole was prepared by decarboxylation of 1-methyl-1,2,3-triazole-4,5-dicarboxylic acid in turn prepared from methyl azide and acetylenedicarboxylic acid.⁴ The two quaternary salts thus prepared were homogeneous and identical on the basis of direct comparison. This is conclusive proof that the alkylation did not occur on the 2-nitrogen in each reaction and that the product is probably 1(3)-benzyl-3(1)-methyl-1,2,3-triazole. It is likely that this behavior is general.

Experimental⁵

Methylation of 1-Benzyl-1,2,3-triazole.—From a mixture of 1.59 g. (0.010 mole) of 1-benzyl-1,2,3-triazole, 1 ml. of methyl iodide (*ca.* 2.5 g., 0.018 mole), 10 ml. of acetone and 5 ml. of ether there precipitated 2.2 g., 74%, of large, colorless, transparent crystals after five days at room temperature. Recrystallization from acetone and ether gave a product, m.p. 135–136°, unchanged on further recrystallizations.

Anal. Calcd. for C₁₀H₁₂N₃I: C, 39.88; H, 4.02. Found: C, 39.96, 40.06; H, 3.99, 4.23.

Benzylation of 1-Methyl-1,2,3-triazole.—To the 1-methyl-1,2,3-triazole prepared by the dry distillation of 5.40 g. (0.0316 mole) of 1-methyl-1,2,3-triazole-4,5-dicarboxylic acid⁴ was added 10 ml. of acetone, 10 ml. of ether and 6 ml. (10.4 g., 0.048 mole) of benzyl iodide. After eight days at room temperature during which time the mixture separated into two liquid layers, the lower of which solidified, there was obtained 7.9 g., 83%, of ether-washed crystals. Recrystallization from acetone gave a product, m.p. 130–132°, mixed m.p. with a sample from the preceding experiment (m.p. 132–134°, 130–134°).

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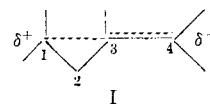
(5) Analyses by Micro Tech Laboratories.

The Reaction of Cyclohexadiene-1,4 with Electrophilic Reagents

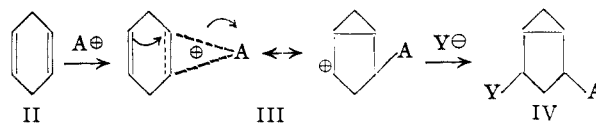
BY EUGENE E. VAN TAMELEN

RECEIVED SEPTEMBER 13, 1954

During recent years considerable attention has been paid to the phenomenon of "homoallylic resonance,"¹ which may be defined as the interaction of an electron-deficient center with a suitably oriented π -electron source in the 3,4-position, thereby involving a mesomeric cation of the type I.²



Interaction at C-4 with a nucleophilic reagent can lead to the formation of a cyclopropyl compound.^{3,4} In an attempt to detect the "i-steroid" effect in simpler systems, we have had occasion to investigate the reactions of cyclohexadiene-1,4 (II), which might be expected, on electrophilic attack, to form a mesomeric cation III and then be converted to IV by subsequent attachment of the nucleophile.



This proposed course of reaction is thus the homoallylic counterpart of the familiar 1,4-addition to a 1,3-diene. Now, several instances of addition reactions of cyclohexadiene-1,4 have appeared in the literature and, in fact, the characteristics of the product resulting from one of these has led us to suspect that III may in reality play a decisive role in determining the course of reaction. Cyclohexadiene-1,4 has been subjected to the Prévost reaction with a controlled amount of silver benzoate and iodine,⁵ and the product obtained was assigned the structure cyclohexenediol-4,5 dibenzoate. This dibenzoate was said not to decolorize an acetone solution of potassium permanganate, and neither the diester nor the diol obtained by saponification was attacked by bromine in carbon tetrachloride.⁶ These properties—hardly in keeping with olefinic structures—can be construed to favor bicyclo-(0,1,3)hexanediol-2,4 (VI) and its dibenzoate V as the true structures, which would result from a II \rightarrow III \rightarrow IV mechanistic sequence.⁷ Further study of

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(2) C. W. Shoppee, *Bull. soc. chim.*, **18**, 120 C (1951).

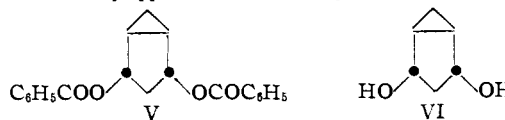
(3) T. Wagner-Jauregg and L. Werner, *Z. physiol. Chem.*, **213**, 119 (1932).

(4) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *THIS JOURNAL*, **72**, 3116 (1950).

(5) G. E. McCasland and E. C. Horswill, *ibid.*, **76**, 1654 (1954).

(6) Bromine water did, however, react positively with both the dibenzoate and the diol. This behavior does not necessarily exclude structures V and VI, since ring opening of the cyclopropyl group could occur with the hydrobromic acid always present (along with hypobromous acid) in equilibrium with bromine and water.

(7) The stereochemistry indicated in formula V follows from considerations already applied in the *i*-steroid system.²

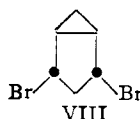
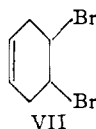


the diol showed, however, that it does possess the structure originally assigned in that it readily consumes periodic⁸ and perbenzoic acids⁸ and absorbs in the infrared at 3.31–3.33 μ , results which clearly indicate the presence of a 1,2-glycol system and an olefinic bond. In order to definitely establish the cyclohexenediol structure, the dibenzoate was catalytically reduced to *trans*-cyclohexanediol-1,2 dibenzoate, which was compared with authentic material.

An attempt to isolate a trace amount of the cyclopropyl dibenzoate V by thoroughly working up mother liquors from a comparatively large run was unsuccessful—only additional small amounts of the previously obtained dibenzoate were found.

In a supplementary experiment, cyclohexadiene-1,4 was transformed by means of perbenzoic acid to the mono-epoxide⁹ which, without isolation, was hydrolyzed with dilute mineral acid to a homogeneous diol, identical with that obtained from the Prévost sequence. Again, no evidence of rearrangement was apparent.

A third transformation previously reported for the diene II is bromination, assumed to give 4,5-dibromocyclohexene (VII), for which proof of structure has never been provided.¹⁰ The reported further bromination under more severe conditions to a tetrabromo compound is consistent with this assignment, although the result can hardly be taken to exclude the homoallylic rearrangement product VIII, the cyclopropyl ring of which constitutes a



site for electrophilic attack. In the repetition of the dibromide preparation, the whole of the crude product was arbitrarily divided during distillation into four approximately equal fractions. With the exception of one of these, which melted over a degree and a half range, the fractions melted over a one degree range; thus no more than a trace of isomeric dibromide can be present. Preliminary evidence for the structure of the dibromo compound was obtained readily through inspection of its infrared absorption spectrum; sharp bands at 3.31 and 6.06 μ , indicative of olefinic bonding, augur for the cyclohexene structure. In order to establish this structural feature, the dibromide was subjected to the action of perbenzoic acid. The rate of peroxidation was inordinately slow, in that a month at 0–5° was required for approximate completion of reaction. That epoxidation was the main reaction, however, was proved by isolation of the product, 4,5-dibromocyclohexene oxide, m.p. 67.5–68.0°, in good yield. Finally, catalytic reduction over palladium or platinum provided complete corroboration for structure VII, in that there was formed *trans*-1,2-dibromocyclohexane, the identity of which was proved by comparison, through infrared spectra, with an authentic sample.

(8) Uptake of these reagents did not cease at one mole, a result consistent with recent observations of McCasland and Horswill (*THIS JOURNAL*, **76**, 2373 (1954)). By contrast, the *dibenzoate* used just one mole of perbenzoic acid.

(9) M. Tiffeneau and B. Tchoubar, *Compt. rend.*, **212**, 581 (1941).

(10) J. P. Wibaut and F. A. Haak, *Rec. trav. chim.*, **67**, 85 (1948).

Experimental¹¹

Cyclohexenediol-4,5.—The diol was obtained essentially according to the directions of McCasland and Horswill.⁵

Oxidation in the dark with standard perbenzoic acid in chloroform at 5° resulted in proximate uptake of one mole after about 24 hours; further contact resulted in additional consumption of reagent. In connection with this result, *trans*-cyclohexenediol was studied and found also to consume perbenzoic acid under similar conditions; the nature of the product was not investigated. After 24 hours, cyclohexenediol-4,5 had used more than three moles of periodic acid (pH 7 at room temperature). The infrared spectra in chloroform and in perfluorokerosene showed absorption at 3.31–3.33 μ , but no well-defined peak in the 6.0–6.1 μ region.

Cyclohexenediol-4,5-dibenzoate reacted at 5° with one mole of perbenzoic acid in chloroform during 24 hours, after which period no further absorption was observed. One gram of the dibenzoate, dissolved in glacial acetic acid, rapidly absorbed just one mole of hydrogen over 10% palladium-on-carbon at 30 lb. initial pressure. Evaporation of the filtrate *in vacuo* left a sirup which crystallized on standing. The product as obtained in this fashion melted at 92.0–93.5° and did not lower the melting point of authentic *trans*-cyclohexenediol dibenzoate, m.p. 93–94°. ¹²

Cyclohexadiene-1,4 also was converted to the unsaturated diol through mono-epoxidation followed by ring opening. One milliliter of cyclohexadiene was added to 25 ml. of 0.209 *N* perbenzoic acid in benzene, and the solution was quickly swirled while being cooled in running water. After a few minutes of such treatment, the solution was allowed to stand in the refrigerator for 24 hours. Washing of the reaction mixture with three portions of dilute sodium hydroxide and with two subsequent portions of water was followed by evaporation *in vacuo* to approximately 2 ml. The liquid residue was swirled on the steam-bath with 5 ml. of 0.1 *N* hydrochloric acid until a homogeneous solution resulted. Evaporation at room temperature of the filtered solution afforded diol melting at 94.5–96°. The melting point was raised to 95–96° on crystallization from benzene, and the mixed melting point with authentic material was undepressed. Volatilization of the intermediate cyclohexadiene-1,4-monoxide during solvent removal was probably the reason for the only fair (41%) yield of final product.

4,5-Dibromocyclohexene.—Repetition of the directions given by Wibaut and Haak¹⁰ led to a 74% yield (total distillate) of dibrominated cyclohexadiene-1,4. This material was separated into four approximately equal fractions on redistillation (total b.p. range 121.0–121.5°), all of which crystallized on standing. The first three melted at 35.5–36.5°, and the highest boiling material at 34.5–36.0°; the reported melting point is 35.1–35.2°.

Catalytic reduction of 4,5-dibromocyclohexene over either 10% palladium-on-carbon or platinum proceeded poorly. In a particular run using 3.45 g. of dibromide, hydrogen was absorbed in increments of 5–15 lb.; after each, fresh catalyst had to be added before absorption again commenced. After a total of about 45 lb. of hydrogen was used (theoretical for one mole, 76 lb.), the reduction mixture was filtered and evaporated *in vacuo* to an oil. In order to remove unreacted dibromocyclohexene by conversion to tetrabromocyclohexane,¹³ this oil was taken up in dry chloroform and treated with excess bromine according to Wibaut and Haak.¹⁰ The dark reaction mixture was evaporated *in vacuo* and diluted with absolute methanol. After the tetrabromide had completely precipitated, it was filtered off, and the filtrate was then evaporated down *in vacuo*. Distillation of this residue afforded 0.80 g. (23%) of *trans*-1,2-dibromocyclohexane, b.p. 115–117° (28 mm.), the infrared of which was indistinguishable from that of the authentic dibromide.

4,5-Dibromocyclohexene Oxide.—4,5-Dibromocyclohexene (0.217 g.) dissolved in benzene containing a slight molar excess of perbenzoic acid was allowed to stand in the refrigerator for about one month. After removal of the or-

(11) Melting points are corrected; boiling points are not corrected. Infrared spectra were measured on a Baird automatic recording infrared spectrophotometer.

(12) N. A. B. Wilson and J. Reed, *J. Chem. Soc.*, 1269 (1935).

(13) Although the *trans*-1,2-dibromocyclohexane could be obtained without this expedient, the final purification was simplified through its introduction.

ganic acids by washing with dilute aqueous sodium carbonate and then with water, the benzene solution was allowed to evaporate at room temperature. The 0.160 g. (69%) of oxide, m.p. 66–67°, which remained was crystallized at 0° from 40–60° petroleum ether, yielding analytically pure material, m.p. 67.5–68.0°.

Anal. Calcd. for $C_6H_5Br_2O$: C, 28.14; H, 3.13. Found: C, 28.56; H, 3.28.

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COMMUNICATIONS TO THE EDITOR

SALT EFFECTS ON NON-ELECTROLYTES IN PARTIALLY AQUEOUS MIXED SOLVENTS¹

Sir:

Previous work on kinetic salt effects^{2,3} had led us to the belief that salt effects on non-electrolytes in mixed, partly aqueous solvents might be quite different from corresponding effects observed in water.

This belief has been borne out by some data recently obtained from solubility measurements in 50% dioxane at 25°, as tabulated in Table I.

Non-electrolyte	Solvent	Salt	<i>k</i>
Benzoic Acid	Water ⁴	NaCl	0.182
		HCl	.121
		KCl	.093
α -Naphthoic Acid	50% Dioxane	KI	.041
		HCl	.011
		KI	.017
		NaCl	– .12
Naphthalene	Water ⁵	KCl	– .15
		NaCl	.260
	50% Dioxane	KCl	.204
		NaCl	– .09
		KCl	– .08

The data show that the salting order of various electrolytes in 50% dioxane is quite different from that generally observed in water.³ This can be seen by comparing the values of *k* in Table I, which were obtained by plotting $\log \frac{S^0}{S}$ versus C_s and measuring the slope. A positive *k* is associated with salting-out while a negative *k* results from salting-in of the non-electrolyte by the salts present. For example, NaCl and KCl, which in water are usually better salting-out agents than HCl and KI, in 50% dioxane actually cause salting-in.

A qualitative understanding of the effect of the mixed solvent on the salting order of electrolytes may be reached on the basis of the preferential hydration of the electrolytes.⁴ Consider, for example, the effects due to KCl.⁵ In water, hydration of KCl leaves less solvent for the non-electrolyte to dissolve in; hence, salting-out. In 50% dioxane, pref-

erential solvation by water leaves an effective solvent richer in dioxane. When the non-electrolyte solubility increases with dioxane content, the net effect may be salting-in. The solubility data for naphthalene and α -naphthoic acid in Table II suggest this as a partial explanation.

Nonelectrolyte	Dioxane, %	Solubility (g./100 ml.)
α -Naphthoic Acid	40	0.89
	50	2.91
	60	7.57
Naphthalene	40	0.44
	50	0.79

The present data suggest that previous treatments of kinetic salt effects as colligative functions of ionic strength, or even on the basis of the Setschenow equation, may be oversimplified in partly aqueous solvents.

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RECEIVED FEBRUARY 10, 1955

AN INVESTIGATION OF THE HYPOTHETICAL ION PAIR INTERMEDIATE IN THE REARRANGEMENT OF 9-DECALYL HYDROPEROXIDE BENZOATE USING OXYGEN-18

Sir:

Recently, ion pairs have been considered as intermediates in a variety of organic reactions.^{1,2,3} The degree of separation of the ions in many of these reactions, particularly those ion pairs which have been dubbed "intimate" or "internal," has remained obscure. We wish to report the results of an oxygen-18 tracer study of the rearrangement of the benzoate of 9-decalyl hydroperoxide (I), a reaction which has the properties of an intimate ion pair reaction.^{4,5}

Benzoyl chloride-O¹⁸, prepared from benzoic acid-O¹⁸, was allowed to react with 9-decalyl hydroperoxide to form I. I was rearranged in both methanol and acetic acid to give 1-benzoyl-1,6-epoxycyclodecane (III) which was reduced with lithium aluminum hydride to benzyl alcohol

(1) This paper is based on research done under contract Nonr 988(02) with the Office of Naval Research.

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