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ELECTROPHILIC ADDITION TO BICYCLO[1.1.0]BUTANE

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The electronic structure of bicyclo[1.1.0]butane (I) [1], in particular the C(1)-C(3) bond, accounts for its capacity to react similar to unsaturated systems with some electrophilic reagents, in particular, with $\text{Hg}(\text{OAc})_2$ [2-4].

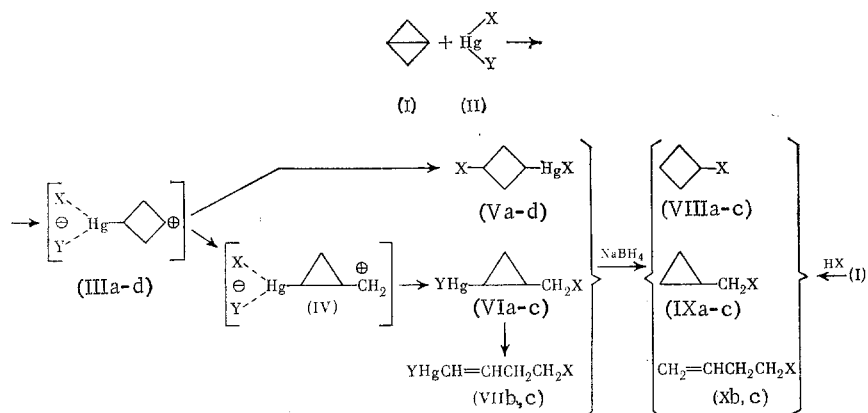
We studied the reaction of (I) with a series of mercury compounds, HgCl_2 , HgBr_2 , HgI_2 , MeHgCl (IIa-d), and Me_2Hg . Compounds (IIa-c) are capable of adding to cyclopropanes, olefins, and acetylenes [5].

Under mild conditions at 20°C in CH_2CH_2 , (I) reacts vigorously with (IIa-c) giving ~70% yields of organomercury salts which are insoluble in organic solvents. The structure of these salts was determined by demercuration of the products formed in alkali medium by the action of NaBH_4 [6] with conversion to the corresponding halides; this method was used for determining the products of the addition of $\text{Hg}(\text{OAc})_2$ to bicyclobutanes [2-4, 7].

The reduction of the products of the addition of (IIa) to (I) gave a 1:3 mixture of chlorocyclobutane (VIIIa) and chloromethylcyclopropane (IXa). Demercuration of the products of the reaction of (I) with (IIb) and (IIc) gave, in addition to (VIII) and (IX), open-ring compounds, 4-bromo-1-butene (Xb) and 4-iodo-1-butene (Xc)

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Scheme



X = Y = Cl (a); X = Y = Br (b); X = Y = I (c); X = Cl, Y = CH₃ (d)

Removal of samples of the reaction mixture over fixed time intervals and analysis of these samples after demercuration showed that halobutenes (Xb) and (Xc) appear only after a certain time period (≥ 10 min) from the reaction onset and their concentration increases over time due to a decrease in the concentration of the cyclopropyl compounds (IXb) and (IXc) (Table 1). In addition, demercuration of the products of the reaction of (I) with (IIb) and (IIc) and maintenance for 24 h led to a mixture virtually lacking (IX).

Thus, halobutenes (X) may be considered to form in the demercuration of the secondary reaction products apparently arising from cyclopropyl organomercury compounds.

The addition of CH₃HgCl to (I) proceeded under the same conditions as the addition of (IIa-c) but at a somewhat lower rate and the product of reduction of the reaction mixture was only chlorocyclobutane (VIIIa).

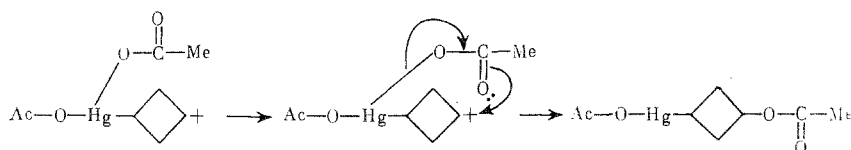
The structure of (VIII), (IX), and (X) was established by convergent synthesis from several of these compounds [(VIIIc) and (Xb, c)] and comparison of the gas-liquid chromatographic and PMR spectral data of the reaction mixtures with mixtures obtained by the reaction of (I) with hydrogen halide acids. This comparison is justified since electrophilic addition to (I) yields mixtures containing cyclobutyl, cyclopropylcarbinyl, and butenyl derivatives [8]. Thus, (I) reacts with mercury halides with the initial formation of halomethylcyclopropylmercury halide (VI) and halocyclobutylmercury halide (V). The addition of (II) leads only to the cyclobutane derivative (Vd).

Since the reactions studied and the addition of Hg(OAc)₂ to (I) described in our previous work [3] proceed readily in low-polarity and nonpolar solvents such as CH₂Cl₂ and CCl₄, we may assume that the addition takes place without prior ionization of the mercury salts. A synchronous process should also apparently be excluded since the reaction does not always proceed by a single pathway with retention of the four-membered ring. The intermediate formation of the bipolar ion (III) is most likely and this is in good accord with the available experimental results. Indeed, the subsequent fate of ions (III) will be a factor of the stabilization either by the transfer of X⁻ to a cationic site or rearrangement [8] to a cyclopropylcarbinyl cation (IV) with subsequent transfer of X⁻. Thus, the ratio of the cyclobutyl products to the cyclopropylcarbinyl products or to the sum of the latter with butenyl products will depend on the capacity of the X⁻ anion to migrate (the strength and length of the Hg-X

TABLE 1

Time from reaction onset, h	Cyclobutyl-X, %		Cyclopropylcarbinyl-CH ₂ X, %		CH ₂ =CHCH ₂ CH ₂ X, %	
	Br	I	Br	I	Br	I
0,1	33,75	33,47	66,25	66,53	—	—
0,5	34,78	34,46	56,52	55,92	8,70	9,62
1,0	34,09	34,21	13,63	26,32	52,27	39,47
2,0	34,48	35,11	4,11	7,40	61,21	57,49
24,0	34,78	35,51	2,17	4,61	63,04	59,78

bond). This is in accord with the observed product ratios: 35:65 for HgBr₂ and HgI₂ and 1:3 for HgCl₂). This scheme also accounts for the addition of CH₃HgCl to (I), in which the exclusive formation of the cyclobutyl derivative may be ascribed to the high nucleophilicity of Cl⁻ in the intermediate (III_d) relative to the adduct with HgCl₂ (III_a). This scheme also readily explains the selective formation of the cyclobutyl derivative in the reaction of Hg(OAc)₂ and (I) [3] due to facile migration of an acetoxy group by means of cyclic electron transfer.



The sole formation of aliphatic products in the reaction of (I) with trialkylboranes [9] may be explained similarly.

In contrast to (Ia-d), the weaker electrophile Me₂Hg does not add to (I) even upon heating in a sealed ampul at 40°C for 24 h. The Grignard reagents, MeMgI and EtMgBr, which are strong nucleophiles, do not add to (I) even upon prolonged heating in THF at 65°C and Bu₂O at 80°C.

EXPERIMENTAL

The PMR spectra were taken on a Varian DA-60-IL spectrometer for 30-35% solutions in CHCl₃ and TMS internal standard. The chemical shifts are given in ppm (δ scale). The gas-liquid chromatographic analysis was carried out on a Pye-104 chromatograph using a 1.5-m glass column packed with 10% PEGA on Celite (100/120 mesh) at 40-100°C.

Reaction of (I) with HgCl₂ (II_a). A sample of 2 g (0.037 mole) (I) was added slowly to a stirred suspension of 10 g (0.037 mole) HgCl₂ in 20 ml dry CH₂Cl₂ at 20°C. The temperature spontaneously rose to 42°C and the color of the suspension turned from white to dark red. After the addition of (I), the mixture was stirred until the temperature dropped to ~20°C. Then, the reaction mixture was reduced with a 3 M solution of NaBH₄ in 3 M aq. NaOH at 20°C. The organic layer was removed and dried. The solvent was evaporated to yield 2.16 g (70%) of a 1:3 mixture of cyclobutyl chloride (VIII_a) and chloromethylcyclopropane (IX_a) (gas chromatographic analysis). The PMR spectrum of the mixture: 0.20-0.85 m (c-C₃H₆, 4H), 0.85-1.35 m (cyclopropane adjacent to CH₂Cl, 1H), 3.20-3.30 d (CH₂Cl, J = 7.0 Hz, 2H), 1.32-2.50 m (c-C₄H₈, 6H), 3.90-4.20 m (CHCl, 1H).

Reaction of (I) with HgBr₂ (II_b). The reaction was carried out similarly to the above. Removal of the solvent yielded 3.53 g (70%) of a mixture consisting of 35% (VIII_b), 17% (IX_b), and 48% (X_b) (gas chromatographic analysis). PMR spectrum of the mixture: 0.21-1.05 m (c-C₃H₆, 4H), 1.05-1.57 m (cyclopropane proton adjacent to CH₂Br, 1H), 3.37-3.50 d (CH₂Br, J = 7.5 Hz, 1H), 1.57-2.37 m (c-C₄H₈, 6H), 4.35-4.80 m (CHBr, 1H), 2.37-2.93 m (CH₂CBr, 2H), 3.58-4.10 m (CCH₂Br, 2H), 4.92-5.30 m (CH₂=C, 2H), 5.50-6.10 m (C=CH, 1H).

Reaction of (I) with HgI₂ (II_c). The reaction was carried out similarly to the above and yielded 2.16 g (50%) of a mixture consisting of 35% (VIII_c), 25% (IX_c), and 40% (X_c). PMR spectrum of the mixture: 0.17-1.03 m (c-C₃H₆, 4H), 1.03-1.62 m (cyclopropane proton adjacent to CH₂I, 1H), 3.09-3.22 d (CH₂I, J = 7.5 Hz, 2H), 1.65-2.47 m (c-C₄H₈, 6H), 4.32-4.65 m (CHI, 1H), 2.20-2.70 m (CH₂CI, 2H), 3.00-3.40 m (CCH₂I, 2H), 4.50-5.00 m (CH₂=C, 2H), 5.30-6.10 m (C=CH, 1H).

Reaction of (I) with MeHgCl (II_d). The reaction was conducted similarly to the above with 5 g MeHgCl and 1 g (I). Reduction with NaBH₄ and removal of the solvent yielded 0.6 g (40%) (VIII_a) identified by gas chromatography.

Reaction of (I) with Grignard Reagent. The reaction was carried out by a modification of our previous method [10]. Starting (I) was isolated.

Reaction of (I) with Hydrogen Halide Acids. A sample of 1 g (I) was added slowly to 5 ml conc. HX at -5°C. After the addition, the mixture was warmed to 20°C. The organic layer was removed washed with sat. aq. NaCl and dried.

The reaction of (I) and HCl yielded 1.5 g (90%) of a 40:60 mixture of (VIII_a) and (IX_a).

The PMR spectrum was identical to that of the mixture of (VIIIa) and (IXa) obtained from the reaction of (I) with HgCl_2 .

The reaction of (I) and HBr yielded 2.25 g (90%) of a 33:60:7 mixture of (VIIIb), (IXb), and (Xb) with PMR spectrum analogous to that obtained for the products of the reaction of (I) with HgBr_2 .

The reaction of (I) and HI yielded 3 g (90%) of a 34:57:9 mixture of (Vc), (IXc), and (Xc) (gas chromatographic analysis with PMR spectrum analogous to that obtained for the products of the reaction of (I) with HgI_2).

Iodocyclobutane (VIIIc). A solution of 4 g (VIIIb) and 8 g LiI in abs. acetone was heated at reflux for 48 h. After removal of the solvent and distillation of the starting (VIIIb), the residue was distilled in vacuum to yield 1.8 g (VIIIc) (35%) with bp 90–92°C (80 mm). PMR spectrum: 1.70–2.47 m ($\text{c-C}_4\text{H}_8$, 6H), 4.33–4.80 m (CHI, 1H).

Allylcarbinol (XI). A solution of 76.6 g $\text{CH}_2=\text{CHCH}_2\text{Cl}$ in 200 ml abs. ether was added slowly to a stirred mixture of 24 g magnesium and 30 g paraform in 250 ml abs. ether heated at reflux. The mixture was heated for an additional 2 h, left overnight, and then poured onto 500 g ice and decomposed with dil. H_2SO_4 . The ethereal layer was removed. A 500-ml distillate fraction was obtained from steam distillation of the aqueous solution. This fraction was dried over K_2CO_3 and extracted with ether. The ethereal extracts were combined with the ethereal layer and dried over anh. Na_2SO_4 . The solvent was evaporated and the residue was distilled to yield 32.4 g (45%) (XI) with bp 112–114°C, n_D^{20} 1.4224.

4-Bromo-1-butene (Xb). A sample of 15.86 g tosylate (XI) obtained from (XI) according to a standard procedure [11] was added to a solution of 12.4 g LiBr in abs. acetone. The reaction mixture was heated at reflux for 1 h and the TsOLi precipitate was removed by filtration. The filtrate was extracted with CHCl_3 and the organic layer was washed with water and dried. The solvent was evaporated and the residue was distilled to yield 3.3 g (98%) (Xb) with bp 98–100°C. PMR spectrum: 2.30–2.85 m (CH_2CBr , 2H), 3.55–3.90 s (CH_2Br , 2H), 4.80–5.28 ($\text{CH}_2=\text{C}$, 2H), 5.40–6.16 m ($\text{CH}=\text{C}$, 1H).

4-Iodo-1-butene (Xc) was obtained by analogy to (Xb) in 98% yield (12.4 g) with bp 85–87°C (120 mm). PMR spectrum: 2.20–2.70 m (CH_2Cl , 2H), 3.00–3.40 m (CH_2I , 2H), 4.50–5.00 m ($\text{CH}_2=\text{C}$, 2H), 5.30–6.10 m ($\text{CH}=\text{C}$, 1H).

CONCLUSIONS

A study was carried out on the electrophilic addition of some divalent mercury compounds to bicyclo[1.1.0]butane and a mechanism was proposed accounting for the ratio of cyclobutyl and cyclopropylcarbinyl products.

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