1,4- AND 1,5-BROMINE SHIFTS IN THE ACYLATION OF ALKYNES

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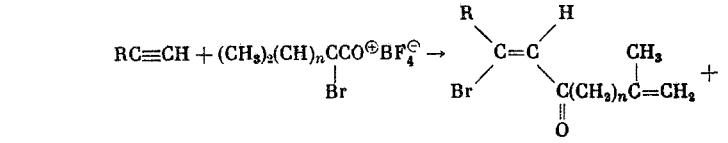
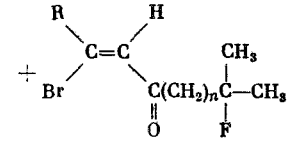
We have shown that acylation of alkynes with α-bromobutyryl tetrafluoroborate involves a 1,4-bromine shift and forms substituted β-bromovinyl ketones [1]. Our intention in the present work was to make a further study of the acylation of alkynes by bromoacylium tetrafluoroborates.

The reactions of methylacetylene (I) or phenylacetylene (II) with α-bromoisobutyryl (III)* and α-bromoisovaleryl tetrafluoroborate (IV)* proceed like those described in [1] and form substituted β-bromovinyl ketones (V)-(VIII) as major products. We also isolated fluorine-substituted β-bromovinyl ketones (IX)-(XI)



$R = CH_3$ (I), C_6H_5 (II), $n = 0$ (III), 1 (IV)

$R = CH_3$, $n = 0$ (V), $R = C_6H_5$, $n = 0$ (VI), $R = CH_3$, $n = 1$ (VII), $R = C_6H_5$, $n = 1$ (VIII),



$R = C_6H_5$, $n = 0$ (IX), $R = CH_3$, $n = 1$ (X), $R = C_6H_5$, $n = 1$ (XI)

These are apparently formed as the result of the reaction of ketones (VI)-(VIII) with HF liberated in the course of the reaction. Their formation is suppressed when acylium hexafluoroantimonate is used for the acylation, which indirectly supports this pathway. Thus the reaction of α-bromoisovaleryl hexafluoroantimonate with butylacetylene forms a single product, bromovinyl ketone (XII) (76% yield)

$$C_4H_9C{\equiv}CH + (CH_3)_2CHCHBrCO^{\oplus}SbF_6^{\ominus} \rightarrow C_4H_9CBr{=}CHCOCH_2C(CH_3){=}CH_2 \quad \text{(XII)}$$

We determined the structures of all the products on the basis of their PMR spectra and verified them from their UV and mass spectra. Comparison of the PMR spectra of (V) and (VII) and of the stereoisomeric ketones (Va) and (VIIa) [prepared by photoisomerization of (V) and (VII)] reveals that the signals of the β-carbon CH_3 group in (V) and (VII) lie ~ 0.3 ppm upfield of their positions in (Va) and (VIIa). They correspond to normal difference in β-CH_3 chemical shifts in α, β-unsaturated ketones between trans and cis methyl and carbonyl groups [1, 3]. Consequently, we assigned the Z configuration to ketones (V) and (VII). By analogy we adopted the same configuration for the other reaction products, (VI), (VIII), and (IX)-(XII).

That β-bromovinyl ketones (V)-(VIII) with the Z configuration are formed compels us to suppose that acylation with α-bromoacylium cationoids apparently generates an intermediate resembling the five-membered cyclic bromonium ion (XIII), which is then either stabilized by elimination of the proton from the β-carbon

*Prepared by exchange reaction of the acid bromides with $AgBF_4$; for the stability of α-haloacylium cationoids see [2].

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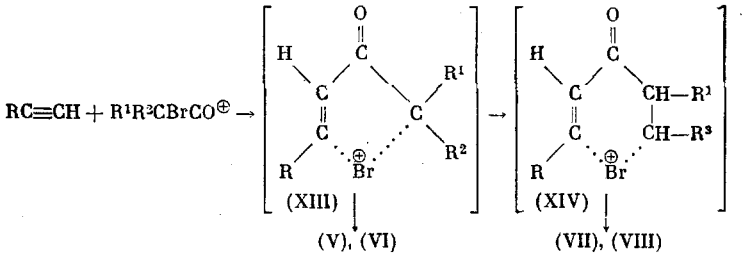
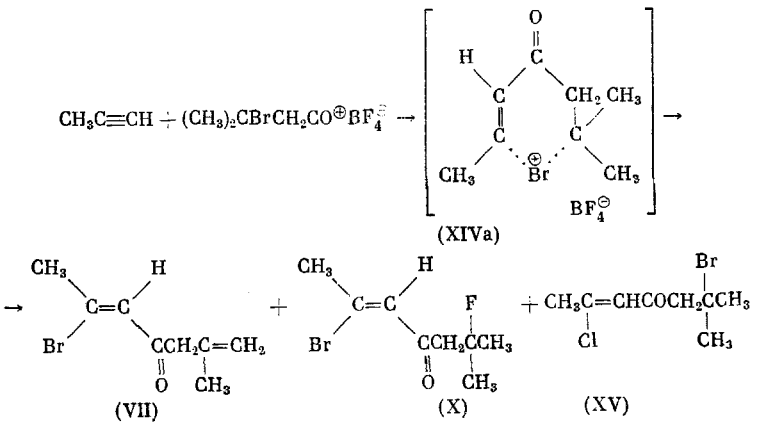
of the acyl group [formation of (V), (VI)] or rearranges to the six-membered cyclic bromonium ion (XIV) by a 1,2-hydride shift from the β- to the α-carbon. Stabilization by proton elimination from the γ-carbon of the acyl group forms ketones (VII) and (VIII)



All attempts to trap the bromonium intermediates by adding nucleophiles (H_2O, CH_3OH, benzene, mesitylene) when the reaction was quenched were unsuccessful. They seem to be extremely unstable and they become stabilized by proton elimination before addition of the nucleophiles. Indirect support for the formation of an intermediate like (XIV) in the reaction with α-bromoisovaleryl tetrafluoroborate is that ketones (VII) and (X) are also formed by the reaction of propyne (I) with β-bromoisovaleryl tetrafluoroborate



In this case the formation of ketones (VII) and (X) demonstrates that the reaction involves a 1,5-halogen shift. However, this reaction produces a considerable quantity of β-chlorovinyl ketone (XV) as a result of intermolecular halogen transfer from the solvent [4]. This compels us to suppose that the generation of six-membered cyclic bromonium ions of type (XIVa) is much more difficult than that of five-membered cyclic intermediates of type (XIII).*

These results together with those of our earlier work [1] show that a 1,4-bromine shift is a fairly general occurrence in the acylation of alkynes by normal or branched α-bromoacylium tetrafluoroborates. The resulting Z-β-bromovinyl ketones are relatively inaccessible compounds that are potentially useful in synthesis.

EXPERIMENTAL

The PMR spectra were recorded on a Varian DA-60-IL instrument in CCl_4 with tetramethylsilane (TMS) as internal standard; the UV spectra were recorded on a Specord UV-VIS instrument in alcohol. The purity of the synthetic compounds was verified by GLC (30 m × 0.4 mm glass capillary columns with SE-30 and XE-60). The synthetic β-bromovinyl ketones were extremely labile compounds; consequently, the majority did not give satisfactory elemental analyses. All synthetic compounds were characterized by their mass spectra.

Z-2-Bromo-5-methyl-2,4-hexadien-3-one (V). To a solution of $AgBF_4$ (0.73 g, 3.75 mmole) in dichloroethane (3 ml) and CH_2Cl_2 (10 ml) at −60°C was added $(CH_3)_2CBrCOBr$ (0.86 g, 3.75 mmole) in CH_2Cl_2 (2 ml). After 5-min vigorous stirring methylacetylene (64 ml, 2.5 mmole) was added by syringe. The mixture was stirred at −60°C for 40 min. A mixture of ether (10 ml) and saturated aqueous $NaHCO_3$ (10 ml) was added. The organic layer was removed and the aqueous layer was extracted three times with ether. The combined extracts were washed with saturated $NaHCO_3$ solution and with water and evaporated. Chromatography of the

*For the preferential formation of five-membered cyclic halonium ions see [5].

residue on silica gel gave (V) (147 mg, 31%). PMR spectrum (δ, ppm): 6.63 q, 5.83-5.66 m, 2.38, 1.88-1.76 m. Mass spectrum: 190 (M^+), 188 (M^+), 175, 173, 149, 147, 109.

Irradiation of a solution of (V) (150 mg) in absolute ether (50 ml) gave the E isomer of (V). PMR spectrum (δ, ppm): 7.03 q, 5.9-5.68 m, 2.7 d, 1.86 m.

Z-1-Phenyl-1-bromo-4-methyl-1,4-pentadien-3-one (VI). To a vigorously stirred solution of $AgBF_4$ (0.73 g, 3.75 mmole) in dichloroethane (3 ml) and CH_2Cl_2 (10 ml) at −60°C was added a solution of $(CH_3)_2CBrCOBr$ (0.86 g, 3.75 mmole) in CH_2Cl_2 (2 ml). After 5 min a solution of phenylacetylene (0.25 g, 2.5 mmole) in CH_2Cl_2 (2 ml) was added. The reaction mixture was then stirred at −60°C for 10 min. After the usual treatment chromatography of the residue on silica gel gave (VI) (231 g, 37%), λ_{max} 238 nm (ε 8460), 295 nm (ε 7060). PMR spectrum (δ, ppm): 7.63-7.16 m, 7.05 s, 5.83 dd (J = 8 Hz), 1.86 d. Mass spectrum: 252 (M^+), 250 (M^+), 211, 209, 183, 181, 129, 102.

Z-1-Phenyl-1-bromo-4-fluoro-4-methyl-1-penten-3-one (IX). The preceding reaction was carried out again but with the length of stirring of the reaction mixture extended to 1 h. Chromatography on silica gel gave (VI) (40 mg) and (IX) (52 mg), yield 8%, λ_{max} 205 nm (ε 12,000), 228 nm (ε 6800), 297 nm (ε 11,900). PMR spectrum (δ, ppm): 7.71-7.21 m, 1.43 d (J_{CH_3-F} = 22 Hz). Mass spectrum 272 (M^+), 270 (M^+), 211, 209, 183, 181, 129, 102.

Reaction of Methylacetylene with α-Bromoisovaleryl Tetrafluoroborate. To a solution of $AgBF_4$ (0.73 g, 3.75 mmole) in dichloroethane (2 ml) and CH_2Cl_2 (5 ml) at −60°C was added methylacetylene (64 ml, 2.5 mmole) by syringe. A solution of $(CH_3)_2CHCHBrCOBr$ (0.91 g, 3.75 mmole) in CH_2Cl_2 (2 ml) was then added with vigorous stirring. The mixture was stirred at −60°C for 10 min. After the usual treatment, chromatography on silica gel gave: 1) (VII) (195 mg, 38%). PMR spectrum (δ, ppm): 6.53 q, 4.86-4.75 m, 3.08 s, 2.38 d, 1.66 d. Mass spectrum: 204 (M^+), 202 (M^+), 149, 147, 123, 121, 119; 2) (X) (100 mg, 18%). PMR spectrum (δ, ppm): 6.55 q, 2.75 d (J_{CH_2-F} = 16 Hz), 2.41 d, 1.38 d (J_{CH_3-F} = 22 Hz). Mass spectrum: 224 (M^+), 222 (M^+), 204, 202, 149, 147, 123, 121, 119.

Irradiation of a solution of (VII) (100 mg) in cyclohexane (50 ml) gave its E isomer. PMR spectrum (δ, ppm): 6.68 q, 4.96-4.75 m, 3.03 s, 2.75 d, 1.73 d.

Reaction of Phenylacetylene with α-Bromoisovaleryl Tetrafluoroborate. To a solution of $AgBF_4$ (0.73 g, 3.75 mmole) in dichloroethane (3 ml) and CH_2Cl_2 (10 ml) at −65°C was added a solution of $(CH_3)_2CHCHBrCOBr$ (0.91 g, 3.75 mmole) in CH_2Cl_2 (2 ml). After 5 min a solution of phenylacetylene (0.25 g, 2.5 mmole) in CH_2Cl_2 (2 ml) was added with vigorous stirring. The mixture was stirred at −60°C for 15 min. After the usual treatment, chromatography gave: 1) (VIII) (277 mg, 42%), λ_{max} 227 nm (ε 9100), 294 nm (ε 17,100). PMR spectrum: (δ, ppm): 7.70-7.25 m, 7.00 s, 5.00-4.80 m, 3.25 s, 1.78. Mass spectrum: 211, 209, 183, 181, 129, 102. 2) (XI) (123 mg, 17%), λ_{max} 237 nm (ε 7300), 290 nm (ε 12,500). PMR spectrum:(δ, ppm): 7.66-721 m, 6.98 s, 2.83 d (J_{CH_2-F} = 16 Hz), 1.41 d (J_{CH_3-F} = 22 Hz). Mass spectrum: 286 (M^+), 284 (M^+), 211, 209, 183, 181, 129, 102.

Photoisomerization of (VIII) apparently formed a mixture of isomeric 1-phenyl-1-bromo-5-methyl-1,4-hexadien-3-ones. PMR spectrum (δ, ppm): 7.63-7.13 m, 6.77 s, 6.60 s, 6.12 q, 5.53 q, 2.13 d, 1.93 d, 1.85 d, 1.57 d.

Reaction of Methylacetylene with β-Bromoisovaleryl Tetrafluoroborate. To a solution of $AgBF_4$ (0.73 g, 3.75 mmole) in dichloroethane (3 ml) and CH_2Cl_2 (10 ml) at −60°C was added methylacetylene (64 ml, 2.5 mmole) by syringe. A solution of $(CH_3)_2CBrCH_2COCl$ (0.75 g, 3.75 mmole) in CH_2Cl_2 (2 ml) was then added with vigorous stirring. The mixture was stirred at −60°C for 10 min. After the usual treatment, chromatography on silica gel gave: 1) (XV) (103 mg, 18%). PMR spectrum (δ, ppm): 6.4 q, 3.0 s, 2.5 d, 1.85 s. Mass spectrum: 240 (M^+), 238 (M^+), 161, 159, 105, 103. The compound was accompanied by (VII) (70 mg, 15%). 2) (X) (94 mg, 18%).

2-Methyl-6-bromo-1,5-dodecadien-4-one (XII). To a vigorously stirred solution of $AgSbF_6$ (1.38 g, 4 mmole) in dichloroethane (7 ml) and CH_2Cl_2 (3 ml) at −50°C was added a solution of $C_4H_9C \equiv CH$ (0.25 g, 3 mmole) and $(CH_3)_2CHCHBrCOBr$ (0.97 g, 4 mmole) in CH_2Cl_2 (3 ml). The mixture was stirred at −55°C for 3 min. After the usual treatment, preparative TLC on silica gel gave (XII) (0.56 g, 76%), λ_{max} 247 nm (ε 7300). Found: C 53.41; H 7.20; Br 31.76%. $C_{11}H_{17}BrO$. Calculated: C 53.87; H 6.99; Br 32.59%. PMR spectrum (δ, ppm): 6.53 t, 4.88-4.71 m, 3.15 s, 2.53 t, 1.73 d, 1.58-0.95 m.

CONCLUSIONS

Acylation of alkynes with α- or β-bromoacylium tetrafluoroborates forms substituted Z-β-bromovinyl ketones as a result of the conjugate addition of the acylium cation and 1,4- or 1,5-bromine migration from the acyl group.

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SYNTHESIS OF SUBSTITUTED CYCLOPROPYLCARBINOLS AND CYCLOPROPYL KETONES BASED ON THE REACTION OF CYCLOPROPENE HYDROCARBONS WITH GRIGNARD REAGENTS

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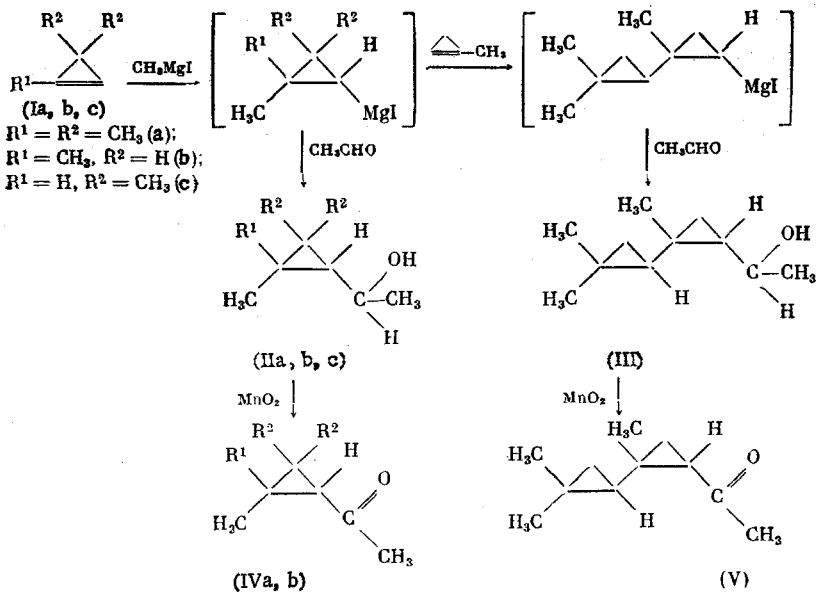
Grignard reagents add cis to the double bond of cyclopropenes under mild conditions. Addition is stereospecific and forms substituted cyclopropylmagnesium halides [1]. 1-Methylcyclopropene can react further with methylmagnesium halide: The intermediate cyclopropylmagnesium halide is capable of adding to a second molecule of 1-methylcyclopropene to form a cyclopropylcyclopropyl magnesium derivative [2].

Here we report a study of the addition of CH_3MgI to 1,3,3-trimethylcyclopropene (Ia), 1-methylcyclopropene (Ib), and 3,3,-dimethylcyclopropene (Ic). Our intention was to prepare methylcarbinols of the cyclopropane and cyclopropylcyclopropane series with methyl substituents on the three-membered ring, (IIa), (IIb), (IIc), and (III), together with the corresponding ketones, (IVa), (IVb), and (V).



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