SYNTHESIS AND CONVERSIONS OF CYCLOPROPYLACETYLENES

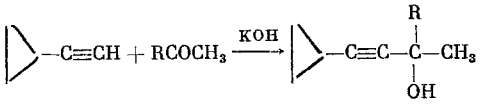
O. M. Nefedov, I. E. Dolgii,
I. B. Shvedova, and É. A. Baidzhigitova,

UDC 542.91:547.512

Acetylene derivatives are widely used in organic synthesis. However, the reactions of the cyclopropylacetylenes, which are difficult to obtain, have hardly been studied. After having developed a simple synthesis of cyclopropylacetylene (I) from methyl cyclopropyl ketone (IIb) [1], in the present work we have investigated the behavior of (I) in some typical reactions of acetylenes, particularly the one with ketones and the further conversion of the cyclopropylethynylcarbinols so obtained.

Condensation of monosubstituted acetylenes with acetone (IIa) under the conditions of the Favorskii reaction leads to the formation of ethynylcarbinols, usually in high yields [2]. The reaction of monosubstituted acetylenes with (IIb) is exemplified by the formation of methyl(cyclopropyl)(phenylethynyl)carbinol from phenylacetylene in 83.5% yield by the Favorskii reaction, and 80-95% yield by the Iotsich reaction [3].

From (I) and (IIa) in the presence of KOH at 20° we obtained by the Favorskii reaction dimethyl(cyclopropylethynyl)carbinol (IIIa) in 50% yield.

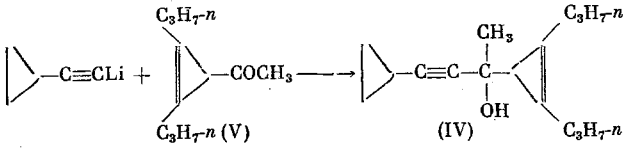


(I) (II) (III)

R = CH_3 (a), Cyclopropyl (b)

When (IIIa) was synthesized from (IIa) and cyclopropylethynylmagnesium bromide [prepared from (I) and C_2H_5MgBr], the yield reached 70%. Analogously, 2,4-dicyclopropyl-3-butyn-2-ol (IIIb) was obtained in 73% yield by the Iotsich reaction. The carbinol (IIIb) is formed in higher yield by the reaction of (IIb) with cyclopropylethynyllithium [obtained from (I) and n-butyllithium].

We then studied the possibility of involving alkyl cyclopropenyl ketones in these reactions; until now these compounds have not been used for ethynylcarbinol synthesis because they are scarce. The instability of methyl cyclopropenyl ketones in the presence of bases, especially at high temperatures, prevents their use in the Favorskii reaction [4]. Alkylmagnesium halides are also reactive toward cyclopropenyl compounds, adding to the transannular multiple bond; this hinders the formation of cyclopropenylethynylcarbinols by way of organomagnesium compounds [5]. In this connection, 2-(1,2-di-n-propylcyclopropen-3-yl)-4-cyclopropyl-3-butyn-2-ol (IV) can be synthesized from methyl 1,2-di-n-propylcyclopropen-3-yl ketone by reaction with cyclopropylethynyllithium.



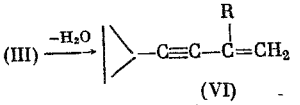
When this reaction is carried out at low temperature (down to −78°) tar formation is essentially avoided, and IV is obtained in 56% yield.

Acetylenic alcohols are usually dehydrated by the action of acidic reagents such as PX_3, POX_3, P_2O_5, $KHSO_4$, or organic or inorganic acids [6]; but these cannot be used to dehydrate (III) because of the lability of the cyclopropane ring. Methylcyclopropylcarbinols are dehydrated without isomerization of the three-membered ring by the action of the cation-exchange resin Amberlite IRC-50 in the H^+ form [7]. However, when carbinol

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1339-1344, June, 1978. Original article submitted February 25, 1977.

 0568-5230/78/2706-1164 $07.50

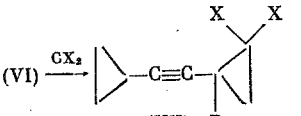
(IIIa) was boiled with this resin in benzene for 60 h, it did not undergo any sort of conversion. When it was boiled for 50 h with Dowex 50 resin, a product was obtained in 30% yield (by gas chromatography); Its IR spectrum contained two bands (1615 and 1680 cm^{-1}) in the region of the C=C valence vibrations which indicate that the ring has been opened. The enynes (VIa) and (VIb) were synthesized in yields of 67 and 26%, respectively, uncontaminated by isomerization products (according to IR and PMR spectra) by heating (IIIa) and (IIb) with an excess of hempa at 220-245°.



(III) $\xrightarrow{-H_2O}$ (VI)

R = CH_3 (a), Cyclopropyl (b)

We then investigated the reaction of the enynes thus obtained with dichloro- and dibromocarbenes. According to [8], enynes with a deactivated double bond, such as 1,4-diphenyl- and 1,4-dialkyl-trans-butenynes, react with dichlorocarbenes predominantly at the triple bond. On the other hand, acyclic conjugated enynes containing alkyl substituents at the 2 position add dihalocarbenes at the double bond to form dihaloethynylcyclopropanes [9]. When dichlorocarbene (generated by the reaction of $CHCl_3$ with aqueous alkali in the presence of an interphase transfer catalyst) reacts with the enynes (VIa) and (VIb), the adducts (VIIa) (X = Cl) and (VIIb) (X = Cl) are formed in yields of 38 and 28%, respectively.

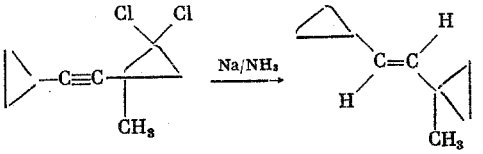


(VI) $\xrightarrow{CX_2}$ (VII)

R = CH_3 (a), Cyclopropyl (b); X = Cl or Br

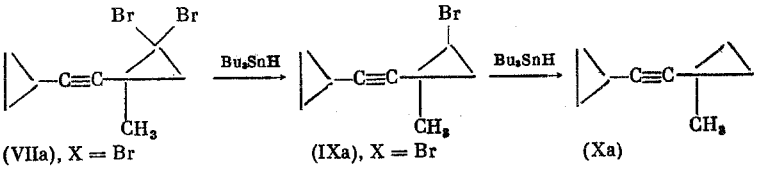
The addition of dibromocarbene (from equivalent amounts of t-C_4H_9OK and $CHBr_3$) to (VIa) yielded 1,1-dibromo-2-methyl-2-(cyclopropylethynyl)cyclopropane (VIIa, X = Br) with 35% reacted and 78% yield based on the amount of (VIa) reacted. With a threefold molar excess of (VIa), the yield of (VIIa) (X = Br) was substantially unchanged.

In order to obtain polycyclopropanes and cyclopropenes the dihaloethynylcyclopropanes were reduced. When (VIIa) (X = Cl) was treated with Na in liquid ammonia according to the procedure of [10], the acetylene bond was simultaneously reduced (as was to be expected [11]) with the formation of trans-1-cyclopropyl-2-(1-methylcyclopropyl)ethylene (VIII) in 35% yield.



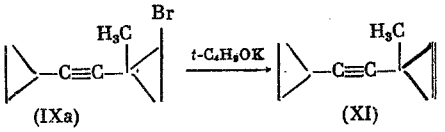
(VIIa), X = Cl $\xrightarrow{Na/NH_3}$ (VIIIa)

On the other hand, when the dibromide (VIIa) (X = Br) was treated with an equimolar amount or a twofold molar excess of tri-n-butylstannane at room temperature, it was reduced to, respectively, a cis — trans mixture of monobromides (IXa, X = Br), or the hydrocarbon (Xa), with preservation of the acetylenic bond (yields were 75-90%).



(VIIa), X = Br $\xrightarrow{Bu_3SnH}$ (IXa), X = Br $\xrightarrow{Bu_3SnH}$ (Xa)

Dehydrobromination of the monobromide (IXa, X = Br) with t-C_4H_9OK in DMSO gave (XI) in 31% yield; this molecule contains cyclopropane and cyclopropene rings and an acetylene bond.



(IXa) $\xrightarrow{t\text{-}C_4H_9OK}$ (XI)

The structure of this hydrocarbon was confirmed by IR and PMR spectra. In the IR spectrum the band at 2225 cm^{-1} corresponds to the acetylene vibration, while that at 1640 cm^{-1} corresponds to the transannular double bond; in the PMR spectrum the protons at the cyclopropene double bond form a singlet with $\delta = 7.2$ ppm.

EXPERIMENTAL

Gas — liquid chromatographic analysis was carried out on an LKhM-8MD apparatus (column 300 by 0.2 cm, 15% Reoplex 400 on silanized Chromaton N-AW-DMCS; katharometer detector; helium carrier gas at 30 ml/min). PMR spectra were obtained on a Varian DA-60-IL apparatus for $CHCl_3$ solutions, with tetramethylsilane as internal standard. IR spectra were recorded on a UR-20 spectrophotometer (in a coating of material between KBr plates).

2-Methyl-4-cyclopropyl-3-butyn-2-ol (IIIa). To a suspension of 14 g of KOH in 17 ml of DMF was added over 20 min a solution of 3.3 g of (I) in 3 ml of DMF, and then over 30 min at 20° a solution of 2.9 g of (IIa) in 3 ml of DMF. The mixture was stirred for 6 h at 20°, then treated with 10 ml of water and extracted with ether. The extract was washed with 5% HCl and with $NaHCO_3$ solution, dried with $MgSO_4$, and concentrated by evaporation. Distillation of the residue yielded 3.1 g (50%) of (IIIa); 96% pure; bp 78-80° at 17 mm; n_D^{20} 1.4707; d_4^{20} 0.9261. Found: C 76.98; H 9.65%. $C_8H_{12}O$. Calculated: C 77.37; H 9.74%. IR spectrum (ν, cm^{-1}); 2235 (C≡C), 3370 (OH). PMR spectrum (δ, ppm): 0.43-0.75 m (2 CH_2 in cyclo-C_3H_5; 0.75-1.28 m (CH in cyclo-C_3H_5); 1.36 s (2 CH_3); 3.05 s (OH).

2,4-Dicyclopropyl-3-butyn-2-ol (IIIb). To a solution of C_2H_5MgBr (from 35.4 g of C_2H_5Br and 7.8 g of Mg) in 180 ml of ether was added, at 0° over 40 min, a solution of 17.7 g of (I) in 17 ml of ether. The mixture was stirred for 3 h at 20°, then a solution of 45.1 g of (IIb) in 45 ml of ether was added at 0°, and the whole was stirred for 8 h at 20°. The mixture was treated with a saturated solution of NH_4Cl and extracted with ether, and the extract was dried with $MgSO_4$. Distillation yielded 29.4 g (73%) of IIIb, bp 92-94° (11 mm); n_D^{20} 1.4908; d_4^{20} 0.9601. Found: C 79.47; H 9.33%. $C_{10}H_{14}O$. Calculated: C 79.96; H 9.40%. IR spectrum (ν, cm^{-1}): 2240 (C≡C), 3410 (OH). PMR spectrum (δ, ppm): 0.2-0.7 m (4 CH_2 in cyclo-C_3H_5); 0.7-1.2 m (2 CH in cyclo-C_3H_5); 1.35 s (CH_3); 2.4 s (OH).

2-(1,2-Di-n-propylcyclopropen-3-yl)-4-cyclopropyl-3-butyn-2-ol (IV). To a solution of 0.93 g of (I) in 33 ml of absolute THF at −78° to −70° was added 10 ml of 1.4 N butyllithium in hexane from a syringe, in an Ar atmosphere over 15 min. The mass was stirred for another 30 min at the same temperature, then a solution of 2.3 g of (V) in 2 ml of THF was added over 5 min. The mixture was stirred for 30 min at −78°, the temperature was allowed to rise to 20°, and the mixture was treated with 7 ml of water, then with anhydrous K_2CO_3. The organic layer was decanted and evaporated in vacuum. Distillation of the residue yielded 1.8 g (56%) of (IV), bp 90-92° (0.3 mm); n_D^{20} 1.4828; d_4^{20} 0.9161. IR spectrum (ν, cm^{-1}): 1850 (C=C); 2240 (C≡C); 3440 (OH). PMR spectrum (δ, ppm): 0.52-0.9 m (2 CH_2 in cyclo-C_3H_5); 0.98 m (CH in cyclo-C_3H_5 and 2 CH_3 in n-C_3H_7); 1.32 s (CH_3); 2.4 m (4 CH_2 in n-C_3H_7); 1.73 s (CH in cyclo-C_3H_5).

Compound (IIIb) was obtained in 82% yield in an analogous manner.

2-Methyl-4-cyclopropyl-1-buten-3-yne (VIa). A mixture of 20 g of (IIIa) and 105 ml of hempa was heated in a bath at 220-245°, while the low-boiling products were distilled off. The distillate was washed with 2% HCl and with saturated $NaHCO_3$, and dried with solid KOH. Distillation yielded 11.5 g (67%) of (VIa), 99% pure, bp 138-139° (750 mm); n_D^{20} 1.4914; d_4^{20} 0.8347. Found: C 90.35; H 9.56%. C_8H_{10}. Calculated: C 90.51; H 9.5%. IR spectrum (ν, cm^{-1}): 895 (C=CH_2), 1612 (C=C), 2228 (C=C). PMR spectrum (δ, ppm): 0.6-0.9 m (2 CH_2 in cyclo-C_3H_5); 0.95-1.62 m (CH in cyclo-C_3H_5); 1.8 d.d ($^4J_{cis}$ = 1.50, $^4J_{trans}$ = 1.12 Hz, CH_3); 5.03-5.22 m (C=CH_2).

2,4-Dicyclopropyl-1-buten-3-yne (VIb). Compound VIb was obtained in analogous manner, in 26% yield, 95% pure, bp 78-80° (15 mm); n_D^{20} 1.5150; d_4^{20} 0.8889. Found: C 90.42; H 9.16%. $C_{10}H_{12}$. Calculated: C 90.85; H 9.15%. IR spectrum (ν, cm^{-1}): 880 (C=CH_2); 1608 (C=C); 2208 (C≡C). PMR spectrum (δ, ppm): 0.47-1.07 m (4 CH_2 in cyclo-C_3H_5); 1.07-1.72 m (2 CH in cyclo-C_3H_5); 5.1-5.17 d.d (J = 2 Hz, C=CH_2).

1,1-Dichloro-2-methyl-2-(cyclopropylethynyl)cyclopropane (VIIa, X = Cl). To a mixture of 10 ml of 50% NaOH, 5.3 g (0.075 mole) of (VIa), and 0.2 g of $(C_2H_5)_3(C_6H_5CH_2)NCl$ was added 6 g (0.05 mole) of $CHCl_3$ dropwise with cooling over 30 min. The mixture was kept at 35-40° for 4 h, diluted with water and extracted with ether. The extract was washed with 3% HCl and with $NaHCO_3$ solution, and dried with $CaCl_2$. Distillation yielded 3.6 g (38%) of (VIIa), bp 91-92° (8 mm); n_D^{20} 1.5110; d_4^{20} 1.1411. Found: C 57.27; H 5.46; Cl 37.28%. $C_9H_{10}Cl_2$. Calculated: C 57.16; H 5.33; Cl 37.51%. IR spectrum (ν, cm^{-1}): 778 (C—Cl); 2245 (C≡C). PMR spectrum

(δ, ppm): 0.5-0.85 m ($2CH_2$ in cyclo-C_3H_5); 0.87-1.28 m (CH in cyclo-C_3H_5); 1.37 d and 1.61 d (J = 6.6 Hz, CH_2 in cyclo-$C_3H_2Cl_2$); 1.48 s (CH_3).

1,1-Dichloro-2-cyclopropyl-2-(cyclopropylethynyl)cyclopropane (VIIb, X = Cl). Compound (VIIb) was obtained in analogous manner in 26% yield, bp 100-102° (2 mm); n_D^{20} 1.5212; d_4^{20} 1.1478. Found: C 61.21; H 5.62; Cl 32.40%. $C_{11}H_{12}Cl_2$. Calculated: C 61.41; H 5.62; Cl 32.96%. IR spectrum (ν, cm^{-1}): 780 (C — Cl); 2245 (C ≡ C).

1,1-Dibromo-2-methyl-2-(cyclopropylethynyl)cyclopropane (VIIa, X = Br). To a suspension of t-C_4H_9OK (from 7 g of K) in 120 ml of absolute pentane was added 16 g (0.15 mole) of (VIa) dropwise in a N_2 atmosphere at −25° to −30°, then 36.8 g (0.15 mole) of $CHBr_3$ over 1 h. The mixture was stirred for 4 h at 0 to −10°. After the usual workup there were separated 8.9 g of unreacted (VIa), and 14.55 g (35%) of (VIIa) (X = Br), 98% pure, bp 113-114° (8 mm); n_D^{20} 1.5567; d_4^{20} 1.6037. Found: C 39.83; H 3.83; Br 55.74%. $C_9H_{10}Br_2$. Calculated: C 38.88; H 3.63; Br. 57.49%. IR spectrum (ν, cm^{-1}): 710 (C — Br); 2245 (C ≡ C). PMR spectrum (δ, ppm); 0.58-0.87 m (2 CH_2 in cyclo-C_3H_5); 1.03-1.38 m (CH in cyclo-C_3H_5); 1.52 s (CH_3); 1.57 d and 1.82 d (J = 7.3 Hz, CH_2 in cyclo-$C_3H_2Br_2$).

1-Bromo-2-methyl-2-(cyclopropylethynyl)cyclopropane (IXa, X = Br). To 35.2 g (0.13 mole) of (VIIa) (X = Br) was added 36.9 g (0.13 mole) of tri-n-butylstannane dropwise in a N_2 atmosphere over 30 min. The mixture was stirred for 4 h at 20°C. Distillation yielded 21.8 g (86.5%) of (IXa) (X = Br), bp 80-85° (5 mm); n_D^{20} 1.5216; d_4^{20} 1.2827. Found: C 53.75; H 5.56; Br 40.06%. $C_9H_{11}Br$. Calculated: C 54.29; H 5.57; Br 40.14%. IR spectrum (ν, cm^{-1}): 555 (C — Br); 2245 (C ≡ C). PMR spectrum (δ, ppm): 0.5-0.88 m (2 CH_2 in cyclo-C_3H_5); 0.9-1.6 m (CH in cyclo-C_3H_5 and CH_2 in cyclo-C_3H_3Br); 1.27 s (CH_3) for trans isomer and 1.37 s (CH_3) for cis isomer (for CH_3 and Br); 2.80 d.d and 3.16 d.d (J_{trans} = 5, J_{cis} = 8 Hz, CH in cyclo-C_3H_3Br).

Compound (IXa) (X = Cl) was obtained in analogous manner in 45% yield, bp 77-82° (14 mm). IR spectrum (ν, cm^{-1}): 680 (C — Cl); 2250 (C ≡ C). PMR spectrum (δ, ppm): 0.5-0.85 m (CH_2 in cyclo-C_3H_5); 0.85-1.6 m (CH in cyclo-C_3H_5 and CH_2 in cyclo-C_3H_3Cl); 1.23 s (CH_3) for trans and 1.35 s (CH_3) for cis isomer; 2.85 d.d and 3.23 d.d (J_{trans} = 5, J_{cis} = 7 Hz, CH in cyclo-C_3H_3Cl).

trans-1-Cyclopropyl-2-(1-methylcyclopropyl)ethylene (VIIIa). To a solution of 9.7 g of Na in 170 ml of liquid NH_3 at −70° was added a solution of 16 g of (VIIa) (X = Cl) in 65 ml of absolute ether dropwise over 15 min in a N_2 atmosphere. The mixture was stirred for 10 min. By means of the usual workup 4.5 g of a fraction boiling at 140-150° (750 mm) was obtained. By means of preparative GLC chromatography (column 450 by 6 mm, 15% Reoplex 400 on silanized HMDS at 90°) a 35% yield of ~100% pure (VIIIa) was obtained; n_D^{20} 1.4723; d_4^{20} 0.8306. Found; C 88.33; H 11.56%. C_9H_{14}. Calculated: C 88.45; H 11.55%. IR spectrum (ν, cm^{-1}): 1665 (C = C); 965 (CH = CH trans). PMR spectrum: (δ, ppm): 0.16-0.95 m (4 CH_2 in cyclo-C_3H_5 and cyclo-C_3H_4); 1.2-1.66 m (CH in cyclo-C_3H_5); 1.06 s (CH_3); 4.88 d.d and 5.12 d.d (J_{trans} = 15, J_{cis} = 6.5 Hz, CH = CH).

1-Methyl-1-(cyclopropylethynyl)cyclopropane (Xa). To a solution of 5.6 g (0.02 mole) of (VIIa) (X = Br) in 4 ml of absolute pentane was added 11.6 g (0.04 mole) of $(n\text{-}C_4H_9)_3SnH$ dropwise at 0°. The mixture was stirred 30 h at 20°. Distillation gave (Xa) in 73% yield, 96.8% pure, bp 150° (754 mm); n_D^{20} 1.4764; d_4^{20} 0.8586. IR spectrum (ν, cm^{-1}): 2240 (C ≡ C). PMR spectrum (δ, ppm): 0.35-0.95 m (4 CH_2 in cyclo-C_3H_5 and cyclo-C_3H_4); 1-1.42 m (CH in cyclo-C_3H_5); 1.17 s (CH_3).

3-Methyl-3-(cyclopropylethynyl)cyclopropene (XI). To a solution of 4.2 g (0.02 mole) of (IXA) in 42 ml of DMSO was added dropwise a solution of 3.6 g (0.03 mole) of t-C_4H_9OK in 96 ml of DMSO at 18-20° in a N_2 atmosphere over 1 h. The mixture was stirred for 1 h at 20°C, 70 ml of ice-cold water was added, and the mixture was extracted with pentane. The extract was dried over $MgSO_4$. Distillation yielded 0.78 g (31%) of (XI), 95% pure, bp 67-68° (23 mm); n_D^{20} 1.4922; d_4^{20} 0.8846. Found: C 91.00; H 8.46%. C_9H_{10}. Calculated: C 91.41; H 8.53%. IR spectrum (ν, cm^{-1}): 1640 (C = C), 2225 (C ≡ C). PMR spectrum (δ, ppm): 0.38-0.82 ($2CH_2$ in cyclo-C_3H_5), 0.87-1.23 m (CH in cyclo-C_3H_5), 1.26 d (J = 0.5 Hz, CH_3), 7.2 s (2CH in cyclo-C_3H_2).

CONCLUSIONS

1. By means of the Favorskii reaction and of organomagnesium and organolithium compounds, cyclopropylethynylcarbinols were synthesized from cyclopropylacetylene and acetone or methyl cyclopropyl ketone in yields of 50-82%.

2. The preparation of 2-(1,2-di-n-propylcyclopropen-3-yl)-4-cyclopropyl-3-butyn-2-ol in 56% yield by the reaction of methyl 1,2-di-n-propylcyclopropen-3-yl ketone with cyclopropylethynyllithium illustrates the possibility of synthesizing cyclopropenylethynylcarbinols, which are difficult to obtain, from labile alkyl cyclopropenyl ketones.

3. The tertiary cyclopropylethynyl-substituted alcohols have been dehydrated at 220-250° in hempa medium to the corresponding enynes uncontaminated by isomerization products of the three-membered ring. Dihalomethylenation of these enynes proceeds at the double bond to form the corresponding dicyclopropylacetylenes.

4. We studied complete and partial reduction of the 1-cyclopropyl-2-(1-methyl-2,2-dihalocyclopropyl)-acetylenes. By dehydrobromination of 1-cyclopropyl-2-(1-methyl-2-bromocyclopropyl)acetylene with potassium tert-butylate in DMSO we synthesized 1-cyclopropyl-2-(3-methylcyclopropen-3-yl)acetylene.

LITERATURE CITED

1. I. E. Dolgii, I. B. Shvedova, K. N. Shavrin, and O. M. Nefedov, Inventor's Certificate No. 555079; Byull. Izobr., No. 15, 65 (1977).
2. I. L. Kotlyarevskii, M. S. Shvartsberg, and L. B. Fisher, Reactions of Acetylene Compounds [in Russian], Nauka, Novosibirsk (1967).
3. T. A. Favorskaya, K. A. Kononova, and M. I. Titov, Zh. Obshch. Khim. 29, 2894 (1959).
4. O. M. Nefedov, I. E. Dolgii, and É. A. Baidzhigitova, Izv. Akad. Nauk SSSR, Ser. Khim., 2842 (1975).
5. M. Yu. Lukina, T. Yu. Rudashevskaya, and O. A. Nesmeyanova, Dokl. Akad. Nauk SSSR, 190, 1109 (1970).
6. A. V. Shchelkunov, R. L. Vasil'eva, and L. A. Krichevskii, Synthesis and Interconversions of Monosubstituted Acetylenes [in Russian], Nauka, Alma-Ata (1976).
7. O. M. Nefedov, I. E. Dolgii, I. B. Shvedova, and R. N. Shafran, Izv. Akad. Nauk SSSR, Ser. Khim., 1885 (1972).
8. E. A. Dehmlow, Tetrahedron Lett., 2317 (1965); 3763 (1966); Chem. Ber., 101, 427 (1968).
9. I. A. D'yakonov, I. A. Favorskaya, L. P. Danilkina, and É. M. Aubinen, Zh. Obshch. Khim., 30, 3503 (1960); L. Vo-Quang and P. Cadiot, Compt. Rend. Acad. Sci., 252, 3827 (1961); M. G. Avetyan, L. L. Nikogosyan, and S. G. Matsoyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 18, 427 (1965).
10. O. M. Nefedov, N. N. Novitskaya, and A. D. Petrov, Dokl. Akad. Nauk SSSR, 152, 629 (1963); O. M. Nefedov, R. H. Shafran, and N. N. Novitskaya, Zh. Org. Khim., 8, 2075 (1972).
11. K. N. Campbell and L. T. Eby, J. Am. Chem. Soc., 63, 216 (1941).

REACTIONS OF 1-FLUORO-1-BROMO-2-ARYLCYCLOPROPANES IN SOLVOLYSIS CONDITIONS IN THE PRESENCE OF ELECTROPHILIC AND NUCLEOPHILIC AGENTS

V. S. Aksenov and G. A. Terent'eva

UDC 542.91:547.512'121

The reactions of compounds of the cyclopropane series in conditions of nucleophilic substitution, as a rule, lead to the formation of allylic derivatives and are accelerated by electrophilic or nucleophilic agents. Lewis bases are used as the electrophilic agents [1, 2] and organic and inorganic bases, as the nucleophilic agents [3]. The reaction rate in the presence of electrophilic agents depends on the nature of the group being cleaved and of the substituent on the cyclopropane ring [4] and on the relative position of the substituent on the three-membered ring and the group being cleaved [5, 6]. In the presence of nucleophilic agents, either ring opening of the cyclopropane ring [1, 3, 7, 8] or reactions with retention of the ring [9, 10] can occur, depending on the nature of the ring substituent. The behavior of unsymmetrical gem-dihalocyclopropanes in conditions of solvolysis has not yet been studied.

The aim of the present study is to establish the structure of the reaction products from 1-fluoro-1-bromo-2-arylcyclopropanes (I) with methanol in the presence of electrophilic and nucleophilic agents, to study the influence of substituents on the aromatic ring on the reaction rate, and to compare the reactivity of the syn and anti isomers.

The I are obtained as mixtures of both isomers [11] from the reaction of the corresponding substituted styrenes with fluorobromocarbene. Solvolysis in the presence of electrophilic agents was conducted by heat-

Institute of Petroleum Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Tomsk.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1344-1350, June, 1978. Original article submitted February 1, 1977.

0568-5230/78/2706-1168$07.50