CODIMERIZATION OF 2-CYCLOPROPYL-1,3-BUTADIENE WITH ETHYLENE

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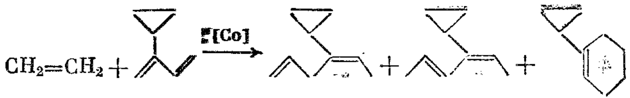
In a continuation of a study of the capacity of cyclopropyl-substituted 1,3-dienes [1, 2] and in order to synthesize linear unsaturated hydrocarbons with cyclopropane fragments, we investigated the codimerization of 2-cyclopropyl-1,3-butadiene (2-CPB) with ethylene by the action of rhodium, nickel, iron, and cobalt catalysts. In the series tested, only the cobalt complexes among the catalysts previously used for the codimerization of ethylene with simple 1,3-butadienes [3-6] displayed any activity.

Thus, in the presence of the $Co(acac)_2$–organophosphorus activator–Et_2AlCl catalytic system at 60°C, ethylene and 2-CPB are converted over 6 h to a mixture of codimers containing E-4-cyclopropyl-1,4-hexadiene (I), E,E-3-cyclopropyl-2,4-hexadiene (II), and 1-cyclopropyl-1-cyclohexene (III):



(I) (II) (III)

The presence and concentration of the organophosphorus activator in the cobalt catalyst have a substantial effect on the product yield and reaction selectivity.

Table 1 shows that the greatest selectivity for linear codimers (I) and (II) in the case of PPh_3 is found for $Co(acac)_2:PPh_3$ = 1:2 (experiment 3), while in the case of the bisphosphines, greatest selectivity is found for 1:1 mole ratio, apparently due to their bidentate nature (experiments 5 and 8). The use of bisphosphines as the activator ligands is preferred since the formation of higher oligomers is virtually eliminated in their presence and the fraction of the cyclic dimer (III) is low.

The structure of (I) separated by distillation on a Widmer column is clearly indicated by its spectral data (see the Experimental section). The upfield shift of the methyl group signal if the ^{13}C NMR spectrum of (I) to about 13 ppm indicates a cis interaction of C^6, most likely, with C^3 since the signal for the methine carbon in the cyclopropane ring (CPR) is at 17 ppm, which is characteristic for the case when this atom does not have a cis interaction. Hence, isomer (I) was assigned the structure E-4-cyclopropyl-1,4-hexadiene.

The structure of cyclic codimer (III) was demonstrated on the basis of its spectral data and comparison with an authentic sample obtained by the Diels–Alder reaction between 2-CPB and ethylene at 150°C over 8 h (58% product yield).

The presence of conjugated isomer (II) was indicated by gas–liquid chromatographic and UV spectral data (characteristic band at λ_{max} 234 nm). By analogy with previous results [3-6], we may assume that the double bonds in (II) have E,E-configuration. Our attempts to carry out the isomerization of (I) to conjugated isomer (II) by the action of t-BuOK or transition metal complexes such as $Fe(CO)_9$ and $PdCl_2 \cdot 2PhCN$ led to the formation of complex mixtures.

Thus, the codimerization of ethylene with e-cyclopropylbutadiene proceeds in the presence of cobalt complex catalysts activated by mono- or bisarylphosphines to form predominantly E-4-cyclopropyl-1,4-hexadiene and slight amounts of E,E-3-cyclopropyl-2,4-hexadiene and 1-cyclopropylhexene. The direction of the codimerization may be controlled by altering the structure of the activating phosphine ligand and reaction conditions.

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TABLE 1. Effect of the Nature and Ratio of the Organophosphorus Activator on the Codimerization of 2-CPB with Ethylene, $Co(acac)_2$:Et_2AlCl = 1:12, Benzene Solvent, 60°C, 6 h

Experiment no.	Organophosphorus activator	$Co(acac)_2$: activator mole ratio	Conversion of 2-CPB	Total yield of (I)-(III), %	Composition, %			Yield of higher oligomers, %
					(I)	(II)	(III)	
1	None		90	—	—	—	—	90
2	PPh_3	1 : 1	85	50	26	21	52	35
3	Same	1 : 2	93	87	80	12	8	5
4	»	1 : 3	92	60	40	9	51	32
5	$Ph_2PCH_2PPh_2$	1 : 1	50	45	74	18	3	5
6	Same	1 : 2	60	58	70	20	10	2
7	»	1 : 3	89	85	73	13	14	4
8	$Ph_2PCH_2CH_2PPh_2$	1 : 1	98	95	79	13	8	3
9	Same	1 : 2	98	95	83	7	10	3
10	»	1 : 3	94	92	80	15	5	2

EXPERIMENTAL

A sample of 2-CPB was obtained according to Golovchanskaya [7]. The PMR spectra was taken on a Tesla BS-497 spectrometer at 60 MHz in CCl_4 relative to TMS. The IR spectra were taken on a UR-20 spectrometer. The ^{13}C NMR spectrum was taken on a Geol FX-90Q spectrometer at 22.50 MHz in $CDCl_3$ with TMS as the internal standard. The gas—liquid chromatographic analysis was taken on a Khrom-41 chromatograph using a 3.5 m × 3 mm column packed with 15% PEG-6000 on Chromaton N-AW-HMDS and 47 ml/min helium carrier gas flow rate. The injector temperature was 200°C, and the temperature mode was 50°C.

General Method for the Codimerization of 2-CPB with Ethylene. A sample of 1.5 g (12 mmoles) Et_2AlCl was added dropwise to a solution of 0.26 g (1 mmole) $Co(acac)_2$ and 1-4 mmoles organophosphorus activator in 10 ml benzene at 0°C in an argon atmosphere. The mixture was stirred for 1 h and transferred in an inert atmosphere to 0.1-liter autoclave previously cooled to 0°C with 4.8 g 2-CPB in 20 ml benzene. The autoclave filled with ethylene to 50 atm. The reaction was carried out at 60°C for 6 h. After cooling of the reaction mass, the catalyst was decomposed with 5 ml methanol, washed with water, and filtered through alumina.

E-4-Cyclopropyl-1,4-hexadiene (I) was separated by distillation, bp 130-131°C, $n^{20}D$ 1.4620. IR spectrum (ν, cm^{-1}): 840 (trisubstituted double bond), 920, 995, 1640 ($CH{=}CH_2$), 1025, 3085 (CPR). PMR spectrum (δ, ppm): 0.3-0.6 (4H, CH_2 in PCR), 1.26-1.37 (1H, CH in CPR), 1.57 (3H, CH_3), 2.75 (2H, CH_2), 4.94 and 5.6-5.9 (3H, $CH{=}CH_2$), 5.2-5.3 (1H, $CH{=}C$). ^{13}C NMR spectrum (δ, ppm): 13.13 q (C^6), 4.92 t (CH_2 in CPR), 17.23 d (CH in CPR), 34.39 t (C^3), 114.75 t (C^1), 118.11 d (C^5), 136.34 d (C^2), 138.36 s (C^4); m/z 122.

Thermal Codimerization of Ethylene with 2-CPB. A mixture of 9.4 g (0.1 mole) 2-CPB and 0.2 g bisphenol was placed in a 0.1-liter steel autoclave and filled with 50 atm ethylene. The autoclave was heated at 150°C for 8 h. After cooling and removal of excess ethylene, we isolated 6.1 g (58%) 1-cyclopropylcyclohexene (III) with bp 90-91°C (50 mm), $n^{20}D$ 1.5090. IR spectrum (ν, cm^{-1}): 820, 1660, 3020 (double bond), 1030, 3085 (CPR). PMR spectrum (δ, ppm): 0.65 (4H, CH_2 in CPR), 0.85-1.4 (1H, CH in CPR), 1.8 (4H, CH_2 in cyclohexene ring), 2.08 (4H, CH_2, allyl), 5.65 (1H, olefin); m/z 122.

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CONCLUSIONS

The codimerization of 2-cyclopropylbutadiene with ethylene by the action of low-valence cobalt complexes was studied. The major reaction product in the presence of the $Co(acac)_2$—$Ph_2PCH_2CH_2PPh_2$—Et_2AlCl catalytic system is E-4-cyclopropyl-1,4-hexadiene.

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POLARITY AND POLARIZABILITY OF ALKOXYACETYLENES

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Alkoxyacetylenes have found various synthetic applications [1], but their electronic structure has not been studied sufficiently. In the present work, we studied the electrical properties of alkoxyacetylenes, viz., polarity distribution and polarizability using birefringence in an electric field.

EXPERIMENTAL

Methoxy- (I), ethoxy- (II), and isopropoxyacetylene (III) were obtained from the corresponding acetals of mono chloroacetaldehyde by reaction with $NaNH_2$ in liquid ammonia according to Eglinton and Jones [2]. Their indices are given in Table 1.

The dipole moments (DM) and molar Kerr constants (KC) were measured in dilute solutions of (I)-(III) in CCl_4 at 25°C according to our previous procedure [3].

RESULTS AND DISCUSSION

The DM values obtained for (I)-(III) are in satisfactory accord with those previously measured in benzene at 20°C [4, 5] and those found using the Stark effect in the gas phase: 1.93 D for (I) [6] and 1.91 and 2.02 D for (II) [7]. Den Engelsen et al. [6] used microwave spectroscopy to determine the structure of (I) and the dipole moment components $\mu_a = 1.41$ and $\mu_b = 1.32$ D. Our coordinate system and arrangement of the major axes a and b according to Den Engelsen [6] are given in Fig. 1. Since component μ_b contains mainly the contribution of the DM m(Alk—O), the orientation of the negative end of the dipole μ_b in the direction of the y axis appears natural. Then, depending on the orientation of μ_a along the x axis or in the opposite direction, the overall DM in (I) forms angle $\varphi_1 \approx 60$ or $\varphi_2 \approx 152°$ relative to the x

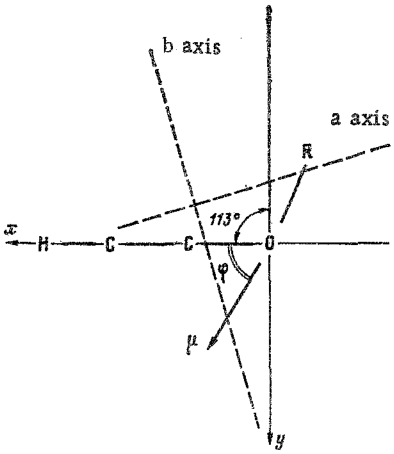

Fig. 1. Coordinate system adopted and orientation of the major inertial axes a and b for (I).

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