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SYNTHESIS OF NEW TYPES OF TETRACYCLO[4.3.0.$0^{2,4}$.$0^{3,7}$]NONANE HYDROCARBONS BY CYCLOCODIMERIZATION OF NORBORNADIENE AND ITS DERIVATIVES WITH DIACETYLENES AND VINYLACETYLENES, CATALYZED BY LOW-VALENCE COBALT COMPLEXES

U. M. Dzhemilev, R. I. Khusnutdinov,
Z. S. Muslimov, and G. A. Tolstikov

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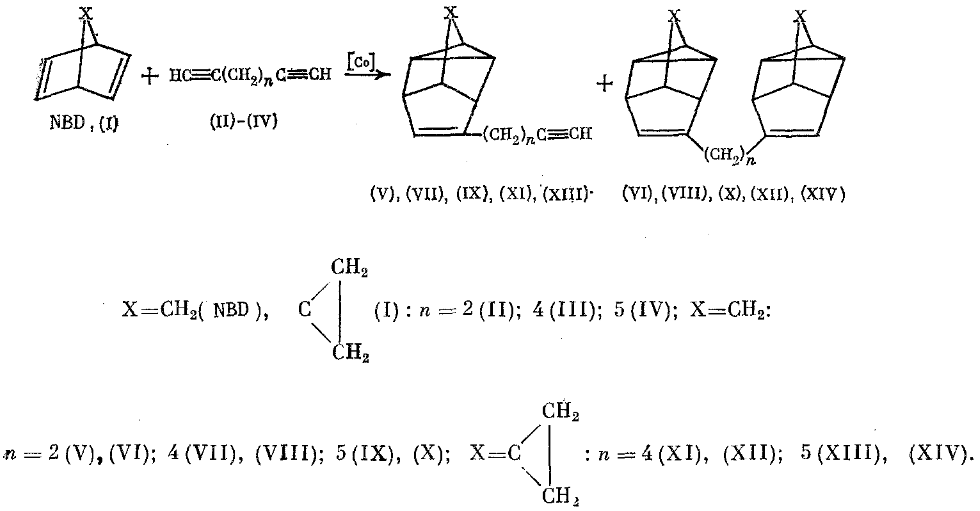
Cyclocodimerization of mono- and dialkyl(aryl)acetylenes with norbornadiene (NBD) according to the [2π + 2π + 2π] scheme, studied in [1-4], represents a convenient route for the synthesis of difficultly obtainable tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane ("deltacyclenic") compounds. The reaction is catalyzed by the $Co(acac)_3$—organophosphorus activator—$AlEt_2Cl$ system, and, to decrease the homodimerization of NBD, a bidentate ligand 1,2-bis(diphenylphosphino)ethane (BPE) is introduced into the composition of the catalyst [1].

To obtain new types of strained polycyclic hydrocarbons and to study the possibilities of introducing conjugated and unconjugated diacetylenes (DA) and vinylacetylenes (VA) into the cyclocodimerization, we studied the reaction of NBD and spiro{bicyclo-[2.3.1]hepta-2,5-diene-7,1'-cyclopropane} (I) with 1,3-, 1,5-, 1,7-, 1,8-diacetylenes and vinyl-1-cyclopentylacetylenes by the action of cobalt complexes, prepared by the reduction of $Co(acac)_2$ by means of $AlEt_2Cl$ in the presence of PPh_3. As the result of replacement of BPE by PPh_3, the cobalt catalyst became more active and selective. Moreover, it was found that acetylenic monomers can be used as activating ligands in the cyclocodimerization. To obtain the required concentration of DA (or VA) at the moment of formation of the catalyst, the reduction of the cobalt salts was carried out in the presence of the entire amount of DA or VA, so that it was possible to shorten the reaction time and to double the yields of the dimers, practically completely, excluding the homodimerization of NBD.

The cyclocodimerization of unconjugated α,ω-diacetylenes (II)-(IV) with NBD and (I), carried out in the presence of the $Co(acac)_2$ $-PPh_3-AlEt_2Cl$ catalytic system (1:1.5:10) at 80°C for 30 min in toluene, is accompanied by the formation of mono- and bitetracyclononane hydrocarbons (V)-(XIV), whose isomeric composition depends on the ratio DA:NBD or (I). At an equimolar ratio of the monomers, besides (V), (VII), (IX), (XI), (XIII), the bideltacyclenic hydrocarbons (VI), (VIII), (X), (XII) and (XIV) are preferentially formed (in a ratio of approximately 1:3-5), and when the concentration of NBD or (I) is doubled, they are the only reaction products.



Institute of Biophysics, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1061-1067, May, 1987. Original article submitted August 22, 1985.

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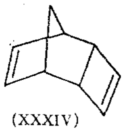
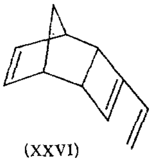
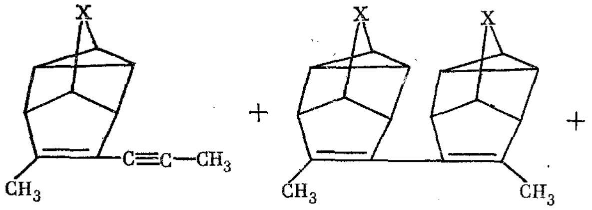
TABLE 1. PMR Spectra of Compounds (XXVI) and (XXXIV) [6]

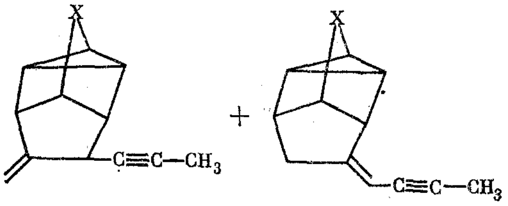
Compound	δ, ppm										
	H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	H^{10}	H^{11}
 (XXXIV)	2.94	2.54	5.76	5.76	2.54	2.94	5.84	5.84	1.85 1.49	–	–
 (XXVI)	2.95	1.75	5.68	5.68	2.50	2.95	5.86	5.68	1.83 1.45	5.88 6.33	4.76 5.05

The yield of (V)-(XIV) depends on the length of the hydrocarbon chain linking the acetylene fragments, reaching ∿95% in the case of 1,7-octadiene and 1,8-nonadiene, while with 1,5-hexadiyne (II) a vigorous polymerization of (II) and NBD takes place. In the case of (I), only trace amounts of the corresponding products could be observed. Therefore, to compare the reactivity of α-ω-diacetylenes with that of conjugated diacetylenes, we studied the cyclocodimerization of 1,3-butadiyne with NBD and (I). It was found that under the cyclocodimerization conditions, unsubstituted 1,3-butadiyne completely polymerizes, while NBD and (I) are completely recovered. At the same time, 1,4-dimethyl-1,3-diacetylene (XV) vigorously reacts with NBD and with (I), forming a mixture of compounds. We assumed that the complexity of the isomeric composition of the hydrocarbons in the case under consideration is due to occurrence of an acetylene-allene isomerization of (XV). Tracing the consumption of (XV) by GLC, we found that together with (XV), two other compounds having bands of the allene group (1955 cm^{-1}) appear in the IR spectrum. It is possible that the appearance of isomeric allene-acetylene (XVa) and diallene (XVb) creates prerequisites for unequivocal occurrence of the codimerization of (XV) with NBD and (I)

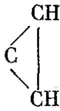
$$(\mathrm{NBD}),\ (\mathrm{I}) + \left\{\begin{array}{l} H_3C{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \\ H_2C{=}C{=}CH{-}C{\equiv}C{-}CH_3 \\ H_2C{=}C{=}CH{-}CH{=}C{=}CH_2 \end{array}\right. \xrightarrow{[\mathrm{Co}]}$$



(XVI), (XVIII)   (XVII), (XIX)

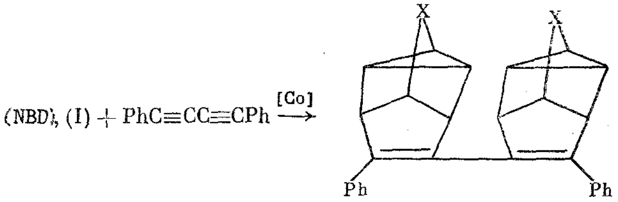


(XXa), (XXb)   (XXIa), (XXIb)

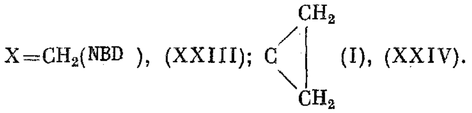
X=CH_2(NBD) (XVI), (XVII), (XXa), (XXIa);  $C\!\left\langle{}^{CH_2}_{CH_2}\right.$ (I), (XVIII), (XIX), (XXb), (XXIb).

The principal compounds among the above isomers (XVI)-(XIX) were not isolated. The presence of the isomers of the (XX), (XXI) type was determined from the signals at 4.5-4.7 ppm ($C{=}CH_2$) and 5.5-5.7 ppm (the norbornene double bond) in the PMR spectrum.

Diphenyldiacetylene (XXII) is less active in cyclocodimerization with NBD and (I), which leads to (XXIII) and (XXIV) in 15 and 12% yields, respectively. It is probable that this behavior of (XXII) is due to the impossibility of acetylene-allene isomerization

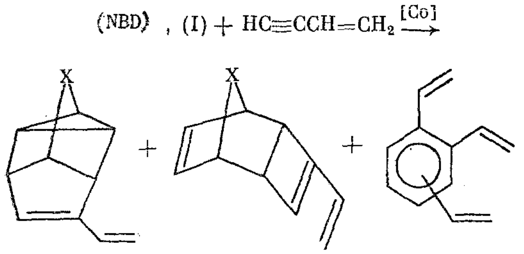


(XXIII), (XXIV)

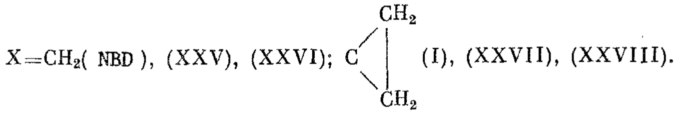


$X{=}CH_2$(NBD), (XXIII); $C(CH_2)_2$ (I), (XXIV).

As far as VA are concerned, their cycloaddition to NBD and (I) proceeds in a nontrivial way, and in the case of the simplest VA, isomers with a deltacyclenic structure (XXV), (XXVII) are formed in small amounts, while the main products are 3-vinyltricyclo-[4.2.1.$0^{2,5}$]nona-3,7-diene- (XXVI) and 3-vinyl-spiro-tricyclo-[4.2.1.$0^{2,5}$]nona-3,7-diene-9,1'-cyclopropane (XXVIII)



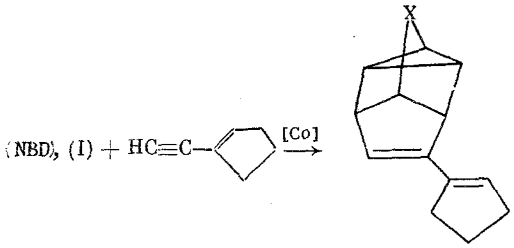
(XXV), (XXVII) (XXVI), (XXVIII) (XXIX)-(XXXI)



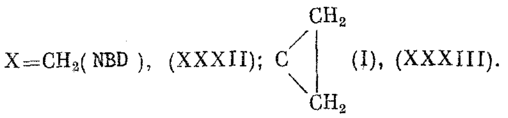
$X{=}CH_2$(NBD), (XXV), (XXVI); $C(CH_2)_2$ (I), (XXVII), (XXVIII).

Moreover, 50% of VA converts into a mixture of three isomeric homocyclotrimers (XXIX-XXX), identified by comparison with known samples. All attempts to suppress the cyclotrimerization of VA by changing the reaction conditions, as well as the nature and concentration of the organophosphorus activator, were unsuccessful.

In contrast to VA, ethynyl-1-cyclopentene adds to NBD and (I), in the presence of the $Co(acac)_2{-}PPh_3{-}AlEt_2Cl$ catalytic system, by the [2π + 2π + 2π] scheme exclusively, giving the corresponding deltacyclenic hydrocarbons (XXXII) and (XXXIII) in an overall yield of 50%



(XXXII), (XXXIII)



$X{=}CH_2$(NBD), (XXXII); $C(CH_2)_2$ (I), (XXXIII).

TABLE 2. Physicochemical and Spectral Characteristics of

Compound	Conv. of NBD (or (I)), %	Conv. of DA or VA, %	Yield of codimer, %	bp, deg C (p, mm Hg)	n_D^{20}	IR spectrum ν, cm^{-1}
(V)	77	100	5	49(5)	1,5427	795, 810, 830, 1620, 3060, 3300
(VI)	95	100	2	66(0,2)	1,5615	798, 808, 835, 1630, 3070
(VII)	99	98	25 *	79(0,2)	1,5080	795, 808, 830, 1620, 3060, 3305
(VIII)	99	98	95	141(0,18)	1,5411	795, 810, 830, 1630, 3080
(IX)	98	98	27 *	91(0,1)	1,5023	796, 808, 830, 1618, 3065, 3300
(X)	98	97	94	152(0,1)	1,5354	790, 805, 835, 1625, 3080
(XVI)	92	87	42	63(0,2)	1,5188	795, 810, 830, 1627, 3070
(XVII)	99	99	38(85) †	135(0,2)	1,5675	798, 805, 830, 1630, 3060
(XXVIII)	87	100	15	mp 175–178°	—	795, 810, 840, 1740, 1803, 1870, 1943, 3070
(XI)	99	98	18	92(0,1)	1,5180	785, 800, 835, 1614, 3050, 3070, 3310
(XII)	99	98	79	169(0,1)	—	786, 800, 840, 1012, 1620, 3050, 3080
(XIII)	97	96	20 *	104(0,1)		787, 802, 840, 1015, 1620, 3050, 3070, 3305
(XIV)	96	97	80	180(0,1)		785, 802, 835, 1010, 1620, 3055, 3070
(XVIII)	93	89	44	74(0,2)		786, 808, 840, 1015, 1615, 3050, 3075
(XIX)	98	97	33(82) †	148(0,2)		796, 810, 1015, 1620, 3060, 3070
(XXIV)	80	150	12	mp 197–201°		797, 808, 840, 1030, 1664, 1739, 1801, 1869, 1943, 3080
(XXV)	76	100	5	73(18)	1,5240	785, 820, 835, 910, 990, 1620, 3070
(XXVI)	76	100	27	76(18)	1,5286	730, 910, 990, 1580, 1630, 3070
(XXVII)	70	100	4	93(15)	1,5350	795, 810, 830, 910, 990, 1630, 3070, 3100
(XXVIII)	70	100	24	98(15)	1,5306	740, 910, 990, 1030, 1575, 1625, 3070
(XXXII)	82	100	50	81(0,1)	1,5145	790, 820, 835, 1630, 3080
(XXXIII)	80	100	41	105(0,1)	1,5210	792, 817, 835, 1030, 1620, 3070, 3100

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*The experiments were carried out at molar ratio of NBD (or

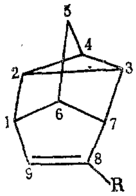
†Overall yield of mixture of codimers.

Compounds Obtained (CPR = cyclopentane ring)

PMR spectrum (δ, ppm)								Side chain proton signals	Mass spectrum (M^+)
H^1	H^2	H^3	H^4	H^5	H^6	H^7	H^9		
2,30	1,15	1,15	1,15	1,45	1,78	2,3	5,48	2,1 (4H, CH_2), 1,8 ($C\equiv CH$)	170
2,37	1,13	1,13	1,13	1,47	1,80	2,37	5,46	2,21 (4H, $CH_2-C=$)	262
2,35	1,10	1,1	1,18	1,40	1,75	2,35	5,50	2,05 (4H, $CH_2-C=$), 1,44 ($4H^1-CH_2$), 1,94 ($\equiv CH$)	198
2,33	1,10	1,15	1,15	1,48	1,78	2,33	5,55	1,42 (4H, CH_2) 2,08 ($4H_3CH_2-C=$)	290
2,40	1,12	1,12	1,12	1,50	1,80	2,40	5,48	1,41 (6H, CH_2), 2,11 (4H, $CH_2-C=$), 1,92 ($\equiv CH$)	212
2,42	1,15	1,15	1,15	1,49	1,79	2,42	5,50	1,38 (6H, CH_2) 2,20 (4H, $CH_2-C=$)	304
2,33	1,0	1,00	1,26	1,30	1,76	2,66	–	1,76 (3H, CH_3), 1,9 (3H, CH_3)	170
2,35	1,02	1,02	1,24	1,4	1,81	2,6	–	1,65 (6H, CH_3)	262
2,96	0,81	0,81	1,62	1,48	2,1	2,5	–	7,1–7,3 (10H, H arom)	294
2,55	1,18	1,18	1,18	–	1,35	2,56	5,53	0,37 (4H, CPR), 1,45 (4H, CH_2), 2,06 (4H, $CH_2-C=$) 1,73 ($\equiv CH$)	224
2,551	1,2–1,35	1,2–1,35	1,2–1,35	–	1,4	2,55	5,58	0,34 (8H, CPR), 1,35 (8H, CH_2), 2,05 (8H, $CH_2-C\equiv$)	342
2,57	1,1–1,25	1,1–1,25	1,2–1,25		1,35	2,57	5,57	0,36 (4H, CPR), 1,45 (6H, CH_2), 2,05 (4H, $CH_2-C=$) 1,75 ($\equiv CH$)	238
2,57	1,16–1,26	1,16–1,25	1,16–1,25		1,37	2,57	5,57	0,34 (8H, CPR), 2,1 (4H, $CH_2-C=$), 1,45 (6H, CH_2)	356
2,60	1,20	1,20	1,20	–	1,42	2,60	–	0,3–0,45 (4H, CPR), 1,66 (3H, CH_3), 1,92 (3H, CH_3)	196
2,35	1,15	1,15	1,15	–	1,45	2,65	–	0,25–0,45 (8H, CPR), 1,60 (6H, CH_3)	314
2,90	1,20	1,2	1,2	–	1,42	1,6	2,62		438
2,46	1,12	1,12	1,12	1,46	1,68	2,63	5,70	4,9–5,0 ($-C=CH_2$), 5,8–6,3 ($CH=C$)	144
2,95	2,75	–	5,68	2,50	2,95	5,68	1,83 1,45	4,76–5,05 ($-C=CH_2$) 5,88–6,33 ($CH=C$)	144
2,57	1,19	1,19	1,19	–	1,50	2,85	5,80	0,2–0,45 (4H, CPR), 4,8–5,0 ($-C=CH_2$) 5,9–6,35 ($-CH=C-$)	170
2,94	2,68	–	5,70	2,45	2,94	5,70	–	0,24–0,40 (4H, CPR) 4,85–5,0 ($C=CH_2$) 5,9–6,33 ($CH=C$)	170
2,54	1,0–1,26	1,0–1,26	1,0–1,26	1,50	1,86	2,76	5,6	1,6 (2H, CH_2), 2,36 (4H, $CH_2-C=$), 5,7 ($CH=C$)	184
2,62	1,23	1,23	1,23	–	1,52	2,90	5,82	0,2–0,52 (4H, CPR), 1,52 (2H, CH_2), 2,40 (4H, $CH_2-C=$), 5,7 ($CH=C$)	210

(I))DA = 1:1.

The structure of the compounds obtained was found from the PMR spectra containing signals at 1.0-1.1 (2H, H^2, H^3), 1.15-1.30 (1H, H^4), 1.45-1.5 (2H, $2H^5$), 1.7-1.9 (1H, H^6), 2.2-2.4 (2H, H^1, H^7) and 5.4-5.7 (1H, H^9) ppm, corresponding to tetracyclo[$4.3.0.0^{2,4}.0^{3,7}$]non-3-ene structure [1]



Moreover, in the IR spectra of these isomers there are absorption bands at 780-820 and 3050-3100 cm^{-1}, which correspond to nortricyclene [5]. In the PMR spectra of the codimers and cooligomers, formed from (I) and DA (VA), a cyclopropane signal appears at 0.1-0.4 ppm instead of the proton signal at C^5, while in the IR spectrum new bands appear at 1010-1030 and 3070-3100 cm^{-1}.

The structure of (XXVI) and (XXVIII) and also the endo-coupling of the cyclobutene and norbornene rings was proved by comparing the PMR spectra with the corresponding spectrum of the model compound endo-tricyclo[$4.2.1.0^{2,5}$]nonadiene (XXXIV) [6] (Table 1).

The codimers of NBD and (I) with VA are unstable and in the course of 2-3 days convert into polymeric products.

EXPERIMENTAL

The VA and DA monomers used, of 99% purity, were synthesized according to [7], and (I) according to [8]. The PMR spectra were recorded on a "Tesla BS-497" spectrometer (100 MHz) in $CDCl_3$ relative to TMS; the IR spectra were run in mineral oil on a UR-20 spectrophotometer. The GLC was carried out on a "Chrom-4" apparatus, using a 3.5 m × 3 mm column with 15% PEG 6000 on chromatone N-AW-HMDS, at a flow rate of He of 47 ml/min, evaporator temperature of 300°C, and at a temperature regime from 50 to 350°C.

General Method of Preparation of the Catalyst and Cooligomerization of NBD and (I) with Diynes and Vinylacetylenes. A 0.28 mole portion of the diyne and 26 g (0.28 mole) of NBD or (I) were added in an Ar current to a solution of 0.35 g (1.36 mmole) of $Co(acac)_2$, 0.54 g (2.04 mmole) of PPh_3 in 20 ml of dry toluene. The mixture was cooled to −15°C and 8.2 ml of a 20% solution (1.64 g, 13.6 mmoles) of Et_2AlCl were added. Five minutes after all the Et_2AlCl has been added, the mixture was transferred into an autoclave and heated at 80°C for 30 min. After cooling, 10 ml of alcohol and 50 ml of ether were added to the mixture, which was filtered through a layer of Al_2O_3 (100 g), and the solvent and the residue were distilled in vacuo. The compounds obtained are listed in Table 2.

CONCLUSIONS

Three-component complex cobalt-containing catalysts are proposed, which are activated by PPh_3 or by an excess of acetylenic hydrocarbons, with which cyclocodimerization of norbornadiene or spiro{bicyclo[2.2.1]hepta-2,5-diene-7,1'-cyclopropane} with diacetylenes can be carried out leading to derivatives of the bitetracyclo[$4.3.0.0^{2,4}.0^{3,7}$]nonane series in high yields.

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