$C_8H_9ClNO_2P$, M = 217.59; a = 7.369(1); b = 15.465(4), c = 8.842(4) Å, β = 107.33(2)°, V = 962(1) Å^3, Z = 4, d_{calc} = 1.502 g/cm^3, $\mu(MoK_\alpha)$ = 5.24 cm^{-1}, space group $P2_1/c$.

The intensities of 2460 reflections were measured in an inverse space quadrant using $\omega/2\theta$ scanning ($2\theta \leq 55°$), of which 1689 independent observed reflections with $I \geq 2\sigma(I)$ were used in the final calculations. Absorption was not taken into account. The structure of (I) was solved by the direct method and refined by the full-matrix method of least squares anisotropically for the nonhydrogen atoms taking account of secondary extinction: $g = 1.2(2)\cdot10^{-6}$. The starting positions of all the hydrogen atoms were determined from the Fourier difference map and their coordinates and B_{iso} values were refined by the method of least squares. In the final cycle of the full-matrix refinement, $|\Delta|/\sigma < 0.45$ for all the 155 parameters varied. The final atomic coordinates for the structure of (I) are given in Table 1.

The final R factors calculated using 1689 observed reflections were: R = 0.031 and R_w = 0.049, the fit quality S = 1.20. In the final Fourier difference map, $\Delta\rho < 0.25$ eÅ^{-3}. The weighting scheme for the reflections in the method of least squares, the f-curves used, and $\Delta f'$ and $\Delta f''$ anomalous dispersion corrections were given, for example, in our previous work [4]. All the calculations were carried out on a PDP 11/23 minicomputer using the Enraf-Nonius SDP-PLUS program system.

LITERATURE CITED

1. V. A. Naumov and L. V. Vilkov, The Molecular Structure of Organophosphorus Compounds [in Russian], Nauka, Moscow (1986).
2. F. H. Allen, O. Kennard, D. G. Watson, et al., J. Chem. Soc., Perkin Trans. 2, No. 12, S1-S19 (1987).
3. R. Taylor and O. Kennard, J. Am. Chem. Soc., 104, 5063 (1982).
4. A. N. Chekhlov, S. P. Ionov, A. N. Bovin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2240 (1985).

SOME NEW TRANSFORMATIONS OF CYCLOPROPYLACETYLENE CATALYZED BY RHODIUM, PALLADIUM, AND COBALT COMPLEXES

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The linear and cyclic dimerization and trimerization of cyclopropylacetylene were carried out by the action of rhodium, palladium, and cobalt catalysts to give 2,4-dicyclopropyl-1-buten-3-yne, 1,3,6-tricyclopropylfulvene, and 1,3,5- and 1,2,4-tricyclopropylbenzenes.

In a continuation of a study of the catalytic transformations of unsaturated compounds containing small rings [1-3], we studied the reaction of cyclopropylacetylene (CPA) in the presence of homogeneous metal complex catalysts containing Rh, Pd, and Co compounds, which, as a rule, permit us to carry out transformations of cyclopropylolefins with the retention of the small rings. Previous attempts to carry out the cyclic oligomerization of CPA by the action of $Fe(CO)_5$ with simultaneous UV irradiation led to Fe(0) complexes with two acetylenic ligands in the coordination sphere of the central atom. In the present work, we achieved both linear and cyclic oligomerization of CPA by the action of the above-mentioned catalytic systems.

The action of the Wilkinson complex, $RhCl(PPh_3)_3$, on CPA leads to linear dimerization with the formation of 2,4-dicyclopropyl-1-buten-3-yne (I). Under optimal conditions, this reaction proceeds in THF at 20°C over 12 h to give a yield of close to 100%

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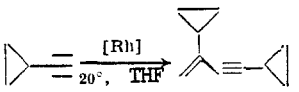
TABLE 1. Dimerization and Trimerization of Cyclopropylacetylene (CPA) by the Action of Rhodium, Palladium, and Cobalt Catalysts ([catalyst]/[CPA] = 1:100)

Catalytic system (mole ratio of components)	Reaction conditions	CPA conversion, %	Yield, %			
			(I)	(II)	(IV)+(V)	higher oligomers
$RhCl(PPh_3)_3Cl$	20°, 12 h, THF	100	100	0	0	0
»	50°, 2 h, THF	100	0	0	0	100
$Rh(acac)_3$–PPh_3–$AlEt_3$ (1:2:4)	100°, 1 h, C_6H_6	25	24,3	0	0	0,7
$Pd(OAc)_2$–PPh_3 (1:1)	20°, 12 h, THF	100	100	0	0	0
»	80°, 1 h, THF	100	100	0	0	0
$Pd_2(DBA)_3CHCl_3$–PPh_3 (1:1) *	100°, 4 h, $CHCl_3$	100	100	0	0	0
$Pd(OAc)_2$	80°, 1 h, THF	100	0	100	0	0
$Co(acac)_2$–PPh_3–$AlEt_3$ (1:1:4)	60°, 2 h, C_6H_6	100	50	0	25	25
$Co(acac)_2$–PPh_3–$AlEt_2Cl$ (1:1:10)	60°, 2 h, C_6H_6	100	0	0	70	30
$Co(acac)_2$–$(Ph_2PCH_2)_2$–$AlEt_2Cl$ (1:1:10)	60°, 2 h	100	0	0	90	10

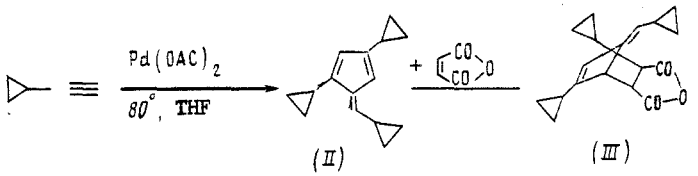
*DBA) dibenzalacetone.



The formation of only oligomers is observed when the reaction temperature is raised to 50°C. The linear dimerization of CPA is achieved using 1:2:4 $Rh(acac)_3$–PPh_3–$AlEt_3$ (see Table 1), but the yield of (I) does not exceed 25%.

The most efficient catalyst for the dimerization of CPA to (I) was found to be $Pd(OAc)_2$ activated by an equivalent of PPh_3 (Table 1), which, in contrast to the $Pd(acac)_2$–PPh_3–$AlEt_3$ catalyst used in our previous work [5], does not require the use of promoters and has selectivity of ~100%.

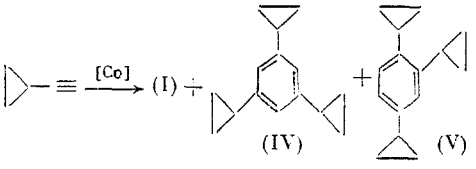
In the absence of triphenylphosphine, $Pd(OAc)_2$ directs the reaction of CPA toward homocyclotrimerization with the formation of 1,3,6-tricyclopropylfulvene (II)



(II) (III)

The formation of fulvene (II) from CPA probably precedes the dimerization of the latter but an attempt to obtain (II) by the cyclodimerization of dimer (I) with CPA by the action of $Pd(OAc)_2$ proved unsuccessful and (I) was recovered unchanged from the reaction. Relatively unstable fulvene (II) was characterized by IR and PMR spectroscopy and as its adduct with maleic anhydride (III).

The three-component cobalt catalysts direct the reaction of CPA toward dimerization or trimerization depending on the activator ligand and reducing agent (see Table 1). If the structure of dimer (I) is identical to that synthesized previously in the presence of the $Pd(OAc)_2$–PPh_3 system, then the trimers obtained are isomeric tricyclopropylbenzenes (IV) and (V)



(IV) (V)

These tricyclopropylbenzenes become the only products when PPh_3 is replaced in the cobalt catalyst by 1,2-bis(diphenylphosphino)ethane and $AlEt_3$ is replaced by $AlEt_2Cl$.

The structures of the products were established using the IR, PMR, ^{13}C NMR, and mass spectra. In particular, the structure of trimers (IV) and (V) follow from an analysis of their ^{13}C NMR spectra. The signals at 144.25 s and 120.62 d are related to symmetrical isomer (IV), while the signals at 141.60 s, 123.10 s, 120.60 d, and 125.57 d belong to isomer (V) [6]. The ratio of these isomers was 3:1.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-497 spectrometer at 60 MHz in CCl_4 and $(CD_3)_2CO$ relative to TMS. The IR spectra were taken on a UR-20 spectrometer. The UV spectra were taken on a Specord UV-VIS spectrometer. The ^{13}C NMR spectra were taken on a Jeol-90QX spectrometer in $CDCl_3$ and $(CD_3)_2CO$ with TMS as the internal standard. The gas-liquid chromatography was carried out on a Chrom-41 chromatograph using a 2.4 × 0.003-m column packed with 5% SE-30 on Chromatone N-AW-HMDS. The helium gas carrier flow rate was 47 ml/min. The temperature was raised from 50 to 250°C. Cyclopropylacetylene (CPA) was obtained according to either Hanack [7] or our previous procedure [8].

Dimerization of CPA. a. A solution of 0.47 g (0.5 mmole) $RhCl(PPh_3)_3$ and 3.3 g (50 mmoles) CPA in 5 ml THF in an argon atmosphere was maintained for 12 h at about 20°C. The reaction mass was filtered through a layer of alumina using hexane as the eluent. After evaporation of the solvent, the residue was distilled in vacuum to give ~3.3 g (100%) 2,4-dicyclopropyl-1-buten-3-yne (I), bp 98°C (10 mm), n_D^{20} 1.5163. IR spectrum (ν, cm^{-1}): 883, 1020, 1040, 1605, 2235, 3020, 3090. PMR spectrum (δ, ppm): 0.47-0.75 (CH_2 in cyclopropyl ring (CPR), 8H), 0.85-1.50 (CH in CPR, 2H), 5.00 ($C=CH_2$, 2H). ^{13}C NMR spectrum (δ, ppm): 5.98 t, 8.58 t (CH_2 in CPR), 16.60 d (CH in CPR), 77.20 s (C^4), 93.49 s (C^3), 117.29 t (C^1), 134.11 s (C^2). Mass spectrum (m/z): 132.

b. A sample of 3.3 g (50 mmoles) CPA was added to a solution of 0.11 g (0.5 mmole) $Pd(OAc)_2$ and 0.062 g (0.25 mmole) PPh_3 in 5 ml THF under argon. The mixture was transferred in an inert atmosphere to a 17-ml steel microautoclave and heated for 1 h at 80°C. Work-up as in the previous procedure gave 3.3 g (~100%) dimer (I).

c. A mixture of 3.3 g (50 mmoles) CPA, 0.1 g (0.25 mmole) $Rh(acac)_3$, 0.13 g (0.5 mmole) PPh_3, and 5 ml benzene was flushed with argon in a Schlenck vessel and cooled to -5°C. Then, 0.22 g $AlEt_3$ was added dropwise. The solution obtained was transferred after 0.5 h to a microautoclave and heated for 1 h at 100°C. Ordinary work-up gave 0.8 g (24%) dimer (I).

1,3,9-Tricyclopropylfulvene (II). A solution of $Pd(OAc)_2$ 0.11 g (0.5 mmole) and 3.3 g (5 mmoles) CPA in 5 ml THF was placed into a microautoclave in an inert atmosphere and heated for 1 h at 80°C. The catalyzate was washed with water, extracted with hexane, filtered through alumina, and eluted with hexane. The solvent was evaporated. The cherry-red oily residue was tricyclopropylfulvene (II). The yield of (II) was ~100%. This product polymerized after several hours. IR spectrum (ν, cm^{-1}): 860, 1030, 1600, 1615, 3020, 3055. PMR spectrum (δ, ppm): 0.33-0.85 (CH_2 in CPR, 12 H), 0.92-1.60 (CH in CPR, 3H), 6.15-6.70 (C=CH, 3H). Mass spectrum (m/z): 198.

The adduct of fulvene (II) with maleic anhydride (III) was obtained at ~20°C as a viscous liquid. IR spectrum (ν, cm^{-1}): 890, 1040, 1660, 1730, 1780, 1850, 3020, 3090. PMR spectrum (δ, ppm): 0.10-0.60 (CH_2 in CPR), 0.90-1.50 (CH in CPR), 3.75-4.20 (3H), 5.83 (C=CH, 1H), 6.80 (C=CH in norbornene fragment, 1H).

Tricyclopropylbenzenes. A sample of 0.6 g (5 mmoles) $AlEt_2Cl$ was added dropwise under argon to a solution of 0.16 g (0.5 mmole) $Co(acac)_2$, 0.3 g (0.5 mmole) $(Ph_2PCH_2)_2$, and 0.5 g CPA in 5 ml benzene cooled to 0°C. After 0.5 h, the solution was transferred to a microautoclave containing 2.8 g CPA and heated for 2 h at 60°C. After cooling, the mixture was treated with 2 ml ethanol and washed with water. The organic layer was filtered through alumina with hexane as the eluent. The solvent was evaporated and the residue was distilled in vacuum to give 3.0 g of a 3:1 mixture of 1,3,5- (IV) and 1,2,4-tricyclopropylbenzenes (V), bp 148-150°C (10 mm), n_D^{20} 1.5490. IR spectrum (ν, cm^{-1}): 830, 900, 1020, 1600, 1630, 1640, 3060. PMR spectrum (δ, ppm): 0.35-0.83 (CH_2 in CPR, 12H), 1.18-1.68 (CH in CPR, 2H), 6.38-6.65 and 7.20-7.41 (aromatic protons). ^{13}C NMR spectrum of (IV) (δ, ppm): 144.25 s (C^1, C^3, C^5), 120.62 d (C^2, C^4, C^6), 9.23 t (CH^2), 15.78 d (CH). ^{13}C NMR spectrum of (V) (δ, ppm): 141.60 s (C^4), 123.10 s (C^1, C^2), 120.60 d (C^3), 13.40 t (CH_2), 7.35 d (CH). Mass spectrum (m/z): 198.

LITERATURE CITED

1. U. M. Dzhemilev, R. I. Khusnutdinov, V. A. Dokichev, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2634 (1979).
2. U. M. Dzhemilev, R. I. Khusnutdinov, N. A. Shchadneva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2294 (1984).
3. R. I. Khusnutdinov, N. A. Shchadneva, and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim., 1196 (1986).
4. R. Victor, R. Ben-Shoshan, and S. Sarel, Tetrahedron Lett., 4211 (1973).
5. F. A. Selimov, O. G. Rutman, and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim., 1853 (1983).
6. E. Pretsch, J. Seibl, and M. Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer-Verlag, Berlin-Heidelberg-New York-Tokyo (1983).
7. M. Schoberth and M. Hanack, Synthesis, 703 (1972).
8. I. E. Dolgii, I. B. Shvedova, K. N. Shavrin, and O. M. Nefedov, USSR Inventor's Certificate No. 555,079; Byull. Izobret., No. 15, 65 (1977).

SYNTHESIS OF ESTERS OF IMINOCARBONIC ACID

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The first syntheses of asymmetrical esters of iminocarbonic acid are reported. These syntheses were carried out without the separation of intermediates.

Esters of iminocarbonic acid are promising reagents in organic synthesis. However, their application is limited by the lack of convenient synthetic methods. The most well-known method for the preparation of iminocarbonic acid esters is based on the chlorination of alcoholic solutions of transition metal cyanides with subsequent reduction of the chloro-iminocarbonic acid esters obtained using alkali metal arsenites [1].

We carried out the syntheses of symmetrical and asymmetrical esters of iminocarbonic acid by the reaction of an alkali metal alcoholate with cyanogen bromide

$$RONa + BrCN + R^1OH \rightarrow \underset{I(a-\ell)}{ROCNHOR^1} + NaBr$$

EXPERIMENTAL

The iminocarbonic acid esters were synthesized by two methods.

Method A: Preparation of Symmetrical Iminocarbonic Acid Esters (Ia)-(If). A sample of 0.1 mole BrCN in THF was added dropwise with rapid stirring and cooling to a solution of 0.1 mole alkali metal in excess alcohol at a rate such that the temperature of the reaction mixture did not exceed 5°C. The precipitate formed was filtered and washed with THF. After distillation of the THF, the residue was distilled in vacuum.

Method B: Preparation of Symmetrical and Asymmetrical Iminocarbonic Acid Esters (Ig)-(Iℓ). A solution of 0.1 mole BrCN in dry THF was added dropwise with rapid stirring and cooling to a suspension or solution of 0.1 mole alkali metal alcoholate in dry THF at a rate such that the temperature of the reaction mixture did not exceed 5°C. After all the reagent was added, the reaction mixture was brought to ~20°C and 0.1 mole alcohol was added dropwise. The precipitate formed was filtered and washed with dry THF. The solvent was removed and the residue was distilled in vacuum. The yield and physical indices of the products are given in Table 1.

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