ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 7, pp. 969–972. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.V. Plemenkov, R.V. Ashirov, O.A. Lodochnikova, I.A. Litvinov, R.N. Zagidullin, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 7, pp. 989–992.

Diels–Alder Reaction of 1-Methylcycloprop-2-ene-1-carbonitrile with Methyl 2-Oxo-2*H*-pyran-5-carboxylate

V. V. Plemenkov[a], **R. V. Ashirov**[a], **O. A. Lodochnikova**[b], **I. A. Litvinov**[b], **and R. N. Zagidullin**[a]

[a] *Kazan State Medical University, ul. Butlerova 49, Kazan, 420012 Tatarstan, Russia*
e-mail: plem-mu@mi.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*

Received July 12, 2005

Abstract—The Diels–Alder reaction of 1-methylcycloprop-2-ene-1-carbonitrile and coumalic acid methyl ester (methyl 2-oxo-2*H*-pyran-5-carboxylate) gave a 2:1 adduct with *endo*-*syn* configuration of both cyclopropane fragments, which was established by X-ray analysis. According to the ^{1}H NMR data, the reaction involves intermediate formation of decarboxylated 1:1 adduct having a cycloheptatriene structure; its isomerization into the corresponding caradiene, followed by addition of the second dienophile molecule, was confirmed by quantum-chemical calculations.

DOI: 10.1134/S1070428006070074

We previously synthesized 1-methylcycloprop-2-ene-1-carbonitrile (**I**) [1] and showed that it can be used as electrophilic reagent in reactions with thiols [2] and dienes [3]. Versatile reactivity of compound **I** is combined with unusually high thermal stability. In the present work we examined the reactivity of cyclopropene derivative **I** as dienophile toward coumalic acid methyl ester (**II**, methyl 2-oxo-2*H*-pyran-5-carboxylate). The latter is an α-pyrone diene which is known to give both normal and decarboxylated Diels–Alder adduct [4, 5]; therefore, coumalic acid and its esters may be regarded as proisoprenoids, i.e., reagents ensuring introduction of an isoprene fragment into Diels–Alder adducts.

The reaction of equimolar amounts of compounds **I** and **II** on heating on a water bath was complete in 2 h. After cooling, the mixture separated into crystalline and liquid phases. When 2 equiv of the dienophile was taken, only the crystalline product was formed in almost quantitative yield. The structure of the crystalline product was determined by X-ray analysis. Unexpectedly, it was a 2:1 dienophile–diene adduct with *endo* configuration of both cyclopropane fragments and *syn* orientation of the cyano groups (Fig. 1). Its molecule in crystal is symmetric; the symmetry plane passes through the bridging $C^1C^9C^{10}C^5$ moiety and ester group. The planar $C^1C^2C^4C^5$ fragment forms dihedral angles of 123.5(2)° and 120.3(3)° with the planes of the $C^1C^{10}C^9C^5$ fragment and cyclopropane ring, respectively.

The structure of the final product implies that the reaction of compound **I** with **II** includes three steps. In the first step, tricyclic monoadduct **III** is formed. Strong steric strain in the tricyclic skeleton of **III** promotes elimination of CO_2 molecule to give caradiene

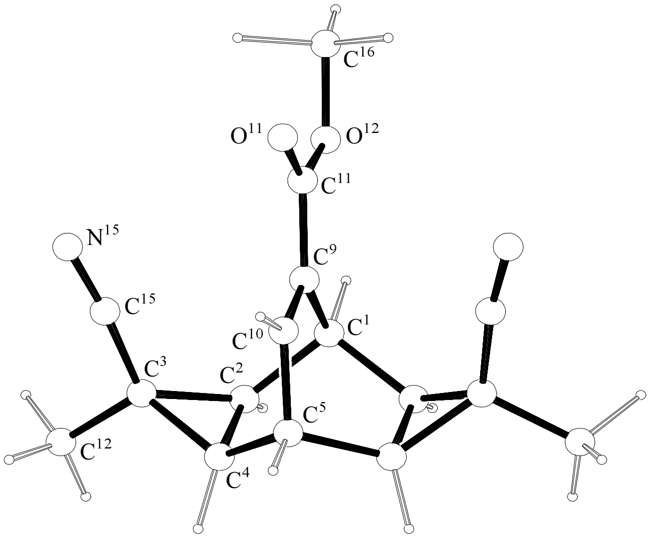
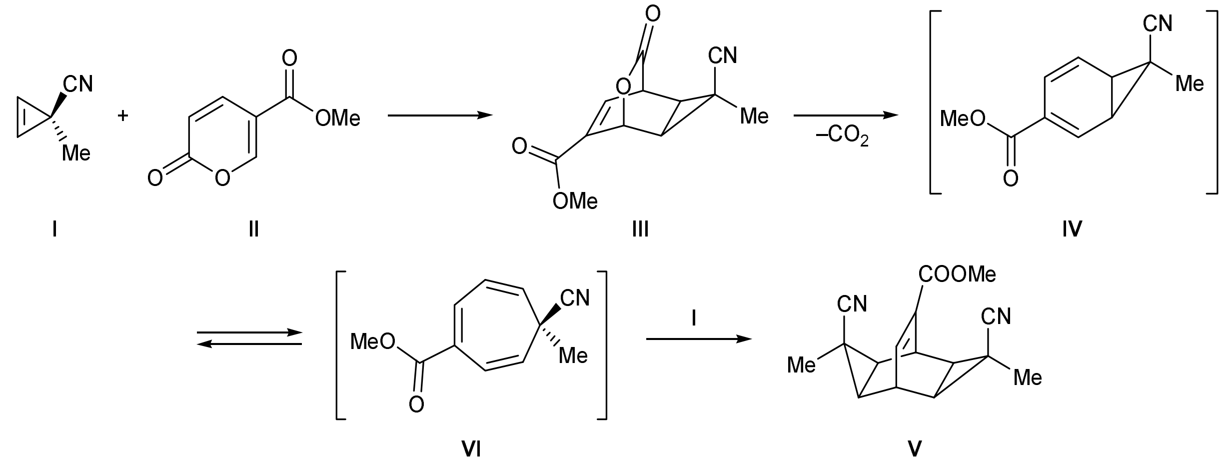


Fig. 1. Structure of the molecule of methyl 3,7-dicyano-3,7-dimethyltetracyclo[3.3.2.0$^{2.4}$.0$^{6.8}$]dec-9-ene-9-carboxylate (**V**) according to the X-ray diffraction data. A half of the molecule is symmetry-dependent.

Scheme 1.



derivative **IV** which takes up the second dienophile molecule with formation of bis-adduct **V** (Scheme 1). If the proposed scheme is valid, intermediate compounds **III** and/or **IV** could be detected in the liquid part of the reaction mixture when the reaction is carried out with equimolar amounts of the reactants. In this case, the reaction mixture could also contain unreacted ester **II** and (what is the most inportant) compound **VI** with a cycloheptatriene skeleton, which should be formed from caradiene **IV**. The interconversion caradiene$\rightleftarrows$cycloheptatriene has been well documented [6, 7].

By column chromatography of the liquid part we isolated its main component as an oily substance. Its IR spectrum contained absorption bands assignable to carbonyl (1723 cm^{-1}) and cyano groups (2233 cm^{-1}). In the ^{1}H NMR spectrum of that product we observed signals from an ester methyl group (δ 3.84 ppm) and another methyl group (δ 1.67 ppm), as well as a set of signals from five olefinic protons. Three of the latter (δ 7.58, 6.96, and 6.41 ppm) were coupled with each other, and the two other appeared at δ 4.65 and 4.77 ppm. These data indicated cycloheptatriene structure **VI** of the product as 1:1 adduct. According to the IR and ^{1}H NMR spectra of the reaction mixture before separation, it contained initial ester **II**, bis-adduct **V**, and cycloheptatriene **VI**, whereas intermediates **III** and **IV** were not detected.

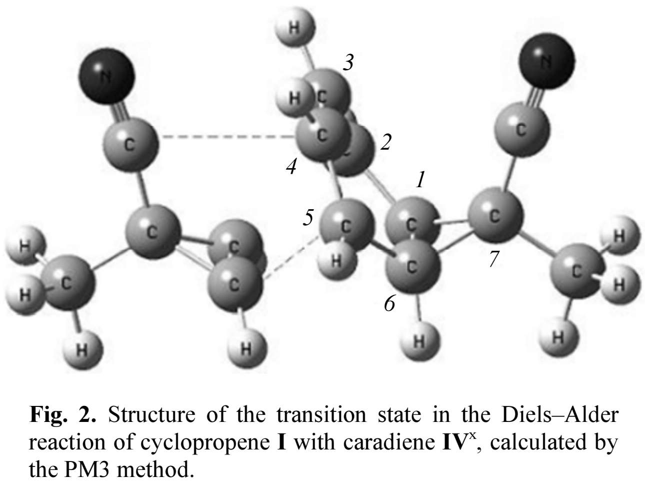


Fig. 2. Structure of the transition state in the Diels–Alder reaction of cyclopropene **I** with caradiene **IV**^{x}, calculated by the PM3 method.

Thus the transformation sequence in the reaction between compounds **I** and **II** may be represented as follows: (1) Diels–Alder reaction of **I** with **II** to give 1:1 adduct **III**, (2) decarboxylation of **III** to caradiene **IV**, (3) reversible transformation of caradiene **IV** into cycloheptatriene **VI**, and (4) Diels–Alder reaction of caradiene **IV** or cycloheptatriene **VI** with the second cyclopropene **I** molecule to yield final product **V** (Scheme 1). Diels–Alder reactions of cycloheptatrienes via preliminary conversion into caradienes were reported in [8].

The X-ray diffraction data (Fig. 1) unambiguously confirmed *syn* orientation of the cyano group in the dienophile molecule with respect to diene in the transition state, regardless of the orientation of the cyclopropene fragment. The *endo* arrangement of the dienophile and diene is determined at the stage of formation of the bisadduct and it cannot be set at the stage of formation of the monoadduct.

However, the question as to which molecule (caradiene **IV** or cycloheptatriene **VI**) acts as diene component at the stage of addition of the second dienophile molecule remains open. Among these, caradiene **IV** is preferred in the Diels–Alder reaction, for participation of cycloheptatriene **VI** as diene component is forbidden by the orbital symmetry conservation rules [9].

On the other hand, distortion of the planar structure of **VI** [10] may partially eliminate this prohibition; therefore, we performed quantum-chemical calculations of possible paths for the formation of the bis-adduct. The reactions of cyclopropene **I** with model dienes **IV**^{x} and **VI**^{x} (having no methoxycarbonyl group) were calculated in terms of PM3 semiempirical method. First, it was found that the most favorable conformation of cycloheptatriene **VI**^{x} is that with the axial CN group and low barrier to the transformation into the equatorial form; second, the cycloheptatriene structure is preferred in the equilibrium system **IV**^{x} $\rightleftarrows$ **VI**^{x} which is characterized by a relatively low barrier to the isomerization into the caradiene structure (~20 kcal/mol). The energy barrier for the reaction of cyclopropene **I** with caradiene **IV**^{x} (~50 kcal/mol) is considerably lower than that found for the reaction of **I** with cycloheptatriene **VI**^{x} (~67 kcal/mol), and the transition states in both reactions are characterized by short distances between carbon atoms involved in formation of new bonds (2.02–2.18 Å) and between the cyano group and the π system of the diene component (2.95 Å). The latter parameter suggests significant secondary orbital interactions and is responsible for the *endo-syn* orientation of dienophile **I** and diene **II** in the transition state (Fig. 2).

EXPERIMENTAL

The ^{1}H NMR spectra were recorded from solutions in $CDCl_3$ on a Varian spectrometer (300 MHz) using tetramethylsilane as internal reference. The IR spectra were measured on a Specord 75IR instrument from samples dispersed in mineral oil. Quantum-chemical calculations of the molecules of cyclopropene **I**, caradiene **IV**^{x}, cycloheptatriene **VI**^{x}, and bis-adduct **V** and transition states were performed by the PM3 method using Gaussian 98 software. Silica gel L (100–160 μm) was used for column chromatography.

Bond lengths and bond and torsion angles in the molecule of methyl 3,7-dicyano-3,7-dimethyltetracyclo[3.3.2.0^{2,4}.0^{6,8}]dec-9-ene-9-carboxylate (**V**)

Bond	*d*, Å	Bond	*d*, Å
$\mathrm{O^{11}{-}C^{11}}$	1.218(8)	$\mathrm{C^{2}{-}C^{4}}$	1.504(7)
$\mathrm{O^{12}{-}C^{11}}$	1.348(8)	$\mathrm{C^{2}{-}C^{3}}$	1.511(8)
$\mathrm{O^{12}{-}C^{16}}$	1.40(1)	$\mathrm{C^{5}{-}C^{10}}$	1.52(1)
$\mathrm{N^{15}{-}C^{15}}$	1.142(8)	$\mathrm{C^{5}{-}C^{4}}$	1.547(8)
$\mathrm{C^{1}{-}C^{9}}$	1.52(1)	$\mathrm{C^{4}{-}C^{3}}$	1.538(8)
$\mathrm{C^{1}{-}C^{2}}$	1.536(7)	$\mathrm{C^{15}{-}C^{3}}$	1.441(9)
$\mathrm{C^{9}{-}C^{10}}$	1.325(9)	$\mathrm{C^{3}{-}C^{12}}$	1.520(9)
$\mathrm{C^{9}{-}C^{11}}$	1.46(1)		
Bond angle	ω, deg	Bond angle	ω, deg
$\mathrm{C^{11}O^{12}C^{16}}$	115.9(7)	$\mathrm{O^{11}C^{11}C^{9}}$	124.3(6)
$\mathrm{C^{9}C^{1}C^{2}}$	108.9(4)	$\mathrm{O^{12}C^{11}C^{9}}$	112.5(7)
$\mathrm{C^{1}C^{9}C^{10}}$	114.5(7)	$\mathrm{C^{2}C^{4}C^{5}}$	110.2(5)
$\mathrm{C^{1}C^{9}C^{11}}$	124.8(6)	$\mathrm{C^{2}C^{4}C^{3}}$	59.6(4)
$\mathrm{C^{10}C^{9}C^{11}}$	120.7(7)	$\mathrm{C^{5}C^{4}C^{3}}$	126.1(5)
$\mathrm{C^{1}C^{2}C^{4}}$	111.2(5)	$\mathrm{N^{15}C^{15}C^{3}}$	172.6(7)
$\mathrm{C^{1}C^{2}C^{3}}$	125.5(5)	$\mathrm{C^{2}C^{3}C^{4}}$	59.1(3)
$\mathrm{C^{1}C^{2}H^{2}}$	94.9(4)	$\mathrm{C^{2}C^{3}C^{15}}$	122.1(5)
$\mathrm{C^{4}C^{2}C^{3}}$	61.3(3)	$\mathrm{C^{2}C^{3}C^{12}}$	116.6(5)
$\mathrm{C^{10}C^{5}C^{4}}$	108.5(4)	$\mathrm{C^{4}C^{3}C^{15}}$	124.4(5)
$\mathrm{C^{9}C^{10}C^{5}}$	114.9(7)	$\mathrm{C^{4}C^{3}C^{12}}$	114.7(5)
$\mathrm{O^{11}C^{11}O^{12}}$	123.2(7)	$\mathrm{C^{15}C^{3}C^{12}}$	111.1(5)
Torsion angle	φ, deg	Torsion angle	φ, deg
$\mathrm{C^{16}O^{12}C^{11}C^{9}}$	–180.0(4)	$\mathrm{C^{4}C^{2}C^{3}C^{12}}$	104.2(5)
$\mathrm{C^{2}C^{1}C^{9}C^{10}}$	–55.3(3)	$\mathrm{C^{4}C^{5}C^{10}C^{9}}$	55.7(4)
$\mathrm{C^{2}C^{1}C^{9}C^{11}}$	124.7(3)	$\mathrm{C^{10}C^{5}C^{4}C^{2}}$	–53.8(6)
$\mathrm{C^{9}C^{1}C^{2}C^{4}}$	52.5(6)	$\mathrm{C^{10}C^{5}C^{4}C^{3}}$	12.6(8)
$\mathrm{C^{9}C^{1}C^{2}C^{3}}$	–16.7(7)	$\mathrm{C^{2}C^{4}C^{3}C^{15}}$	110.0(6)
$\mathrm{C^{1}C^{2}C^{4}C^{5}}$	0.9(7)	$\mathrm{C^{2}C^{4}C^{3}C^{12}}$	–107.3(6)
$\mathrm{C^{1}C^{2}C^{4}C^{3}}$	–119.9(5)	$\mathrm{C^{5}C^{4}C^{3}C^{2}}$	–93.8(6)
$\mathrm{C^{3}C^{2}C^{4}C^{5}}$	120.8(6)	$\mathrm{C^{5}C^{4}C^{3}C^{15}}$	16.2(9)
$\mathrm{C^{1}C^{2}C^{3}C^{4}}$	96.7(6)	$\mathrm{C^{5}C^{4}C^{3}C^{12}}$	158.8(5)
$\mathrm{C^{1}C^{2}C^{3}C^{15}}$	–17.0(7)	$\mathrm{N^{15}C^{15}C^{3}C^{2}}$	–125(5)
$\mathrm{C^{1}C^{2}C^{3}C^{12}}$	–159.1(5)	$\mathrm{N^{15}C^{15}C^{3}C^{4}}$	163(5)
$\mathrm{C^{4}C^{2}C^{3}C^{15}}$	–113.7(6)	$\mathrm{N^{15}C^{15}C^{3}C^{12}}$	19(5)

Crystallographic data for bis-adduct **V** at 20°C: rhombic crystals, $C_{16}H_{16}N_2O_2$, space group $Cmc2_1$; $a = 9.256(9)$, $b = 12.76(2)$, $c = 11.882(6)$ Å; $V = 1403(3)$ Å^3; $Z = 8$; $M = 268.31$; $d_{\mathrm{calc}} = 1.27$ g/cm^{-3}; μ(Mo) = 6.8 cm^{-1}; $F(000) = 568.0$. Intensities of 833 reflections were measured on an Enraf–Nonius CAD-4 automatic diffractometer at 20°C (λCuK_α, ω scanning), 534 reflection were with $I > 3\sigma$. The structure was solved by the direct method using SIR program [11] and was refined first in isotropic and then in anisotropic approximation. Hydrogen atoms were visualized from the difference series of electron density, and their contribution to the structure amplitude was taken into account with fixed thermal and positional parameters. All calculations were performed using MOLEN software package [12] on an AlphaStation 200 PC. The final divergence factors were $R =$

0.058, R_w = 0.074 (from 534 independent reflections with $F^2 \geq 3\sigma$). The bond lengths and bond and torsion angles in molecule **V** are given in table.

1-Methylcycloprop-2-ene-1-carbonitrile (**I**) was synthesized by the procedure described in [1].

Methyl 2-oxo-2*H*-pyran-5-carboxylate (II). A solution of 5 g (35.7 mmol) of 2-oxo-2*H*-pyran-5-carboxylic acid in 50 ml of tetrahydrofuran was mixed at 5°C with 100 ml of a solution of diazomethane [prepared from 8 g (77.7 mmol) of *N*-methyl-*N*-nitrosourea] in diethyl ether. The mixture was kept for 3 h at room temperature (20°C), the solvent was distilled off under reduced pressure, and the residue was recrystallized from methanol. Yield 4.2 g (76.4%), crystalline substance, mp 65–66°C. ^{1}H NMR spectrum, δ, ppm: 8.30 d (1H, 6-H, ^4J = 2.6 Hz), 7.79 d.d (1H, 4-H, ^4J = 2.6, ^3J = 9.8 Hz), 6.34 d (1H, 3-H, ^3J = 9.8 Hz), 3.89 s (3H, CH_3).

Methyl 3,7-dicyano-3,7-dimethyltetracyclo-[3.3.2.0$^{2.4}$.0$^{6.8}$]dec-9-ene-9-carboxylate (V) (2:1 adduct). *a.* A mixture of 0.31 g (2 mmol) of compound **II**, 0.16 g (2 mmol) of cyclopropene **I**, and 5 mg of hydroquinone was heated for 3 h at 90–100°C in a sealed ampule on a water bath. The mixture was dissolved in 5 ml of diethyl ether on heating; after 15 min, crystals precipitated and were separated by decanting. Yield 0.17 g (63.4%), mp 158–159°C. ^{1}H NMR spectrum, δ, ppm: 6.92 d.d (1H, C=CH, ^3J = 9.5, ^4J = 2.3 Hz), 4.23–4.31 m (1H, 1-H), 3.72–3.83 m (1H, 5-H), 3.82 s (3H, $COOCH_3$), 1.31 s (6H, $2CH_3$), 1.53–1.73 m (4H, 2-H, 4-H, 6-H, 8-H).

The liquid phase was subjected to column chromatography using petroleum ether–diethyl ether (1:1) as eluent, R_f(**VI**) 0.35 (Silufol). Yield 0.12 g (31.7%), oily substance; the product was identified as 1:1 adduct of cyclopropene **I** and ester **II**, methyl 5-cyano-5-methylhepta-1,3,6-triene-1-carboxylate (**VI**). ^{1}H NMR spectrum, δ, ppm: 1.67 s (3H, CH_3), 3.84 s (3H, $COOCH_3$), 6.41 d.d (1H, 3-H, ^3J = 8.4, $^{3'}J$ = 7.4 Hz), 6.96 d (1H, 4-H, ^3J = 8.4 Hz), 7.58 d (1H, 2-H, $^{3'}J$ = 7.4 Hz), 4.77 d (1H, 6-H, $^{3''}J$ = 11.4 Hz), 4.65 d (1H, 7-H, J = 11.4 Hz).

b. A mixture of 0.12 g (0.63 mmol) of compound **VI** and 0.055 g (0.70 mmol) of cyclopropene **I** was heated for 3 h at 90–100°C in a sealed ampule on a water bath. After cooling, the mixture crystallized. The product was recrystallized from acetone. Yield 0.16 g (94.8%), mp 158–159°C.

REFERENCES

1. Latypova, M.M., Plemenkov, V.V., Kalinina, V.N., and Bolesov, I.G., *Zh. Org. Khim.*, 1984, vol. 20, p. 542.
2. Plemenkov, V.V., Gritsenko, E.I., Butenko, G.G., and Bolesov, I.G., *Dokl. Akad. Nauk SSSR*, 1986, vol. 281, p. 99.
3. Rul', S.V., Plemenkov, V.V., Gubaidullin, A.T., Litvinov, I.A., Kataeva, O.N., and Appolonova, S.A., *Russ. J. Org. Chem.*, 1999, vol. 35, p. 1121.
4. Pilet, O., Birbaum, J-L., and Vogel, P., *Helv. Chim. Acta*, 1992, vol. 66, p. 19.
5. Onishchenko, A.S., *Dienovyi sintez* (Diels–Alder Reaction), Moscow: Akad. Nauk SSSR, 1963.
6. Takahashi, K., Takase, K., and Toda, H., *Chem. Lett.*, 1981, p. 979.
7. Ishiwata, A., Yamabe, S., Minato, T., and Machiguchi, T., *J. Chem. Soc., Perkin Trans. 2*, 2001, p. 2202.
8. Saracoglu, N., Menzek, A., and Balci, M., *Turk. J. Chem.*, 2001, vol. 25, p. 123.
9. Stegemann, J. and Lindler, H.J., *Acta Crystallogr., Sect. B*, 1980, vol. 36, p. 2363.
10. Butcher, S.S., *J. Chem. Phys.*, 1965, vol. 42, p. 1833.
11. Altomare, A., Cascarano, G., Giacovazzo, C., and Viterbo, D., *Acta Crystallogr., Sect. A*, 1991, vol. 47, p. 744.
12. Straver, L.H. and Schierbeek, A.J., *MolEN. Structure Determination System*, Delft, Netherlands: Nonius B.V., 1994, vols. 1, 2.