[2 + 4] CYCLOADDITION OF TETRACYANOETHYLENE WITH DIALKYL ESTERS

OF 3-DIALKYLAMINO-1, 3-ALKADIENE-2-PHOSPHONIC ACID

V. K. Brel', E. V. Abramkin, and I. V. Martynov

UDC 66.095.252+542.955:547.339.1:547.1'118

Dialkyl esters of 3-dialkylamino-1,3-alkadiene-2-phosphonic acid undergo [2 + 4] cycloaddition with tetracyanoethylene to give 1-(0,0-dialkylphosphono)-2-dialkyl-amino-3,3-dimethyl-4,4,5,5-tetracyano-2-cyclohexenes.

Tetracyanoethylene (TCE) is capable of reacting with various 1,3-dienes to give products of [2 + 4] cycloaddition [1]. TCE does not react with phosphorus-containing 1,3-alkadienes. In a continuation of a study of the reactivity of 1,3-alkadiene-2-phosphonates [2], we carried out the [2 + 4] cycloaddition of TCE with the dialkyl esters of 3-dialkylamino-1,3-alkadiene-2-phosphonic acid

 $\begin{array}{c} \begin{array}{c} & & & \\ H_2C = C & & \\ H_2C = C & C = C(CH_3)_2 + (NC)_2C = C(CN)_2 \longrightarrow \end{array} \xrightarrow[]{(RO)_2P} & & \\ H_2C = C & & \\ H_2C = C & & \\ (RO)_2P & & \\ H_2C & & \\ H_2C & & \\ CN & & \\ R_2'N &$

The reaction was carried out at room temperature in diethyl ether with the subsequent separation of adducts (I)-(IX) by crystallization. Low-melting (V), (VII), and (VIII) were first purified by column chromatography on silica gel 100/250 using 2:1 hexane-ether as the eluent. Adducts (I)-(IX) are stable crystalline compounds with high solubility in polar solvents. The structures of (I)-(IX) were established by PMR, ³¹P NMR, and IR spectroscopy. The spectral indices of these products are given in Table 1, while their physicochemical indices are given in Table 2.

EXPERIMENTAL

The ¹H and ³¹P NMR spectra were taken on a Bruker CXP-200 spectrometer at 200 and 188 MHz, respectively, with TMS as the internal standard for the ¹H NMR spectra and H_3PO_4 as the external standard for the ³¹P NMR spectra. The IR spectra were taken on a Bruker IFS-113 spectrometer for samples in vaseline oil.

1-(0,0-Dipropylphosphono)-2-dimethylamino-3,3-dimethyl-4,4,5,5-tetracyano-2-cyclohexene (IV). A solution of 1.45 g (0.005 mole) dipropyl ester of 3-dimethylamino-4-methyl-1,3pentadiene-2-phosphonic acid in 5 ml ether was added slowly with stirring to a suspension of 0.64 g (0.005 mole) tetracyanoethylene in 5 ml abs. ether. Then, 10 ml hexane was added and the reaction mixture was evaporated. The precipitate was filtered off and recrystallized from 1:5 hexane-ether to give 1.05 g (50.4%) (IV).

Adducts (I)-(III) and (V)-(IX) were obtained by procedures analogous to the procedure for the preparation of (IV).

Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2843-2845, December, 1989. Original article submitted December 5, 1988.

TABLE 1. Spectral Indices of Adducts (I)-(IX)

Com- pound	^{3 1} P NMR spectrum, δP, ppm	PMR spectrum, δ, ppm (J, Hz)	IR spectrum V, cm ⁻¹
(I)	13,83	1.33 t (6H, 2CH ₃ , J_{H-H} =7,2), 1,78 s (6H, 2CH ₃), 2,86 s (6H, 2NCH ₃), 3.63 d (2H, CH ₂ , J_{H-P} =6,0), 444 d a (4H, 2CH ₂ O, J_{H-P} =8,0)	1253(P=0), 1616(C=C), 2253(C=N)
(11)	14,40	1.15 t (6H, 2CH ₃ , $J_{H-P}=7.4$), 1.33 t (6H, 2CH ₃ , $J_{H-P}=7.4$), 1.35 t (6H, 2CH ₃ , $J_{H-P}=7.4$), 1.78 s (6H, 2CH ₃), 3.26 * (4H, 2CH ₂ N), 3.61 d (2H, CH ₂ $J_{H-P}=6.0$), 4.13 d.q (4H, 2CH ₂ O), $J_{H-P}=8.0$ $J_{H-P}=7.0$)	$\begin{array}{c} 1268(P=0), \\ 1542(C=C), \\ 2252(C=N) \end{array}$
(111)	13,02	$J_{H-P}=0,0, J_{H-H}=1,0)$ 1,34 t (6H, 2CH ₃ , $J_{H-H}=7,0)$, 1,60 m (6H, 3CH ₂), 1,76 s (6H, 2CH ₃), 2,96 *, 3,44 * (4H, 2CH ₂ N), 3,58 s (2H, CH ₂ , $J_{H-P}=6,0)$, 4,12 d.q (4H, 2CH ₂ O), $J_{U}=7,8$)	$\begin{array}{c} 1278(P=0), \\ 1602(C=C), \\ 2252(C=N) \end{array}$
(IV)	13,62	$J_{H-P} = 7.07$ 0.95 t (6H, 2CH ₃ , $J_{H-H} = 7.0$), 1.71 m (4H, 2CH ₂ , $J_{H-H} = 7.0$), 1.78 d (6H, 2CH ₃ , $J_{H-P} \sim 1.0$), 2.86 s (6H, 2NCH ₃), 3.65 d (2H, CH ₂), 4.05 d.t (4H, 2CH ₄ O, $J_{H-P} = 7.5$, $J_{H-H} = 7.5$)	$\begin{array}{c} 1257 (P=0), \\ 1609 (C=C), \\ 2251 (C=N) \end{array}$
(V)	14,20	0.96 t (6H, 2CH ₃ , J_{H-H} =7.0), 1.16 t (6H, 2CH ₃ , J_{H-H} =7.4), 1.71 m (4H, 2CH ₂), 1.78 s (6H, 2CH ₃), 3.31 * (4H, 2CH ₂ N), 3.62 d (2H, CH ₂ , J_{H-P} =6.0), 4.08 d, t (4H, 2CH ₂ , J_{H-P} =8.0, J_{H-H} =7.5)	1239, 1266(P=O), 1548(C=C), 2252(C=N)
(VI)	13,86	0.93 t (3H, 2CH ₃ , $J_{H-H}=7,0)$, 1.59 m (6H, 3CH ₂), 1.72 m (4H, 2CH ₂), 1.75 s (6H, 2CH ₃), 2.96 *, 3.44 * (4H, 2CH ₂ N), 3.65 d (2H, CH ₂), 4.05 d.t (4H, 2CH ₂ O, $J_{H-P}=8.0$, $J_{H-H}=7,5$)	$\begin{array}{c} 1259(P=O), \\ 1608(C=C), \\ 2248(C=N) \end{array}$
(VII)	13,96	0.94 t (6H, 2CH ₃ , $J_{H-H}=7.5$), 1.44 m (4H, 2CH ₂), 1.96 m (4H, 2CH ₂), 1.79 s (6H, 2CH ₃), 2.87 s (6H, 2CH ₃), 3.65 d (2H, CH ₂ , $J_{H-P}=6.0$), 4.09 d.t (4H, 2CH ₂ O, $J_{H-P}=7.8$)	1262(P=O), 1558, 1606(C=C) 2252(C=N)
(VIII)	14,2	0,93 t (6H, 2CH ₃ , $J_{H-H}=7,5$), 1,15 t (6H, 2CH ₃ , $J_{H-H}=7,3$), 1,41 m (4H, 2CH ₂), 1,66 m (4H, 2CH ₂), 1,78 s (6H, 2CH ₃), 3,31 * (4H, 2CH ₂ N), 3,6 d (2H, CH ₂ , $J_{H-P}=6,0$), 4,08 d.t (4H, 2CH ₂ O, $J_{H-P}=7,8$)	1258(P=O), 1545, 1591(C=C), 2253(C=N)
(IX)	13,7	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} 1259 (P=0) \\ 1609 (C=C), \\ 2250 (C=N), \end{array}$

*Broad signal.

TABLE 2. Physicochemical Indices of Adducts (I)-(IX)

Com- pound	Yield, %	Mp,°C	Found, %		Chemical for-	Calculated, %	
			N	P	mula	N	Р
(I) (II) (III) (IV) (V) (VI) (VII) (VIII)	36,4 38,7 35,5 50,4 22,0 58,0 39,0 40,8	$\begin{array}{r} 64-62\\ 113-114,5\\ 87-88,5\\ 110,5-112\\ 37-37,5\\ 71,5-72\\ 24-22\\ 31-31,5\end{array}$	17,60 16,71 16.03 16,56 15,64 15,20 15,80 14,23	7.48 7.40 7,11 7,20 6,67 6,73 6.88 6,35	$\begin{array}{c} C_{18}H_{24}O_3N_5P\\ C_{20}H_{28}O_3N_5P\\ C_{21}H_{28}O_3N_5P\\ C_{20}H_{28}O_3N_5P\\ C_{20}H_{32}O_3N_5P\\ C_{22}H_{32}O_3N_5P\\ C_{23}H_{32}O_3N_5P\\ C_{22}H_{32}O_3N_5P\\ C_{24}H_{36}O_3N_5P \end{array}$	17,99 16,77 16.29 16,77 15,71 15,07 15,71 14,78	7.96 7,42 7,21 7,42 6,95 6,77 6,95 6,54

LITERATURE CITED

- 1. A. I. Konovalova, Usp. Khim., <u>52</u>, No. 11, 1852 (1983).
- V. K. Brel', V. Ya. Komarov, B. I. Ionin, and A. A. Petrov, Zh. Obshch. Khim., <u>53</u>, No. 1, 66 (1983).

AN EMPIRICAL ANALYSIS OF THE CONTRIBUTIONS OF INTERMOLECULAR

DISPERSION INTERACTIONS TO THE VAPORIZATION ENTHALPY OF

NONELECTROLYTES

V. F. Nikolaev, A. N. Vereshchagin,* and S. I. Strobykin

UDC 539.196.3:536.722

A parameter was proposed, which is linearly related to the energy contribution of the dispersion interactions to the vaporization enthalpy. We showed the applicability of this parameter for the analysis of the energy characteristics of intermolecular interactions calculated from the internal pressure in liquids.

The vaporization enthalpy ΔH_{vap} is related to the energy of the intermolecular interaction U_{in} using Eq. (1) [1]:

$$U_{\text{in}} = -\Delta U_{\text{vap}} \approx -\Delta H_{\text{vap}} + RT \left(Z^{\text{v}} - Z_{\text{k}} \right)$$
(1)

where Z^{v} and Z^{ℓ} are the compressibility factors of the vapor and liquid. When the vapor obeys the ideal gas laws and far from the critical conditions when $Z^{v} \gg Z^{\ell}$ and $Z^{v} = 1$, Eq. (1) simplifies to

$$U_{\rm in} = -\Delta H_{\rm vap} + RT \tag{2}$$

If the liquids studied are nonpolar, the intermolecular dispersion interactions and repulsion forces make the predominant contribution to U_{in} . Our preliminary analysis showed that the parameter $I((n^2 - 1)/(n^2 + 2))^2$ (I is the ionization potential and n is the refraction index), used by Perov [2] as an index of the energy of dispersion interactions in liquids, leads to a curvilinear dependence of ΔH_{vap} on $I((n^2 - 1)/(n^2 + 2))^2$ foralkanes, which is quite likely since the contribution related to repulsion forces is not reflected in this term.[†] However, a similar analysis of ΔH_v using Eq. (3), where M is the molecular mass and d is the liquid density

$$\Delta H_{\text{vap}} = \alpha + \beta I \frac{M}{d} \left(\frac{n^2 - 1}{n^2 + 2}\right)^2$$

alkylbenzenes: $\beta = 0.4552, n = 3, r = 0.9999$ (a)
cycloalkanes; $\beta = 0.4517, n = 4, r = 0.9961$ (b)
n-alkanes: $\beta = 0.4108, n = 6, r = 0.9988$ (c)
isoalkanes: $\beta = 0.3998, n = 3, r = 0.9994$ (d)
(3)

for nondipolar liquids such as alkanes, alkylbenzenes, and cycloalkanes, leads to rather linear behavior (Fig. 1). The value of the intercept α is in good accord with the value RT = 2.48 kJ/mole (T 298 K). Thus, although the analytical form of the contribution of short-range repulsion to Δ Hvap is unknown, it is directly proportional to the contribution of the dispersion interaction energy.

*Deceased.

[†]The vaporization enthalpies given by Lebedev [3] were used and the vertical ionization energies were taken from the work of Viselov [4].

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2846-2848, December, 1989. Original article submitted December 6, 1988.