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ETHYNYL CARBONIUM IONS.

3.* DIENE SYNTHESIS WITH 4-PHENYLETHYNYLPYRYLIUM SALTS

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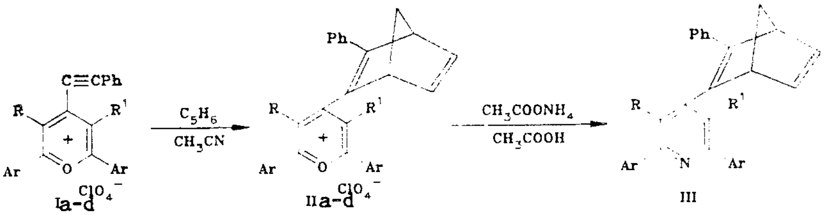
Norbornadiene derivatives of pyrylium salts were obtained for the first time by [4 + 2] cycloaddition of cyclopentadienes and 2,6-diaryl-4-phenylethynylpyrylium salts with and without methyl groups in the 3 and 5 positions. Their photochemical transformations were studied.

The synthesis developed by us [2] of 4-phenylethynylpyrylium salts that contain an activated (by the electron-acceptor pyrylium cation) C≡C bond for the first time opened up the possibility of introducing a labile carbocyclic group such as a norbornadienyl group into a charged heteroring. These molecules could become a convenient model in the study of processes involving the accumulation and utilization of the energy of visible light.

To obtain 4-norbornadienylpyrylium salts we set out to construct a carbocycle on an unsaturated substituent in the pyrylium cation using the Diels–Alder reaction.

We showed that refluxing 2,6-diphenyl-, 2,6-di(p-methoxyphenyl)-, 2,6-diphenyl-3-methyl-, and 2,6-diphenyl-3,5-dimethyl-4-phenylethynylpyrylium perchlorates Ia-d with cyclopentadiene in absolute acetonitrile leads to the formation of 2,6-diphenyl[di(p-methoxyphenyl)]-4-(2'-phenyl-3'-norbornadienyl)pyrylium and 2,6-diphenyl-3-methyl(3,5-dimethyl)-4-(2'-phenyl-3'-norbornadienyl)pyrylium perchlorates IIa-d in high yields (Table 1); the formation of other products of addition to the triple bond was not noted.



I, II **a,c,d** Ar=Ph, **b** Ar=*p*-$OCH_3C_6H_4$; **a,b** R=H; **c,d** R=CH_3; **a-c** R^1=H, **d** R^1=CH_3;
III Ar=Ph, R=CH_3, R^1=H

The results of cycloaddition provide evidence that the charge in 4-norbornadienylpyrylium salts Ia-d is concentrated primarily in the pyrylium ring, while the unsaturated substituent retains the properties of a triple bond, i.e., 4-norbornadienylpyrylium salts are ethynyl carbonium ions rather than allenyl cations, for which [2 + 2]-cycloaddition reactions are generally characteristic on reaction with cyclopentadiene [3-5].

Pentamethylcyclopentadiene is also capable of reacting with 4-ethynyl-substituted pyrylium salts. Using this method we were able to synthesize 2,6-di(p-methoxyphenyl)-4-(2'-phenyl-1',4',5',6',7'-pentamethyl-7'H-3'-norbornadienyl)pyrylium perchlorate (IIa). However,

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*See [1] for Communication 2.

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TABLE 1. Characteristics of 4-Norbornadienylpyrylium Perchlorates IIa-d

Compound	Empirical formula	mp, °C	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm (in CF_3COOH)	Yield, %
IIa*	$C_{30}H_{23}ClO_5$	195...196	425 (33,0), 495 (19,5)	1626, 1600, 1573, 1546, 1286, 1273, 1100, 846, 780, 680	1,96...2,26 (2H, m, 7-2H), 3,73...4,0 (2H, m, 1-H, 4-H); 6,58...6,90 (2H, m, 5-H, 6-H); 6,9...7,74 (17H, m, Ar)	85
IIb	$C_{32}H_{27}ClO_7$	218...219	372 (10,6), 488 (54,5)	1626, 1600, 1570, 1546, 1265, 1233, 1173, 1100, 853, 754, 700	2,08 (2H, m, 7-2H); 3,67...3,93 (2H, m, 1-H, 4-H); 3,48 (6H, s, 2OCH₃); 6,65...8,12 (17H, m, 15H-Ar, 2H—5-H, 6-H)	92
IIc	$C_{31}H_{25}ClO_5$	198	407 (26,1), 482 (13,0)	1614, 1567, 1554, 1287, 1214, 1080, 774, 747, 687	1,62 (3H, s, CH₃); 1,82...2,12 (2H, m, 7-2H); 3,78 (2H, m, 1-H, 4-H); 6,5...7,6 (18H, 16H-Ar, 2H—5-H, 6-H)	78
IId	$C_{32}H_{27}ClO_5$	228...229	389 (26,0), 474 (9,4)	1607, 1594, 1573, 1300, 1087, 780, 700, 634	1,47 (3H, s, CH₃); 1,9...2,17 (5H, m, CH₃, 7-2H); 3,75 (2H, s, 1-H, 4-H); 6,47...7,6 (17H, m, 15H-Ar, 2H—5-H, 6-H)	76

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*The PMR spectrum of IIa in CF_3COOD was recorded with a Varian XL-100 spectrometer (100 MHz).

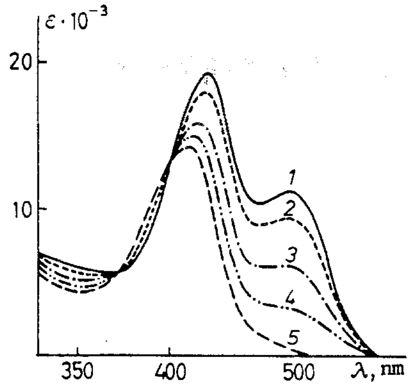


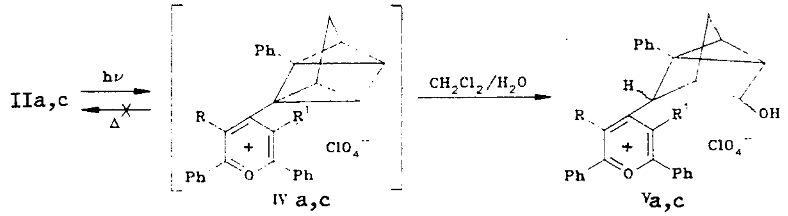
Fig. 1. Electronic absorption spectra of IIa in CH_2Cl_2: 1) before irradiation; 2) after irradiation for 10 sec; 3) after irradiation for 40 sec; 4) after irradiation for 120 sec; 5) after irradiation for 360 sec (λ_{irr} 546 nm).

hexachlorocyclopentadiene, which has electron-acceptor substituents, does not react with 4-phenylethynyl-substituted pyrylium salts under the same conditions.

The absorption bands of the pyrylium cation, which are overlapped with the absorption bands of aromatic double bonds at 1600-1620 and 1553-1580 cm^{-1}, and the absorption band of the ClO_4^- anion at 1090-1100 cm^{-1} are retained in the IR spectra of the synthesized II. In addition to a multiplet signal of 7-H bridge protons at 1.96-2.26 ppm, signals of the 5-H and 6-H olefinic protons of the norbornadiene residue at 6.58-6.90 ppm are present in the PMR spectrum of IIa.

The characteristic (for pyrylium salts) conversion to pyridine derivatives under the influence of ammonium acetate in acetic acid could be accomplished only for the 2,6-diphenyl-3-methyl-4-(2'-phenyl-3'-norbornadienyl)- and 2,6-di(p-methoxyphenyl)-4-(2'-phenyl-1',4',5',6',7'-pentamethyl-7'H-3'-norbornadienyl)pyrylium salts. The corresponding pyridines were not obtained from salts IIa,b, which are unsubstituted in the 3 and 5 positions of the pyrylium ring.

The electronic absorption spectra of II contain intense bands at 470-500 nm (Table 1), which is close to the maximum of solar radiation. Thus the long-wave shift of the absorption as compared with the most similarly constructed 2,3-dipyridinianorbornadienes [6] is 110-130 nm. The introduction of bulky methyl substituents into the 3 and 5 positions of the pyrylium cation leads to acoplanarization of the molecule and to a decrease in the conjugation between the pyrylium ring and the double bond of the norbornadiene fragment. The maximum of the long-wave absorption in IIa → IIIc → IIId experiences a small hypsochromic shift with a simultaneous decrease in intensity (Table 1). Its most intense long-wave bands are observed for 2,6-di(p-anisyl)-substituted IIb,e.



Irradiation of solutions of norbornadiene derivatives II in the region of the long-wave absorption maximum with the light of a mercury lamp (λ_{max} 546 nm) or with sunlight causes a fast photoreaction (Fig. 1), which is characterized by a decrease in the band at 500 nm, the development of a new band at 400 nm, and the presence of a distinct isobestic point. In the case of norbornadiene IIa the reddish color of a solution ($c = 2 \cdot 10^{-5}$ M in CH_2Cl_2) changes completely to light yellow after 2-3 min in diffuse light.

The quantum yield of the photoreaction decreases with the introduction of alkyl groups into the 3 and 5 positions of the pyrylium ring from 0.52 (IIa) to 0.11 (IIc) and 0.01 (IId).

Compounds Va, c formed after irradiation of norbornadienes IIa, c were isolated preparatively. According to the results of elementary analysis and IR, PMR, and mass-spectrometric data they are products of hydration of quadricyclane derivatives IVa, c, which proceeds with cleavage of the $C_{(3)}-C_{(5)}$ bond of the cyclopropane ring. This sort of transformation was described in [6] in the case of pyridinium derivatives of norbornadiene. The observed pattern of the UV spectra is characteristic for reactions of both the II → IV type and the II → V type; this is confirmed by the coincidence of the UV spectrum of photoproduct Va (Fig. 1) with the spectrum of the model 2,6-diphenyl-4-propylpyrylium perchlorate. An absorption band of a hydroxy group at 3400 cm^{-1} and a group of absorption bands of the pyrylium cation and the ClO_4^- anion (1663, 1608, 1520, 1100 cm^{-1}) are present in the IR spectrum of Va. Signals of olefinic protons in the 5 and 6 positions of the norbornadiene skeleton are absent in the PMR spectrum, and the overall integral area and the positions of the signals of the protons correspond to the selected structure. A peak of a cation with m/z 417, which is due to splitting out of perchloric acid from salt Va, is present in the mass spectrum of Va. The unsuccessful attempts at catalytic isomerization to norbornadiene II utilizing catalysts that are widely used for these purposes, viz., tetraporphyrincobalt(II), $SnCl_2$, and $PdCl_2$, can be explained by the formation of product V.

Thus 4-ethynyl-substituted pyrylium salts can be used for the synthesis of norbornadiene derivatives of pyrylium salts that absorb in the visible region of the spectrum; this distinguishes them extremely favorably with respect to their spectral characteristics from known systems [6] and makes promising the search in this direction for accumulators of light energy and photosensitive materials for recording optical information.

EXPERIMENTAL

The IR spectra of thin layers of suspensions of the compounds in mineral oil (NaCl prism) were recorded with a Specord IR-75 spectrometer. The PMR spectra were recorded with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The electronic absorption spectra of solutions in methylene chloride were obtained with a Specord UV-vis spectrophotometer. The molecular mass was determined with a Finnigan 4021 chromatographic mass spectrometer (70 eV).

The characteristics of IIa-d are presented in Table 1. The results of elementary analysis of II-V for C, H, and Cl were in agreement with the calculated values.

4-phenylethynylpyrylium perchlorates Ia-d were synthesized by the methods in [1, 7].

4-Norbornadienyl-Substituted Pyrylium Perchlorates IIa-d. A 7-8-fold excess of cyclopentadiene was added with stirring to a solution of 3 mmole of perchlorate Ia-d in 50 ml of absolute acetonitrile, and the mixture was refluxed for 30 min. The polymeric precipitate was separated, the mother liquor was evaporated, and the residue was triturated with a small amount of chloroform and recrystallized from acetonitrile. When perchlorates Ic, d were used in the reaction, the mixtures were refluxed for 1 h.

The reaction of 2,6-diaryl-4-phenylethynyl-substituted pyrylium perchlorates with cyclopentadiene could be carried out at room temperature (the reaction time increased to 20-25 h).

2,6-Di(p-methoxyphenyl)-4-(2'-phenyl-1',4',5',6',7'-pentamethyl-7'H-3-norbornadienyl)-pyrylium Perchlorate (IIe, $C_{37}H_{37}ClO_7$). A 0.5-ml (3 mmole) sample of pentamethylcyclopentadiene was added to a solution of 0.98 g (2 mmole) of perchlorate Ib in 35 ml of absolute acetonitrile, and the mixture was allowed to stand at 20°C for 18 h. It was then evaporated, and the orange precipitate was triturated with acetone to give 1.02 g (82%) of a product with mp 241-242°C (from acetonitrile). IR spectrum: 1620, 1600, 1560, 1513 (C=C), 1250, 1233 (C-O-C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (in CF_3COOH): 3.47 (6H, s, $2OCH_3$), 6.55-7.57 ppm (15H, m, Ar); (in nitrobenzene) with HMDS as the external standard: 0.46 (3H, d, 7'-CH_3), 0.60-1.67 (12H, m, $4CH_3$), 2.35 (1H, m, 7'-H), 3.43 ppm (6H, s, $2OCH_3$).

2,6-Diphenyl-3-methyl-4-(2'-phenyl-3'-norbornadienyl)pyridine (III, $C_{31}H_{25}N$). A tenfold excess of ammonium acetate was added to a solution of 0.51 g (1 mmole) of perchlorate IIc in 20 ml of acetic acid, and the mixture was refluxed for 3 h. It was then poured into water, and the product was extracted with benzene. The extract was evaporated, and the residue was purified by chromatography with a column (30 by 1.5 cm) packed with Al_2O_3 by elution with benzene. Removal of the solvent and recrystallization of the residue from ethanol-hexane (1:1) gave 0.22 g (54%) of the pyridine with mp 144-145°C and R_f 0.82 (Al_2O_3, benzene). IR spectrum: 1580, 1573, 1543 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 1.85-3.85 (7H, m, CH_3, 1-H, 4-H, 7-2H), 6.75-8.05 ppm (18H, m, 16H-Ar, 5-H, 6-H).

2,6-Di(p-methoxyphenyl)-4-(2'-phenyl-1',4',5',6',7'-pentamethyl-3'-norbornadienyl)pyridine (IIIa, $C_{37}H_{37}NO_2$). A tenfold excess of ammonium acetate was added to a solution of 0.44 g (0.7 mmole) of perchlorate IIe in 20 ml of acetic acid, and the mixture was refluxed for 30 min. The reaction product was isolated and purified as in the case of III to give 0.2 g (55%) of a product with mp 154°C (from propanol) and R_f 0.7 (Al_2O_3, benzene). IR spectrum: 1607, 1600, 1540, 1520 (C=C), 1255, 1240 cm^{-1} (C-O-C). PMR spectrum ($CDCl_3$: 1.12-2.1 (16H, m, $5CH_3$, 7-H). Found: M 527. Calculated: M 527.

2,6-Diphenyl-4-(2'-phenyltricyclo [2.2.1.0^{2,6}]heptan-5'-ol-3'-yl)pyrylium Perchlorate (Va, $C_{30}H_{25}ClO_6$) (mixture of isomers). A solution of 0.49 g (1 mmole) of perchlorate IIa in 500 ml of methylene chloride was irradiated for 10-15 min in a quartz photoreactor with a DRT-250 mercury lamp. The solvent was then removed by distillation in the vacuum created by a water aspirator, leaving 3-5 ml of solution. The residue was reprecipitated from absolute acetonitrile by means of absolute ether to give 0.44 g (86%) of Va in the form of a yellow-orange powder with mp 184°C. IR spectrum: 3400 (OH), 1633, 1608, 1520 (C=C), 1100 cm^{-1} (ClO_4^-). Found: $[M - HClO_4]^+$ 417. Calculated: $[M - HClO_4]^+$ 417.

2,6-Diphenyl-3-methyl-4-(2'-phenyltricyclo[2.2.1.0^{2,6}]-heptan-5'-ol-3'-yl)pyrylium Perchlorate (Vc) (mixture of isomers). This compound was isolated in the same way as Va. Workup gave a product with mp 209°C in 89% yield. IR spectrum: 3394 (OH), 1620, 1580, 1520 (C=C), 1100 cm^{-1} (ClO_4^-).

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