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SYNTHESIS OF 3,3-DIMETHYL-1-PHENYL-2-PHENYLETHYNYLCYCLOPROPENE - THE FIRST CONJUGATED ALKYNYLCYCLOPROPENE †

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Abstract. *The 1,3-cycloaddition reaction of 2-diazopropane with diphenyldiacetylene leads to the mixture of 3,3-dimethyl-5-phenyl-4-phenylethynyl-3H-pyrazole, 3,3-dimethyl-4-phenyl-5-phenylethynyl-3H-pyrazole, and 3,3,3',3'-tetramethyl-4',5-diphenyl-4,5'-bi-3H-pyrazolyl. Photolysis of both 3H-pyrazoles gives the title phenylethynylcyclopropene.*

1. INTRODUCTION

Derivatives of cyclopropene - the most strained carbomonocycle - attract the constant and growing attention of organic chemists[1-3]. The unique electronic structure of the unsaturated three-membered ring is interesting from the theoretical point of view; the synthetic value of cyclopropene derivatives is frequently determined by their high reactivity, the negative respect of which often displays itself as the relatively low stability. Undoubtedly, the unsaturated cyclopropene derivatives, including alkynylcyclopropenes with one more (except the three-membered ring) endothermic fragment, the triple bond, are of great theoretical and practical interest. In spite of the synthesis of a vast number of different vinylcyclopropenes, only a few derivatives of 3-methyl-3-ethynylcyclopropene have been obtained up to now[4,5], and to our knowledge the information on 1-alkynylcyclopropenes is absent in the literature at present. But in the course of our investigation of aminoaziridination of a variety of conjugated compounds, particularly conjugated enynes[6-8] and cyclopropene derivatives[9], we became interested in such objects and in this connection we now report on the synthesis of the first representative of conjugated alkynylcyclopropenes, 3,3-dimethyl-1-phenyl-2-phenylethynylcyclopropene **1**.

The choice for synthesis alkynylcyclopropene **1** with phenyl substituents at both ends of the conjugated system is determined by the desired stabilization of the potentially highly reactive strained unsaturated system. Two methyl groups also serve this purpose and moreover allow to avoid some side processes in the course of the synthesis.

† To the memory of RRB.

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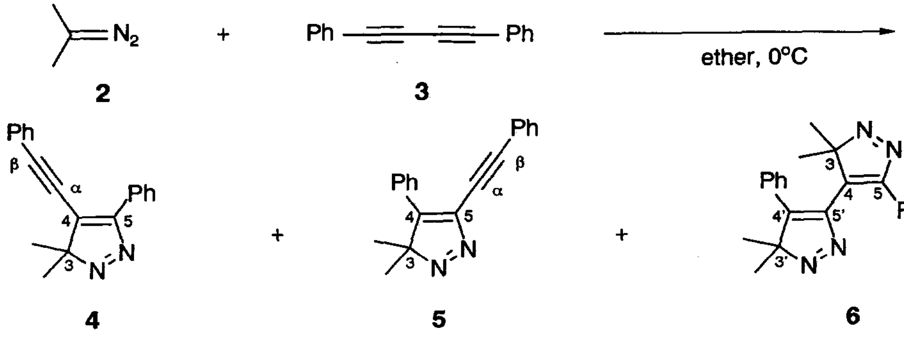
On the face of it, the reaction of carbenes or carbenoids with diacetylenes might be the straightest and the most natural way to conjugated alkynylcyclopropenes. But one must take into account that the reaction of carbenes with acetylenes rarely gives satisfactory results (the relatively successful syntheses of cyclopropenes by this way are summed up in the reviews[1,2]). Even such a convenient and synthetically useful reagent as dichlorocarbene reacts with C≡C bond with extreme reluctance[10] giving usually not the initially formed dichlorocyclopropenes but the products of their further transformations, mostly, cyclopropenones, and with low yields as a rule. That is why one is not surprised at the fact that in the unique work on dichlorocarbene (and generally carbenes) addition to diacetylenes only small amounts of cyclopropenone derivatives were isolated instead of alkynylcyclopropenes[11].

The construction of cyclopropene framework as a result of intramolecular cyclization of vinylcarbene[2,12] seemed to us to be the most promising of all other approaches. The source of the required vinylcarbenes might be the photolysis of the corresponding *3H*-pyrazoles, which, in their turn, in principle are directly accessible by the 1,3-dipolar cycloaddition of diazocompounds to diacetylenes. But in these cases the choice is limited to only disubstituted diazocompounds, because the addition of diazomethane and its monosubstituted derivatives to the C≡C bond leads to *3H*-pyrazoles with an active hydrogen in the position *3*; these pyrazoles immediately rearrange to the much more stable aromatic *1H*-pyrazoles[12,13], which are not suitable for vinylcarbene generation. 2-Diazopropane **2** and diphenyldiazomethane are most widely used for the syntheses of *3H*-pyrazoles. So long as the photolysis of 3,3-diphenyl-*3H*-pyrazoles is accompanied usually by indene formation[12,13], we chose 2-diazopropane **2**, all the more that its reactivity is usually higher than that of diphenyldiazomethane.

2. 1,3-DIPOLAR CYCLOADDITION OF 2-DIAZOPROPANE TO DIPHENYLDIACETYLENE

Thus, the first part of this work describes our results on the study of the reaction of 2-diazopropane **2** with diphenyldiacetylene **3**. To perform this reaction an ethereal solution of 2-diazopropane **2** (5-10-fold excess) is added to the cold ether solution of diphenyldiacetylene **3**. After 2 days at 0°C the reaction mixture contains at least four substances - the unreacted diphenylbutadiyne **3** and three products. The separation of this mixture by column chromatography on silica gives the starting diacetylene **3**, two regioisomeric *3H*-pyrazoles - the major component **4** and the minor one **5** - and a small amount of bi-*3H*-pyrazolyl **6**, which is formed during the addition of the diazocompound to both triple bonds.



The compounds **4** and **5** are light yellow, and the compound **6** - white prismatic crystals, all of them melting with decomposition. All three products can be stored at room temperature.

The composition of the compounds **4-6** is confirmed by the elemental analysis data; their structure is unambiguously proved by their spectra, first of all, by the ^{1}H and ^{13}C NMR spectra. Actually, according to the elemental analysis data, two 1:1 adducts - compounds **4** and **5** - are obtained as the result of the reaction. The same fragments reveal themselves in their ^{1}H and ^{13}C NMR spectra: there are the signals of two equivalent methyl groups, the complete sets of signals of two different phenyl rings. Besides that, in the ^{13}C NMR spectra of both 1:1 adducts, weak signals due to quaternary carbon atoms at 94-97 ppm, a pair acetylenic carbons and two sp^2-hybridized carbons, not attributed to aromatic rings, are present. It is easy to demonstrate that only the molecules of two regioisomeric *3H*-pyrazoles **4** and **5** can be put together using this fragments. The final structural assignments for each regioisomer are based upon the analysis of aromatic region of their ^{1}H NMR spectra. The basis of the assignments is the position of the most downfield doublet-like signals of the *ortho*-protons of the phenyl substituent in pyrazole ring (8.50 ppm for the adduct **4** and 7.94 ppm for the isomer **5**). A rather more complex multiplets of the *ortho*-protons of the phenylethynyl substituents are situated in the usual (*cf.*[6,7]) narrow region of δ 7.55-7.60 ppm for both isomers; there are no anomalies in the shielding of all *meta*- and *para*-protons, while the chemical shifts of the aromatic *ortho*-protons nearest to the pyrazole ring differ very much for the two regioisomeric products **4** and **5**.

We consider that the origin of this difference lies in the fact that in the molecule **5** the phenyl substituent at C^4 is situated between the phenylethynyl and two methyl groups and, owing to the strong steric interactions with its neighbours, must be twisted out of the plane of the pyrazole ring, thus resulting in its *ortho*-protons being placed in the shielding region of the π-system of the heterocycle. On the contrary, in the case of pyrazole **4**, the phenyl ring at C^5 is in the neighbourhood of the rod-like phenylethynyl substituent, which does not create any serious sterical hindrance (*cf.*[7,8]). Therefore, this phenyl group can stay in the conjugation with the pyrazole ring and its *ortho*-protons lie in the nodal plane of the π-system of the heterocycle, just in the region of deshielding. For the same reason in the compound **4** these phenyl protons turn out to be in the region of strong deshielding by the neighbouring C≡C bond, but in the twisted molecule **5** they are more remote from this triple bond. Finally, one must take into account the fact that in *3H*-pyrazole **4** the phenyl substituent is near to the electron-withdrawing azo-group N=N, but not the $C(CH_3)_2$ group, as in the case of isomer **5**.

In agreement with the considerations mentioned above, the structure of 3,3-dimethyl-5-phenyl-4-phenylethynyl-*3H*-pyrazole **4** was attributed to the major product of the reaction, which exhibits in its ^{1}H NMR spectrum a very downfield signal for *ortho*-protons, while the structure **5** was attributed to the second monoadduct. The interpretation of the ^{13}C NMR spectra of the adducts **4** and **5** is carried out on the basis of the common criteria such as the additive rules[14], literature analogies[7] and the spectrum of diphenylbutadiyne **3** (see Exp.). Besides that, for pyrazole **4** there was obtained the proton coupled ^{13}C NMR spectrum, which helps to make signal assignments for a great number of fully substituted carbon atoms; in particular, it allows to identify the signals of C^{α} (δ 81.8 ppm, singlet) and C^{β} (δ 108.9 ppm, triplet, ^3J 5.0 Hz) atoms of the ethynyl substituent, and also of the pyrazole carbons. It is necessary to mention that the deshielding of the outward carbon atoms of the enyne chain, especially the acetylenic carbon C^{β} in the compound **4**, is extremly high.

It is also interesting to note, that the chemical shifts of the pyrazole carbon atoms C^4 and C^5 is mainly determined by the neighbourhood of the phenyl or phenylethynyl substituent, but practically insensitive to the replacement of the $C(CH_3)_2$ moiety by the azo-group. But it is worth mentioning, that for example, in the series of monosubstituted benzenes, isopropyl- and *tert*-butyl- substituents on one hand, and Ph-N=N- group on the other , influence on the chemical shifts of aromatic carbons also similarly[14].

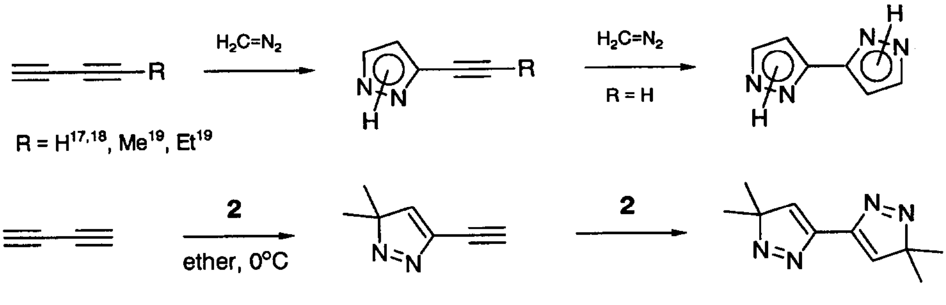
The intense bands of π-π^*-transitions in the UV spectra of compounds **4** and **5** have the maxima at 240-250 nm and 335-345 nm with a poorly marked shoulder at about 360-370 nm. The weak band of n-π^*-transition in the azo-group, common for *3H*-pyrazoles, is obviously hidden by the strong longwave band of the π-π^*-type, but may probably be detected as weak shoulder. The comparison of the spectra of both isomers shows that for more sterically strained *3H*-pyrazole **5** one can observe the hypsochromic shift of all bands by ~10 nm and some decrease of extinction. Both facts can be easily connected with the conjugation gap in the molecule **5** caused by the twisting of the phenyl ring out of the plane of the rest part of π-system. However, one must take into consideration that this distinction may be caused simply by the different topology of π-systems of these two isomers (the different connectivity of the azo-group and the 1,4-diphenylbutenyne moiety).

The structure of the isolated bis-adduct has also been deduced from its ^1H and ^{13}C NMR spectra, which proves it to be 3,3,3',3'-tetramethyl-4',5-diphenyl-4,5'-bi-*3H*-pyrazolyl **6**. First of all the signals of acetylenic carbons are not present in its ^{13}C NMR spectrum, but there are two additional signals for sp^2-hybridized carbons. This indicates that 2-diazopropane **2** adds to the both triple bonds of the starting diacetylene **3**, consequently the bis-adduct must have the structure of one of three isomeric bi-*3H*-pyrazolyls (two symmetric and one asymmetric). Meanwhile, there is a double set of signals in the ^1H and ^{13}C NMR spectra of this compound, so it is obvious that it has the unsymmetrical structure **6**. The proton coupled ^{13}C NMR spectrum of bis-adduct **6**, and also one with selective irradiation of methyl protons confirm the connectivity of the molecule and allow us to assign the signals of the sp^2-carbons of both pyrazole rings. As in the case of monoadducts **4** and **5**, one may note, that the shielding of this atoms is mainly influenced by the attached substituents, but not by their position in the *3H*-pyrazole ring.

The π-π^*-bands in the UV spectrum of bi-pyrazolyl **6** are shifted markedly to the shortwave region and are essentially less intense than that in the case of the adducts **4** and **5** and even of 3,3,5-triphenyl-*3H*-pyrazole (λ_{max} 236 nm (ε 32000), a shoulder at 300 nm (ε 4600)[15]) with formally much shorter chain of conjugation. Probably, it is a consequence of a drastic twisting of this molecule about the 4-5' bond because of steric reasons.

The addition of relatively inert diazocompound **2** to the unactivated triple bonds of diphenyldiacetylene **3** proceeds slowly, and a considerable amount of diacetylene **3** does not participate in this reaction even in the presence of large excess of 2-diazopropane **2**. Since both the starting diyne and the products of reaction do not contain groups sensitive to HgO or KOH, in repeated experiments we have used the simplified procedure which avoids the labourious work of obtaining a 2-diazopropane solution. This method includes the addition of excess acetone hydrazone to a stirred and cooled suspension of yellow mercury oxide in alkaline ethereal solution of diphenyldiacetylene **3**. When the noticeably exothermic reaction has ceased, the solution is left at 0°C till the crimson color vanishes, then the precipitate is filtered off and the filtrate is worked up in the usual way.

In both variants the 1,3-dipolar addition of 2-diazopropane **2** to diphenyldiacetylene **3** proceeds regioselectively and leads mainly to 3,3-dimethyl-5-phenyl-4-phenylethynyl-*3H*-pyrazole **4** and to only one of three possible bis-adducts. In few other works on the cycloaddition of diazoalkanes to diacetylenes one also observes a high regioselectivity of this reaction. Thus, the addition of diazomethane to the conjugated diynone system, which takes place only upon C≡C bond activated by the adjacent carbonyl group, leads mainly (or exclusively) to 3(5)-acyl-4-arylethynylpyrazoles[16] in full accordance with the Auwers rule. At the same time, the interaction of diazomethane with the parent diacetylene[17,18] and its monoalkyl derivatives* (in this case only terminal triple bond participates in a reaction)[19] and also the addition of 2-diazopropane **2** to diacetylene[20] results in 3(5)-alkynylpyrazoles only, which are able to add a second molecule of diazoalkane also fully regioselectively with the formation of 5,5'-bipyrazolyls[17,18,20].



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In our case, in the reaction of 2-diazopropane **2** with the diphenyldiacetylene **3** we observe reverse regioselectivity for the addition of the first molecule of the diazocompound with the preferential formation of 4-alkynyl-*3H*-pyrazole **4**. However, it seems possible that the outcome of both reactions with 2-diazopropane **2** can be explained by taking into account the influence of the steric factors (*cf.*[21]). Actually, in both cases we see the formation (preferentially or exclusively) these adducts, in which the bulky $C(CH_3)_2$ group is connected with the triple bond carbon carrying the less sterically demanding substituent (H < C≡CR < Ph < pyrazolyl). Thus, it is not surprising that the reaction of 2-diazopropane **2** with diphenyldiacetylene **3** leads mainly to 4-phenylethynylpyrazole **4**, while the same reaction with diacetylene results in the formation of 5-ethynylpyrazole **7**.

Obviously bi-*3H*-pyrazolyl **6** is obtained as a result of addition of the second molecule of 2-diazopropane **2** to the major 1:1 adduct **4**, and this reaction also proceeds *via* the sterically more favourable way (as also bis-adduct **8** formation). This possibility has been proved by obtaining of bi-pyrazolyl **6** directly from the reaction of *3H*-pyrazole **4** with large excess of 2-diazopropane **2** in good yield.

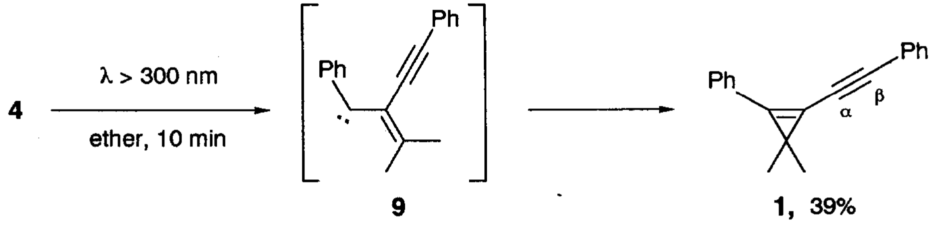
* It is interesting to note, that an attempt to add diazomethane to diphenyldiacetylene **3** met no success. According to authors[18] the mixing of reagents leads to a rapid decomposition of diazomethane accompanied by the evolution of nitrogen and the formation of polymethylene compounds. Unchanged diphenyldiacetylene is recovered quantitatively.

To complete the comparison of our data with Franck-Neumann results[20], one may note the higher reactivity of the simplest diacetylene compared with its diphenyl derivative. Similar yields of the cycloadducts are obtained with only 50-100% excess of 2-diazopropane **2** in the reaction with the parent diacetylene.

3. PHOTOLYSIS OF 3H-PYRAZOLES

The first photolytical conversion of 3,3,5-trimethyl-*3H*-pyrazole into cyclopropene was carried out in 1961[22], and since that time this method has been used for obtaining various cyclopropenes[1,2,12,13], but not alkynylsubstituted ones. For example, Franck-Neumann has reported that the photolysis of 3,3-dimethyl-5-ethynyl-*3H*-pyrazole **7** in CH_2Cl_2 or ether gives only the mixture of unstable compounds and their separation was unsuccessful[20]. According to spectral data, the reaction products contain isobutylenic fragment, ethynyl group, but no cyclopropene moiety. The corresponding ethynylcyclopropenes have also not been detected among the products of photolysis of the ethynylsubstituted analogs (≡C-Br, $-CH_3$, $-COOCH_3$) of compound **7**[23].

Thus, in the light of these facts, the possibility to obtain the ethynylcyclopropene **1** by the photolysis of *3H*-pyrazole **4** or **5** seemed to be doubtful, all the more that in the first experiments, when photolysis of the compound **4** was carried out in CH_2Cl_2 in quartz reaction vessel, we observed only rapid formation of tar. However the change of reaction condition (filter, solvent) allowed us to isolate the desired 3,3-dimethyl-1-phenyl-2-phenylethynylcyclopropene **1** with satisfactory yield.



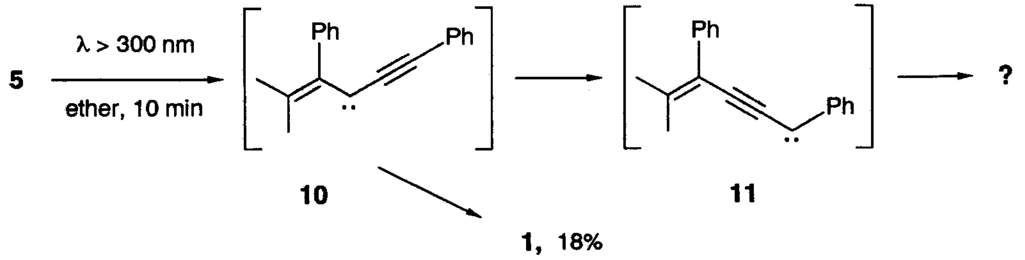
The initially white, slightly oily crystals of cyclopropene **1** rapidly turn yellow in air at room temperature and melt with decomposition. A dark resinous precipitate starts to fall out from a $CDCl_3$ solution after several days. At temperatures below 0°C, ethynylcyclopropene **1** can be stored at least for several weeks without visible changes.

The composition of ethynylcyclopropene **1** is confirmed by the elemental analysis, its molecular mass - by the presence of the intense peak of molecular ion at *m/z* 244 in its mass-spectrum. The structure of this compound is established by combined spectral data. The most valid information is provided by the ^{13}C NMR spectra obtained with full and selective ^1H decoupling and also without decoupling. Such spectral combination allows to pick up two sets of signals for two phenyl groups, peaks of the quaternary cyclopropene carbon C^3 (δ 25.6 ppm) and of two equivalent methyl groups (δ 25.3 ppm). Besides that, there are signals of sp^2-carbons of cyclopropene ring at δ 132.8 and 108.3 ppm (*cf.*[5,24]) and also of acetylenic carbons at δ 79.7 and 104.2 ppm (we note once more the extremely downfield signal of the acetylenic carbon at the end of the butenyne fragment). Thus, there are two phenyl rings, sp^3-hybridized quaternary carbon atom, two equivalent methyl groups and fully substituted C=C and C≡C bonds. Considering the mass-spectroscopic and elemental analysis data and using this "blocks" one cannot assemble any molecule other than **1**.

The ^{1}H NMR and mass-spectra of **1** are in accordance with the proposed structure. In the mass-spectrum one can mark (except the molecular ion peak) the most intensive peak at *m/z* 229 (M-15), which indicates the loss of a methyl group and the formation of the stable aromatic cyclopropenyl cation, and a peak at *m/z* 202, which obviously corresponds to the cation-radical of diphenyldiacetylene. This fragmentation pattern of the molecular ion $\mathbf{1}^{+\cdot}$ with the loss of $C(CH_3)_2$ is the so called "retrocarbenic" fragmentation, which is typical for cyclopropenes.

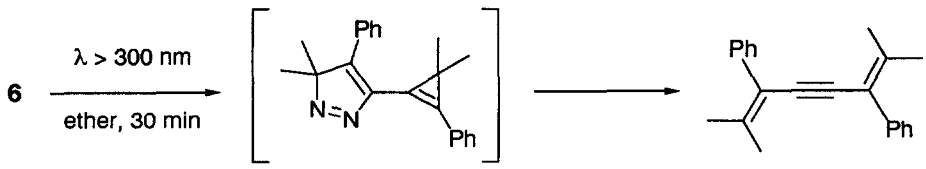
The considerable conjugation in the 1,4-diphenylbutenyne chain reveals itself in the Raman spectrum of cyclopropene **1** with a certain decrease in the frequencies of the very strong bands of valence vibrations ν(C≡C) (2188 cm^{-1} *vs.* 2230-2235 cm^{-1} for other enynes with the disubstituted triple bond[25]) and cyclopropene C=C bond (1797 cm^{-1}; *cf.* 1840 cm^{-1} for methyl 2,3-diphenyl-2-cyclopropene-1-carboxylate[26]). The UV spectrum of ethynylcyclopropene **1** contains intensive bands due to the π–π*-transitions at 234 nm (ε 19800), 332 nm (ε 27500) and 354 nm (ε 20000). One can consider the two last maxima as an indication of a fine vibrational structure of the longwave band at 332 nm with Δν ~2000 cm^{-1}, which is in a good agreement with ν(C≡C) in Raman spectrum. The comparison of UV spectra of compound **1** and *E*-1,4-diphenylbutenyne (λ_{max} 223 nm (ε 17000) and 312 nm (ε 39000)[27]), which formally has the same π-system, demonstrates that the passing from the unstrained disubstituted C=C bond with *trans*-configuration to the strongly distorted tetrasubstituted one in the cyclopropene **1** (with *cis*-configuration of the conjugated π-system) causes a significant bathochromic shift in both absorption maxima and a marked decrease in intensity of the longwave band.

Using the mechanism commonly accepted for the photolysis of *3H*-pyrazoles[12,13,23], one may suppose that the photolytic decomposition of 4-phenylethynyl-*3H*-pyrazole **4** into phenylethynylcyclopropene **1** proceeds *via* singlet vinylcarbene **9** and its following cyclization. The photolysis of the regioisomeric 5-phenylethynyl-*3H*-pyrazole **5** must proceed *via* another vinylcarbene **10**, which, unlike intermediate **9**, in principle, is able to undergo the so-called propargylene-propargylenic rearrangement[20,23] into carbene **11**, which is unable to cyclize into cyclopropene.



In agreement with this, in the photolysis of *3H*-pyrazole **5**, alkynylcyclopropene **1** is isolated from the complex reaction mixture with a rather low yield. Since Franck-Neumann earlier[20,23] subjected only 5-ethynyl-*3H*-pyrazole derivatives to photolysis, it is possible that the lack of alkynylcyclopropene in the reaction products is caused by the rapid propargylene-propargylenic rearrangement of intermediate vinylcarbene. In this connection one may note, that the trapping of intermediate carbenes with furan[20], cyclopentadiene or vinyl ether[23] gives as a rule the main products which correspond to the addition of not the "starting" vinylcarbene but rearranged alkynylcarbene upon C=C bond.

We have also studied the photolysis of bis-adduct **6** in the hope to obtain the conjugated 1,1'-bicyclopropene system (*cf.*[28]). But the maximum of absorbance for the compound **6** lies in much more shortwave region than for the *3H*-pyrazoles **4** and **5**, and it is very likely that due to this fact its photolysis slows down strongly. In spite of the increasing of the photolysis time up to 30 min, a part of the starting compound (~20%) is recovered from the reaction. At the same time, according to TLC, a complex mixture of products is obtained as a result of the photolysis, and we were able to isolate only one individual component from it. A structure of 2,7-dimethyl-3,6-diphenyl-2,6-octadien-4-yne **12** was attributed to this product on the basis of its ^1H and ^{13}C NMR spectra and also mass-spectrum.



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The analogous compound - 2,7-dimethyl-2,6-octadien-4-yne - was obtained by Franck-Neumann in the course of the photolysis of bi-*3H*-pyrazolyl **8**[20]. However, it is curious that, unlike the latter reaction, in our case the dienyne **12** cannot arise from the bi-pyrazolyl **6** directly as a result of the elimination of nitrogen (2 moles), but forms obviously in the course of the closure and then the opening of at least one three-membered ring.

EXPERIMENTAL

The elemental analyses are performed on the C,H,N-analyser Hewlett-Packard 185B. The ^1H NMR spectra are obtained on the Bruker AC-200 (200 MHz) and WM-400 (400 MHz) and Varian XL-500 (500 MHz) spectrometers in $CDCl_3$ solutions and are referenced to internal HMDS (δ 0.05 ppm) or residual $CHCl_3$ resonance (δ 7.25 ppm). The ^{13}C NMR spectra are recorded for $CDCl_3$ solutions on the AC-200 instrument (50.3 MHz) with TMS or $CDCl_3$ (triplet 76.90 ppm) as internal standard. UV spectra are obtained on the Specord M-40 spectrophotometer in hexane solutions, Raman spectrum of compound **1** in an interval 1500-2400 cm^{-1} - on Spex Scamp instrument with green Ar laser (514.5 nm) excitation. Mass-spectra (EI) are recorded at 70 eV on the chromato-mass-spectrometer LKB-2091.

The preparative separations were performed by column chromatography on silica (40/100 μm, Chemapol) with eluents of different polarity. The composition of the reaction mixtures and of the fractions obtained during separation, and also the purity of the substances were controlled by TLC on the Silufol UV 254 plates (eluent hexan-ether 3:1). A burner from the high-pressure lamp DRL-252 with pyrex filter (λ>300 nm) was used as a source of UV light for photolysis.

The solution of 2-diazopropane **2** in ether was obtained by oxidation of the acetone hydrazone with yellow mercury oxide[29]. 1,4-Diphenylbutadiyne **3** was synthesized by the oxidation of phenylacetylene[30]. M.p. 87°C; ^{1}H NMR (200 MHz): 7.25-7.34 (m, 6H, H^m and H^p), 7.49 (distort. dm, 4H, H^o, ^3J ~8 Hz); ^{13}C NMR: 73.82 ($C^{2,3}$, s*), 81.43 ($C^{1,4}$, t, ^3J 5.4 Hz), 121.59 (C^i, t*), 128.08 (C^m, dd), 129.05 (C^p, dt), 132.32 (C^o, dt). Lit.: m.p. 87-88°C[30]; ^{1}H NMR: 7.34 (d, H^o, ^3J 7.9 Hz)[31]; ^{13}C NMR: 74.9 and 82.2 ($C^{1,4}$ and $C^{2,3}$)[31].

The reaction of diphenyldiacetylene 3 with 2-diazopropane 2. Method A. An ether solution of 2-diazopropane **2**, obtained from 15 g (208 mmol) of the acetone hydrazone, was added to the solution of 7.2 g (36 mmol) of diphenyldiacetylene **3** in 50 ml of ether, and the mixture was left at 0°C until the crimson color vanished (it took about 2 days). The ether was evaporated *in vacuo*, and the yellow oily residue was put on the top of the column packed with 70 g of SiO_2. The unreacted diphenyldiacetylene (4.5 g, 62.5%) was eluted by pentane, and the products by pentane-ether 4:1. After the removal of the solvent the substances were recrystallized from the ethanol-water 1:1. There was obtained 2.23 g (23%) of 3,3-dimethyl-5-phenyl-4-phenylethynyl-*3H*-pyrazole **4**, 0.56 g (5.7%) of 3,3-dimethyl-4-phenyl-5-phenylethynyl-*3H*-pyrazole **5**, and 0.14 g (1.2%) of 3,3,3',3'-tetramethyl-4',5-diphenyl-4,5'-bi-*3H*-pyrazolyl **6**. Taking into account the return of the started diphenyldiacetylene **3**, the yields of the compounds **4-6** are 61, 15 and 3% respectively.

3,3-Dimethyl-5-phenyl-4-phenylethynyl-3H-pyrazol 4. M.p. 71-73°C, R_f 0.51. UV: 249 (22500), 346 (15200), ~370 sh (~10000). ^{1}H NMR (400 MHz): 1.59 (s, 6H, CH_3), 7.39-7.43 (m, 3H, 4-Ph, H^m and H^p), 7.44 (tt, 1H, 5-Ph, H^p, ^3J 7.5 Hz, ^4J 1.3 Hz), 7.52 (tm, 2H, 5-Ph, H^m, ^3J 7.7 Hz), 7.54-7.59 (m, 2H, 4-Ph, H^o), 8.50 (dm, 2H, 5-Ph, H^o, ^3J 7.2 Hz). ^{13}C NMR: 21.28 (CH_3, qq, ^1J 137.4 Hz, ^3J 4.4 Hz), 81.81 (C^α, s) 97.27 (C^3, septet, ^2J 4.2 Hz), 108.92 (C^β, t, ^3J 5.0 Hz), 122.4 (4-Ph, C^i, t), 127.44 (5-Ph, C^o, dt), 128.39 and 128.50 (C^m, dd), 129.23 (C^p, dt), 130.84 (5-Ph, C^i), 131.44 (4-Ph, C^o, dt), 134.07 (C^4, br.s), 151.99 (C^5, t, ^3J 3.5 Hz). The *para*-carbon atoms of both phenyl rings give the common signal with δ 129.23 ppm. The weak *ipso*-carbon signal at 130.84 ppm in the spectrum without decoupling is hidden by the half of the multiplet of C^o at 131.44 ppm. Found: C, 83.89; H, 5.98; N, 10.35%. $C_{19}H_{16}N_2$ requires C, 83.82; H, 5.88; N, 10.29%.

3,3-Dimethyl-4-phenyl-5-phenylethynyl-3H-pyrazol 5. M.p. 87-88°C, R_f 0.38. UV: 239 (20200), 334 (16400), ~362 sh (~6300). ^{1}H NMR (200 MHz): 1.63 (s, 6H, CH_3), 7.35-7.55 (m, 6H, H^m and H^p), 7.59 (m, 2H, 5-Ph, H^o), 7.94 (dm, 2H, 4-Ph, H^o, ^3J 8.0 Hz). ^{13}C NMR: 21.80 (CH_3), 82.84 (C^α), 94.09 (C^3), 96.14 (C^β), 122.12 (5-Ph, C^i), 127.93 (4-Ph, C^o), 128.38 and 128.73 (C^m), 129.05 and 129.83 (C^p), 130.05 (4-Ph, C^i), 131.75 (5-Ph, C^o), 134.4 (C^5), 156.43 (C^4). Found: C, 83.94; H, 5.90; N, 9.87%. $C_{19}H_{16}N_2$ requires C, 83.82; H, 5.88; N, 10.29%.

* In brackets are given the multiplicities of the signals and the values of the coupling constants $J(^{13}C\text{-}H)$ in the proton coupled spectra. As a rule, in phenyl nuclei the ^1J values are 160-165 Hz, ^2J < 1 Hz, ^3J 6-8 Hz, this trivial values are not given.

3,3,3',3'-Tetramethyl-4',5-diphenyl-4,5'-bi-3H-pyrazolyl 6. M.p. 166-168°C, R_f 0.11. UV: 229 (11300), 296 (11800), ~365 sh (~2200). ^1H NMR (400 MHz): 1.53 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 6.73 (dm, 2H, 4'-Ph, H^o, ^3J ~8 Hz), 7.07 (tm, 2H, 4'-Ph, H^m, ^3J 7.5 Hz), 7.15 (tt, 1H, 4'-Ph, H^p, ^3J 7.5 Hz), 7.22-7.30 (m, 3H, 5-Ph, H^m and H^p), 7.50 (dm, 2H, 5-Ph, H^o, ^3J 7.5 Hz). The signal assignments for H^m and H^p are confirmed by the double-resonance experiments with irradiation of doublets H^o at δ 6.73 and 7.50 ppm. ^{13}C NMR: 20.55 and 21.01 (CH_3, qq), 95.74 and 97.61 (C^3 and $C^{3'}$, septets, ^2J ~4.2 Hz), 126.81 and 128.02 (C^o and $C^{o'}$, dt), 128.31 (C^m and $C^{m'}$, dd) 128.63 and 128.84 (C^p and $C^{p'}$, dt), 130.90 and 131.05 (C^i and $C^{i'}$, t), 142.67 (C^4, br. m), 143.83 ($C^{5'}$, s), 153.13 (C^5, t, ^3J 3.5 Hz), 156.82 ($C^{4'}$, m). In the ^{13}C NMR spectrum, obtained with selective irradiation of the methyl protons, the signals at δ 95.74, 97.61 and 142.67 ppm collapse into singlets, and the multiplet at 156.82 ppm - into a triplet. Found: C, 77.36; H, 6.55; N, 16.43%. $C_{22}H_{22}N_4$ requires C, 77.16; H, 6.48; N, 16.36%.

In an another run same quantity of 2-diazopropane **2** reacted with 3 g (15 mmol) of diphenyldiacetylene **3**. The recovery of the diyne **3** was 1.06 g (35%). There were obtained 1.93 g (74% on the consumed diacetylene) of *3H*-pyrazole **4** and 0.03 g (1.2%) of its isomer **5**. The bis-adduct **6** was not isolated from this reaction mixture.

Method B. Forty grams (185 mmol) of yellow mercury oxide, 7.5 g (37 mmol) of diphenyldiacetylene **3**, 200 ml of ether and 4.5 ml of 3M KOH solution in methanol were placed into a 250 ml round-bottom flask fitted with a pressure-equalizing dropping funnel. Acetone hydrazone (5.4 g, 74 mmol) was added dropwise with intensive stirring and cooling at such a rate, that ether boiled gently. The reaction mixture was stirred for additional 2 hours and was left at 0°C until the crimson colour completely vanished (it took about 2 days). The precipitate was filtered off and the solution was washed with water to remove the unreacted hydrazone, dried over $CaCl_2$ and worked up in the usual way. There were isolated: 3.27 g (44%) of starting diacetylene **3**, 4.3 g (76%) of 4-phenylethynyl-*3H*-pyrazole **4**, 0.1 g (2%) of 5-phenylethynyl-*3H*-pyrazole **5** and 0.55 g (8%) of bi-pyrazolyl **6** (the yields of **4-6** are calculated on the consumed diphenyldiacetylene).

Carring out this reaction according to method **B** with 20-fold excesse of acetone hydrazone (14.5 g (201 mmol) of hydrazone and 2.06 g (10.2 mmol) of diphenyldiacetylene **3**) resulted in the isolation of 0.7 g (34%) of diacetylene **3** followed by 0.45 g (25%) of *3H*-pyrazole **4**, 0.19 g (11%) of its isomer **5** and 1.33 g (58%) of bis-adduct **6**.

The reaction of 3,3-dimethyl-5-phenyl-4-phenylethynyl-3H-pyrazole 4 with 2-diazopropane 2 was carried out according to method **B**. 87 mg (0.3 mmol) of pyrazole **4** were dissolved in 100 ml of ether, and to this solution there were added the following reagents: 20 g (90 mmol) of yellow mercury oxide, 3 ml of 3M KOH solution in methanol, and then 3 g (42 mmol) of acetone hydrazone. When the addition of hydrazone was completed, and the exothermic reaction has ceased, the solution was filtered from the precipitate and left at 0°C until its colour vanished. In such a way 69 mg (67%) of bi-pyrazolyl **6** were obtained. It was identical to the previously obtained samples according to m.p., R_f and ^1H and ^{13}C NMR spectra.

The general procedure of photolysis of 3H-pyrazoles 4-6. The solution of *3H*-pyrazole (1-3 mmol) in 120 ml of absolute ether was placed into reactor. The inert gas was bubbled through the solution for 20 min, and then it was irradiated for 10 min on cooling with a running water (5-12°C). The course of the reaction was controlled by TLC. Ether was evaporated *in vacuo*, and the residue was separated on 70 g SiO_2.

Photolysis of 3,3-dimethyl-5-phenyl-4-phenylethynyl-3H-pyrazole 4. From 456 mg (1.7 mmol) of pyrazole 4, 163 mg (39%) of **3,3-dimethyl-1-phenyl-2-phenylethynylcyclopropene 1** was obtained. M.p. 56-58°C, after recrystallization from pentane at -20°C or from methanol m.p. 63-63.5°C; R_f 0.86. UV: 234 (19800), 332 (27500), 354 (20000). Raman: 2188 (vs, C≡C), 1797 (vs, C=C), 1596 (s, Ph). ^{1}H NMR (500 MHz): 1.45 (s, 6H, CH_3), 7.33 (tt, 1H, 1-Ph, H^p, ^3J 7.5 Hz, ^4J ~1.3 Hz), 7.34-7.38 (m, 3H, 2-Ph, H^m and H^p), 7.42 (tm, 2H, 1-Ph, H^m, ^3J 7.4 Hz), 7.54 (m, 2H, 2-Ph, H^o), 7.56 (dt, 2H, 1-Ph, H^o, ^3J ~8 Hz). ^{13}C NMR: 25.25 (CH_3, qq), 25.55 (C^3, septet), 79.68 (C^α, s), 104.25 (C^β, t, ^3J 5.8 Hz), 108.32 (C^2, septet, ^3J ~4.8 Hz), 123.26 (2-Ph, C^i, m), 128.23 and 128.58 (C^m, dd), 128.37 and 128.78 (C^p, dt), 128.87 (1-Ph, C^i, t), 128.90 (1-Ph, C^o, dt), 131.44 (2-Ph, C^o, dt), 132.77 (C^1, m). The weak signal at δ 128.87 ppm is seen only in the proton coupled spectrum. Selective irradiation of CH_3 protons turns the C^2 signal to a singlet and C^1 - to a triplet. MS, *m/z (I,%)*: 245 (16), 244 (68, $M^{+\cdot}$), 243(42), 230(30), 229 (100, M-CH_3), 228 (87), 227 (35), 226 (42), 215 (19), 203 (10), 202 (34, M-$C(CH_3)_2$), 200 (15), 189 (15), 167 (16), 165 (31), 152(18), 151 (13), 150 (11), 129 (11),128 (16), 127 (15), 126 (10), 115 (27), 114 (22), 113 (15), 101 (17), 91 (15), 77(25), 63 (11), 51 (18). Found: C, 93.28; H, 6.62%. $C_{19}H_{16}$ requires C, 93.40; H, 6.60%.

Photolysis of 3,3-dimethyl-4-phenyl-5-phenylethynyl-3H-pyrazole 5. There were obtained 40 mg (18%) of cyclopropene 1 with m.p. 56-57°C as a result of the photolysis of 245 mg (0.9 mmol) of pyrazole 5. This sample of cyclopropene 1 was identical to the previously synthesized one according to m.p, R_f and ^{1}H NMR spectrum.

Bi-3H-pyrazolyl 6 photolysis. A complex mixture of compounds was obtained as a result of the 30 min photolysis of 1.05 g (3.1 mmol) of bis-adduct 6. The separation of this mixture gives 200 mg (19%) of starting compound and 60 mg (7%) of a white crystalline solid. The structure of **2,7-dimethyl-3,6-diphenyl-2,6-octadien-4-yne 12** was attributed to it on the basis of its ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (200 MHz): 1.83 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 7.17-7.34 (m, 10H, C_6H_5). ^{13}C NMR: 21.43 and 23.98 (CH_3), 93.28 ($C^{4,5}$), 119.52 ($C^{3,6}$), 126.42 (C^p), 127.77 (C^m), 129.04 (C^o), 139.63 ($C^{2,7}$), 141.34 (C^i). MS, *m/z (I,%)*: 287 (19), 286 (80, $M^{+\cdot}$), 271 (31), 256 (24), 221 (30), 207 (36), 165 (28), 147 (32), 131(39), 129 (44), 128 (36), 115 (52), 105 (42), 91 (100), 77 (50). As it has been reported earlier, the dienyne **12** with m.p. 87-88.5°C has a very similar ^{1}H NMR spectrum[32], but a markedly different mass-spectrum[33].

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