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# REACTION OF AZOLONES WITH ACETYLENE

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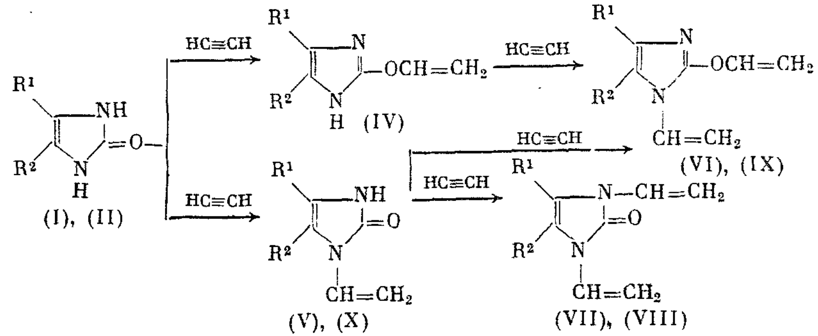
UDC 542.97:547.785.5:547.783:547.779:547.314.2

An investigation of the reaction of benzimidazole-2-, 4,5-diphenylimidazole-2-, and 1,2,4-triazole-3-thiones with acetylene in the presence of KOH showed that regardless of the structure of the starting azole the reaction occurred primarily at the more nucleophilic sulfur atom. The use of copper monochloride as a catalyst led to addition of acetylene at a second center, the nitrogen atom [1-4].

In the present paper, we used 4,5-diphenylimidazol-2-one (I) and benzimidazol-2-one (II) and also indazol-3-one (III) in the reaction with acetylene. Under the conditions of [1-4], azolones (I)-(III) do not react with acetylene, or they form vinyl derivatives in significant amounts. When the reaction temperature was increased to 240°C, it was possible, in the presence of KOH, to obtain the N,N-divinyl derivative of azolone (I) in 36% yield and the $N^2$,O-divinyl derivative of azolone (III) in 10% yield. In the presence of CuCl, the azolones do not react with acetylene.

It was determined that the most efficient catalyst for the vinylation of azolones is $Cd(OAc)_2$. Apparently, because of the comparable activity of both nucleophilic centers (N, O) in cyclic amides (I)-(III), we were unable to direct the reaction toward the formation of only the monovinyl product. In almost all cases, we observed exhaustive vinylation at the two reaction centers. However, in the reaction of azolone (I) with acetylene, we were able to recover all the possible mono- and divinyl derivatives.

Previously only azolone (VIII) was obtained by the reaction of (II) with acetylene under the conditions of alkaline catalysis [5]. We determined that in the presence of $Cd(OAc)_2$



$R^1 = R^2 =$ Ph(I), (IV)—(VII); $R^1 + R^2 =$ CH=CH—CH=CH(II), (VIII)—(X).

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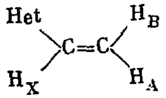
TABLE 1. Vinyl Derivatives of Azolones

| Compound | Bp, °C (p, torr) mp, °C | Found, % |  |  | Empirical formula | Calc., % |  |  | Yield, % | IR spec. ν, cm$^{-1}$ |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | C | H | N |  | C | H | N |  | OCH=CH$_2$ | NCH=CH$_2$ | C=O |
| (IV) | 130–131 | 77,6 | 5,6 | 10,8 | $C_{17}H_{14}N_2O$ | 77,8 | 5,4 | 10,7 | 29 | 1631 | – | – |
| (V) | 227–228 | 78,2 | 5,3 | 11,1 | $C_{17}H_{14}N_2O$ | 77,8 | 5,4 | 10,7 | 14 | – | 1625 | 1690 |
| (VI) | 194–200(2) | 78,6 | 5,9 | 9,2 | $C_{19}H_{16}N_2O$ | 79,1 | 5,6 | 9,7 | 39 | 1659 | 1622 | – |
| (VII) | 121–122 | 79,3 | 5,5 | 10,0 | $C_{19}H_{16}N_2O$ | 79,1 | 5,6 | 9,7 | 36 | – | 1615 | 1690 |
| (VIII) | 149–150(2) | 71,1 | 5,4 | 14,9 | $C_{11}H_{10}N_2O$ | 71,0 | 5,4 | 15,0 | 34 | – | 1634 | 1720 |
| (IX) | 105–106(2) | 71,2 | 5,5 | 15,0 | $C_{11}H_{10}N_2O$ | 71,0 | 5,4 | 15,0 | 20 | 1615 | 1640 | – |
| (X) | 152–153 | 67,4 | 5,0 | 17,6 | $C_9H_8N_2O$ | 67,4 | 5,0 | 17,5 | 5 | – | 1640 | 1720 |
| (XII) | 111–112(1) | 71,0 | 5,5 | 14,9 | $C_{11}H_{10}N_2O$ | 71,0 | 5,4 | 15,0 | 69 | 1634 | 1622 | – |

TABLE 2. Parameters of Proton NMR Spectra

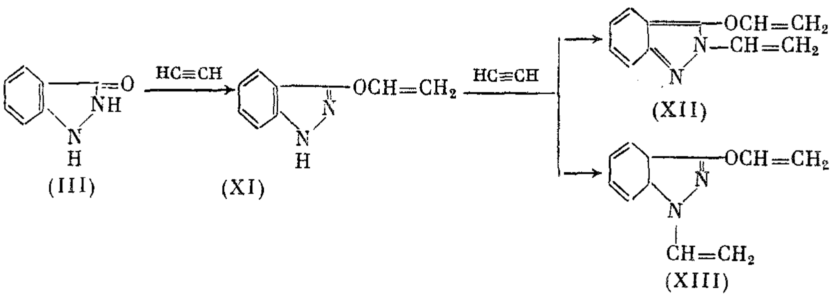


| Compound | Position of vinyl group | δ, ppm |  |  | J, Hz |  |  |
|---|---|---|---|---|---|---|---|
|  |  | H$_A$ | H$_B$ | H$_X$ | $J_{AB}$ | $J_{AX}$ | $J_{BX}$ |
| (IV) | O | 4,46 | 4,82 | 7,27 | −2,0 | 6,1 | 13,8 |
| (V) | N$^1$ | 4,73 | 5,56 | 6,43 | 0 | 9,7 | 16,0 |
| (VI) | N$^1$<br>O | 4,83<br>4,61 | 5,26<br>4,98 | 6,43<br>7,48 | −0,7<br>−2,0 | 9,5<br>6,1 | 16,2<br>13,8 |
| (VII) | N$^1$<br>N$^3$ | 4,73 | 5,54 | 6,46 | 0 | 9,5 | 16,2 |
| (VIII) | N$^1$<br>N$^3$ | 5,03 | 5,63 | 6,97 | −0,9 | 9,7 | 16,3 |
| (IX) | N$^1$<br>O | 5,08<br>4,72 | 5,56<br>5,08 | 7,03<br>7,47 | −1,2<br>−2,3 | 9,4<br>6,1 | 16,1<br>13,7 |
| (X) | N$^1$ | 4,97 | 5,53 | 7,00 | −0,8 | 9,7 | 16,3 |
| (XI) | O | 4,54 | 4,96 | 7,29 | −1,9 | 6,1 | 13,9 |
| (XII) | N$^2$<br>O | 5,12<br>4,55 | 6,06<br>4,77 | 7,20<br>6,84 | −0,7<br>−2,9 | 8,9<br>6,1 | 15,6<br>13,7 |
| (XIII) | N$^1$<br>O | 4,70<br>4,59 | 5,46<br>5,01 | 7,16<br>7,41 | −0,5<br>−1,9 | 9,1<br>6,1 | 15,4<br>13,9 |

at 230°C a mixture of divinyl derivatives of (VIII) and (IX) was formed with predominance of (VIII). When the reaction temperature was increased, the proportion of compound (IX) increased somewhat. The addition product of one molecule of acetylene (X) was recovered in a small amount.

The reaction of indazolone (III) with acetylene in the presence of CdO gave a product which, according to the data of [6], was 1-vinyl-3-hydroxyindazole. However, according to our data, this product was 3-(vinyloxy)indazole (XI) because the region of the proton NMR spectrum at 4.55-5.05 ppm assigned by Shatalov et al. [6] to AB protons of the vinyl group at the nitrogen atom characterizes, in fact, the corresponding protons of the vinyloxy group, which was shown in a systematic study of the proton NMR spectra of vinyloxy derivatives of nitrogen-containing heterocycles [7].

In the reaction with acetylene in the presence of $Cd(OAc)_2$, indazolone (III) formed 2-vinyl-3-(vinyloxy)indazole (XII) as the main product. Other acetylene-addition products (XI) and (XIII) were found in the reaction mixture in a small amount (their presence was recorded by proton NMR). Compound (XI), formed as an intermediate, added a second acetylene molecule primarily at the N$^2$ atom, which was possible due to the electron-acceptor effect of the adjacent vinyloxy group.



The properties of the obtained compounds are given in Tables 1 and 2.

The position of the vinyl group in the synthesized compounds was determined by proton NMR. In compounds (V), (VII), (VIII), and (X) the vicinal spin–spin coupling constants $^3J_{AX}$ and $^3J_{BX}$ for the vinyl group are 9.5-9.7 and 16.0-16.3 Hz, respectively (Table 2). Such values correspond to the N-vinyl group. In compounds (IV) and (XI) the values of $^3J_{AX}$ (6.1 Hz) and $^3J_{BX}$ (13.8-13.9 Hz) indicate the presence of a vinyloxy group [7]. Compounds (VI), (IX), (XII), and (XIII) have two nonequivalent vinyl groups, in which the spin–spin coupling constants are 8.9-9.5 or 6.1 Hz ($^3J_{AX}$) and 15.4-16.2 or 13.7-13.9 Hz ($^3J_{BX}$).

## EXPERIMENTAL

The proton NMR spectra were recorded on a Tesla BS-497 spectrometer (100 MHz), the solvent was $CDCl_3$, and the internal standard was HMDS. The concentration of the samples was 5%, and the recording was carried out at ~20°C. The IR spectra were recorded on a Specord IR-75 spectrophotometer in a thin layer or in tablets with KBr. Preparative GLC was carried out on a PAKhV-07 instrument, with stationary phase PFMS-4, 20% on Chromaton, temperature 190°C, and column 5 m × 10 mm.

2-(Vinyloxy)-4,5-diphenylimidazole (IV). In a steel rotating autoclave were placed 5 g (0.02 mole) of azolone (I), 1 g (20%) or $Cd(OAc)_2$, and 200 ml of dioxane. Acetylene was fed from a cylinder with an initial pressure of 17 atm. The reaction mixture was heated for 4 h at 240°C. After cessation of the reaction, the precipitate was filtered off, the solvent was driven off, and the residue was passed through a column with $Al_2O_3$; the solvent was chloroform–benzene (5:1). The recovered substance was purified by recrystallization from an ether–hexane mixture. The yield was 1.6 g.

1-Vinyl-4,5-diphenylimidazol-2-one (V). This compound was synthesized and recovered similarly to compound (IV), with reaction time 3 h, initial acetylene pressure 12 atm, and yield 0.8 g.

1-Vinyl-2-(vinyloxy)-4,5-diphenylimidazole (VI). This compound was obtained similarly to (IV) in the presence of 1.5 g (30%) of $Cd(OAc)_2$. Vacuum distillation gave 2.4 g of (VI), $n_D^{20}$ 1.5850.

1,3-Divinyl-4,5-diphenylimidazol-2-one (VII). This compound was synthesized under conditions similar to those in the synthesis of (IV), with catalyst KOH, 1 g (20%), and yield 2.2 g.

1,3-Divinylbenzimidazol-2-one (VIII). Into an autoclave were placed 6.7 g (0.05 mole) of azolone (II), 1.34 g (20%) of $Cd(OAc)_2$, and 200 ml of dioxane. The reaction mixture was saturated with acetylene and heated for 1 h at 230°C. After cooling, the precipitate was filtered off, the dioxane was driven off, and the residue was distilled *in vacuo*. We obtained a mixture of divinyl derivatives (VIII) and (IX). By preparative GLC we recovered 3.2 g of (VIII), $n_D^{20}$ 1.6125 [5].

1-Vinyl-2-(vinyloxy)benzimidazole (IX). This compound was obtained similarly to compound (VIII). By preparative GLC we recovered 1.8 g of (IX), $n_D^{20}$ 1.5825.

1-Vinylbenzimidazol-2-one (X). This compound was recovered by chromatography of the reaction mixture on a column with $Al_2O_3$, and the eluent was chloroform–benzene (5:2).

2-Vinyl-3-(vinyloxy)indazole (XII). This compound was obtained similarly to (IV), but at 220°C with an initial acetylene pressure of 12 atm. By vacuum distillation we recovered (XII), $n_D^{20}$ 1.6175.

## CONCLUSIONS

The reaction of 4,5-diphenylimidazol-2-, benzimidazol-2-, and indazol-3-ones with acetylene gave their N- and O-mono- and N,N- and N,O-divinyl derivatives.

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# ESTERS OF TRIFLUOROVINYLPHOSPHONIC ACID

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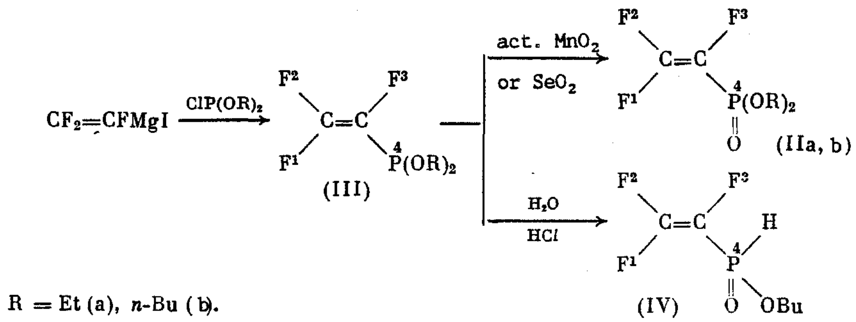
The high electrophilicity of pentafluoroisopropenylphosphonic acid esters $CF_2=C(CF_3)-PO(OR)_2$ (I) [1], containing a terminal C=C bond, is due to a combination of electron drawing off action of the $CF_3$ and $PO(OR_2)_2$ substituents; it was therefore of interest to study the properties of the simplest representatives of perfluoroalkenylphosphonates, the esters of of trifluorovinylphosphonic acid (II).

It was found that phosphonates (II) can be obtained by the reaction of trifluorovinylmagnesium iodide with dialkyl chlorophosphites, followed by oxidation of the esters of trifluorovinylphosphorous acid (III) formed. A similar sequence of reactions has already been used for the synthesis of vinylphosphonic acid esters [2].



R = Et (a), *n*-Bu (b).

Trifluorovinyl phosphonites are readily isolated from the reaction mixture by extraction with pentane or hexane; it is clear that these esters, in contrast to vinyl phosphonites, either do not form adducts with magnesium salts, or give very unstable adducts. On prolonged standing, phosphonites (III) decompose with the formation of unidentified products. Hydrolysis of ester (IIIb) with dilute HCl under mild conditions leads to a mono butyl ester of trifluorovinylphosphonous acid (IV).

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