Journal of Organometallic Chemistry, 87 (1975) 247—256
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REACTIONS OF PHENYLBROMOACETYLENE WITH HETEROCUMULENES IN THE PRESENCE OF IRON PENTACARBONYL

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(Received October 2nd, 1974)

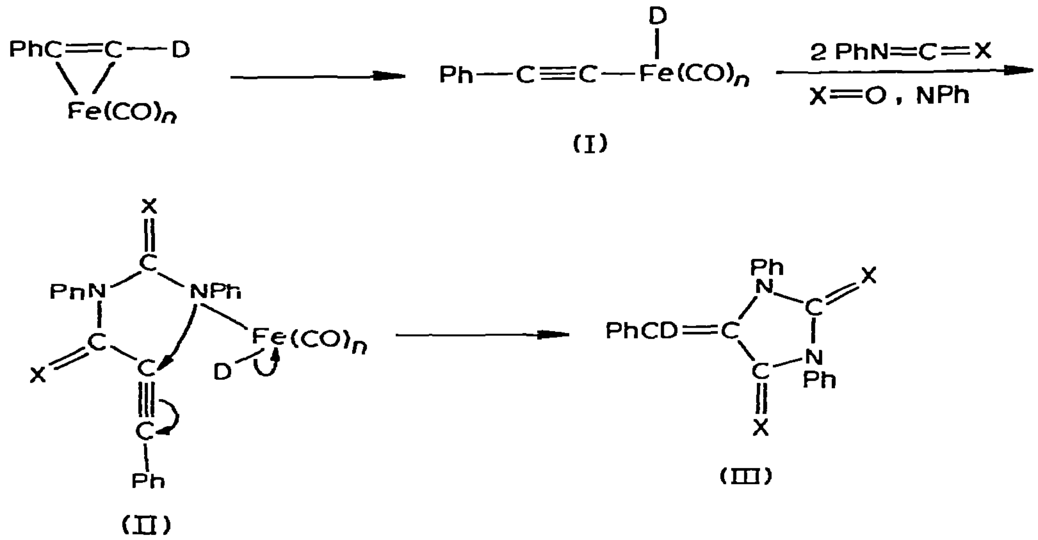
Summary

Reactions of phenylbromoacetylene with heterocumulenes in the presence of iron pentacarbonyl have been studied. The reactions with arylcarbodiimides gave diazepinone derivatives in 41-17% yields. The reaction with phenyl isocyanate gave two hydantoin derivatives, in 18 and 8% yields. On the other hand, the reaction with diphenylketene was not catalysed by iron pentacarbonyl and gave 2-bromo-3,4-diphenyl-1-diphenylacetoxynaphthalene. In all cases coupling of phenylbromoacetylene to give diphenylbutadiyne was also observed. Reaction mechanisms are discussed.

Introduction

We have reported previously [1] that phenylacetylene reacts with isocyanates or carbodiimides in the presence of iron pentacarbonyl to give imidazolidine derivatives III. It was suggested that isocyanates or carbodiimides were inserted into the C—Fe bond of the complex I, and that the hydrogen atom attached to the iron of intermediate II returned to the acetylenic carbon in the ring closure step to III.

When phenylbromoacetylene is employed instead of phenylacetylene, some significant differences in the observed reaction is expected due to the affinity of bromine for iron. When we investigated reactions of phenylbromoacetylene with heterocumulenes in the presence of iron pentacarbonyl, this was indeed found to be the case. In the cyclization step of these reactions, coupling reactions of phenylbromoacetylene should have occurred. We had noticed such a coupling reaction of phenylbromoacetylene to give diphenyldiacetylene in the presence of iron pentacarbonyl in our preliminary experiments and it has been reported to be effected by cuprous salts [2] as well.


(I)

(II)

(III)

Results and discussion

Reactions with carbodiimides

Reactions of phenylbromoacetylene with arylcarbodiimides IVa-IVc in the presence of iron pentacarbonyl at 90-100° gave the benzodiazepinone derivatives Va-Vc and the diacetylene VI. It seemed that the benzodiazepinones Va-Vc were formed from an arylcarbodiimide, an aryl isocyanate and two moles of phenylethynyl groups, and that the diacetylene VI was formed by the coupling reaction of phenylbromoacetylene. The reactions proceeded with violence unless they were controlled by adding a solvent such as tetrahydrofuran.

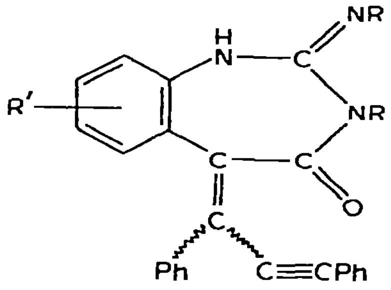
$$RN{=}C{=}NR \quad + \quad PhC{\equiv}CBr \quad + \quad Fe(CO)_5 \xrightarrow[THF]{}$$

(IV)

a, R = Ph, R′ = H

b, R = p-tolyl
R′ = 4-Me

c, R = o-tolyl
R′ = 2-Me


(V)

$+ \quad (PhC{\equiv}C\text{—})_2$

(VI)

The results of the reactions are shown in Table 1.

The structure of the benzodiazepinone Va was determined by spectral data. In the IR spectrum, the absence of the absorption due to the triple bond implied its strong conjugation with the double bond. The NMR spectrum showed the

TABLE 1

THE REACTIONS OF PhC≡CBr WITH RN=C=NR

R	Molar ratio					Yield[b] (%)	
	PhC≡CBr	RN=C=NR	$Fe(CO)_5$	Temp. (°C)	Time (h)	V	VI
Phenyl	1	1	2	90-100	2	41	23
Phenyl	1	1	1	90-100	2	40	19
Phenyl	1	1	0.8	90-100	2	29	25
Phenyl	1	1	0.5	90-100	2	14	30
p-Tolyl	1	1	1	90-100	2.5	33	17
o-Tolyl	1	1	1	90-100	4	17	36
c-Hexyl[a]	1	1	1	90-100	4.5	0	88

[a] This reaction was carried out without solvent, and all other reactions were carried out in THF. [b] Based on phenylbromoacetylene.

signal of amine proton at δ 7.7 in DMSO-d_6. In the product Va, the configuration of the phenyl group attached to the olefinic carbon was not determined.

A decrease in the mole ratio of $Fe(CO)_5$ to the acetylene to unity led to a decrease in the yield of the product Va, but an increase in the mole ratio caused no remarkable effect. These results indicate that an equimolar amount of iron pentacarbonyl is necessary for the reaction. A substituent on the *ortho* position of the arylcarbodiimide depressed the formation of the benzodiazepinone Vc by its steric hindrance. In the case of cyclohexylcarbodiimide, no benzodiazepinone was obtained because of poor reactivity of the carbodiimide, and the diacetylene VI was formed quantitatively.

We assume the reaction mechanism as shown in the Scheme 1 in analogy with the proposed mechanism for the reaction between phenylacetylene and a carbodiimide [1]. The smooth formation of the acetylide complex VII would be followed by successive insertion of two moles of the carbodiimide giving the intermediate VIII. Both the fission of the iron—nitrogen bond and the attack of the π-electrons of the C≡C bond at the iron atom will lead to the intermediate IX without a shift of bromine to the acetylenic carbon, although the ring closure of II which corresponds to VIII was accompanied by a prototropic shift in the reaction of phenylacetylene. This is because of the higher affinity of bromine for iron as compared with that of hydrogen. The subsequent coupling reaction between the intermediate IX and the acetylide complex VII which gives the benzodiazepine derivative X could be deduced from the results of couplings of organohalo compounds by iron carbonyls [3]*. The benzodiazepine X was not isolated but was obtained as the hydrolyzed product, the diazepinone V, after chromatographic treatment on alumina.

Reaction with phenyl isocyanate

The reaction of phenylbromoacetylene with phenyl isocyanate in the presence of an equimolar amount of iron pentacarbonyl gave the hydantoin derivatives XI and XII instead of a diazepinone. The structure of XI was determined by means of spectral and analytical data (see Experimental).

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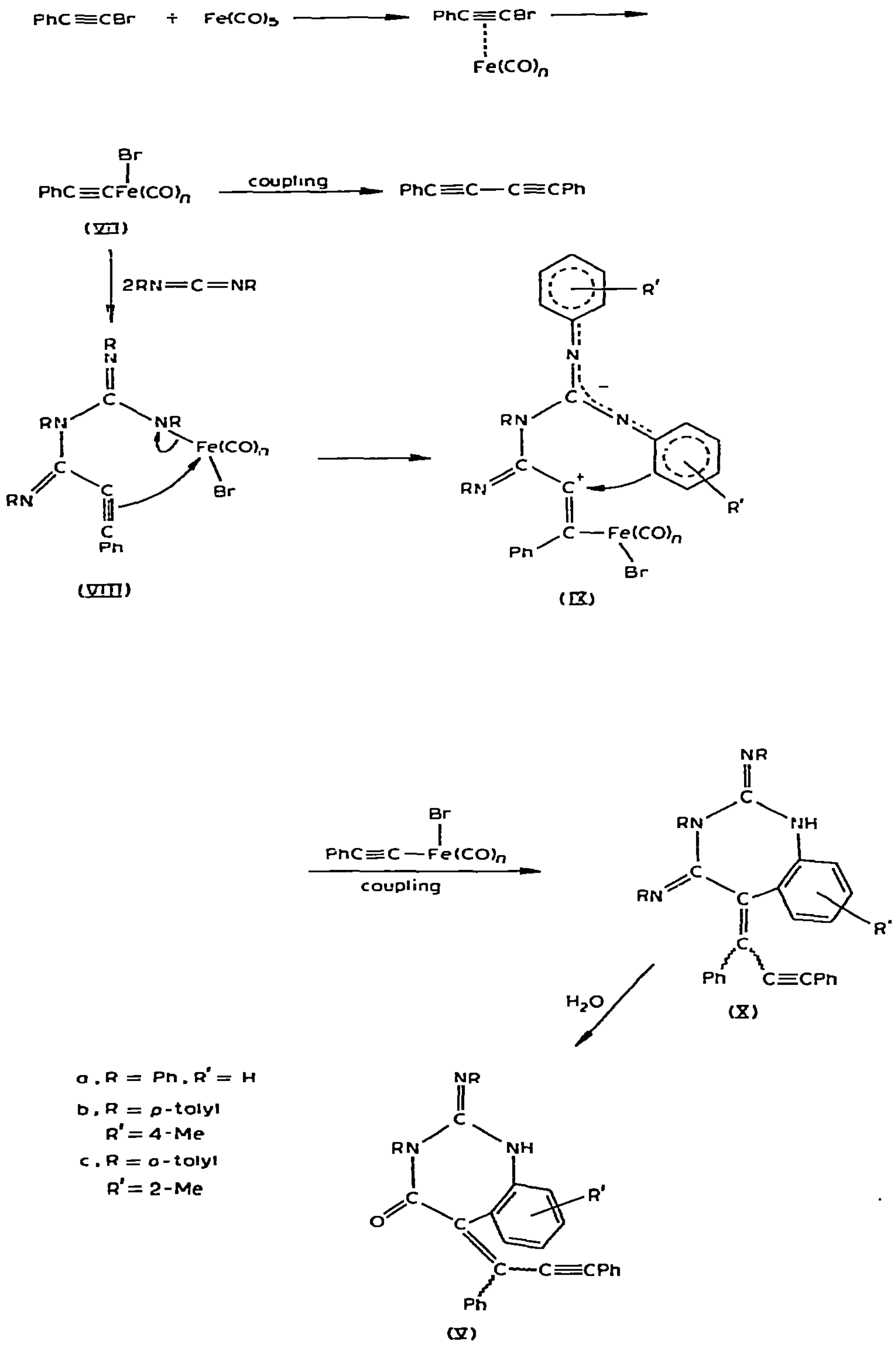
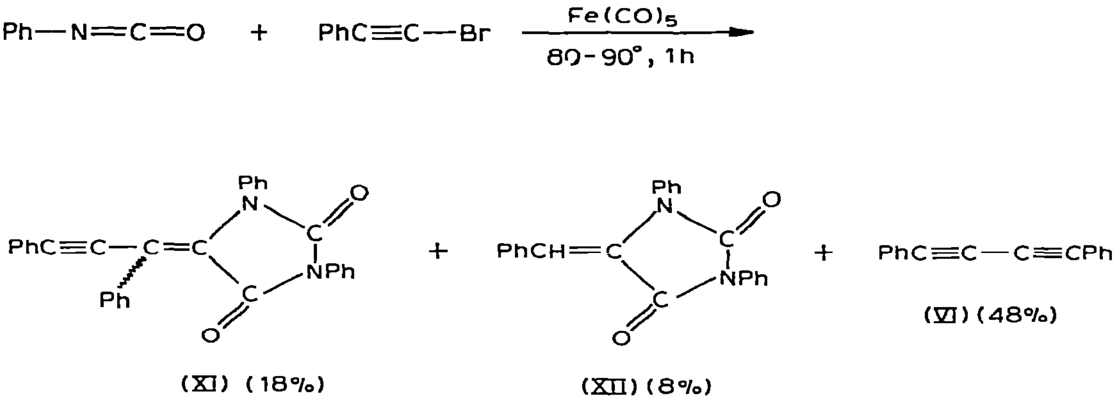
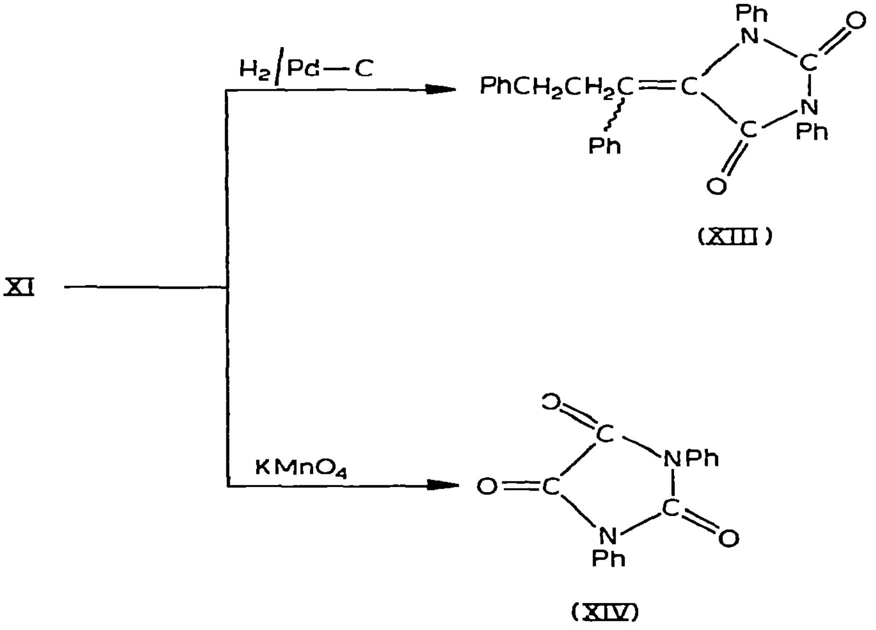
* The same author has reported that phenylbromoacetylene was coupled by $Fe(CO)_5$ (private communication).

SCHEME 1


PhC≡CBr + Fe(CO)5
PhC≡CBr
Fe(CO)n
PhC≡CFe(CO)n
Br
(VII)
coupling
PhC≡C—C≡CPh
2RN=C=NR
(VIII)
(IX)
R'
Fe(CO)n
Br
PhC≡C—Fe(CO)n
coupling
(X)
H2O
(V)
a, R = Ph, R' = H
b, R = p-tolyl
R' = 4-Me
c, R = o-tolyl
R' = 2-Me



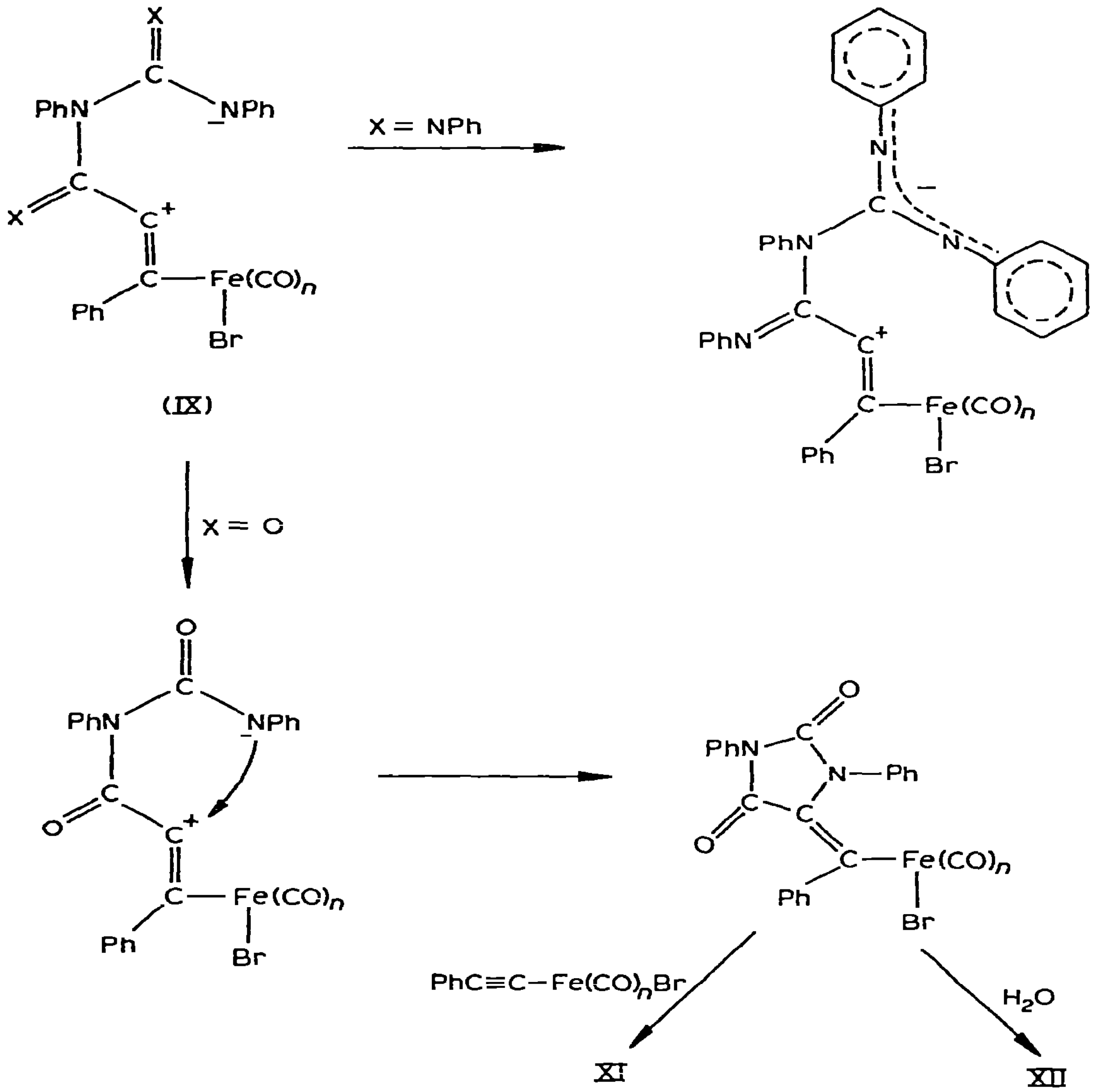
In the hydrogenation of the hydantoin XI with Pd/C catalyst, only the acetylenic group was reduced to give the hydantoin XIII, and the carbon—carbon double bond remained unchanged under such conditions. In the IR spectrum, the hydantoin XIII showed an absorption band which was assigned to the C=C group at 1630 cm^{-1}. The hydantoin XI was oxidized with $KMnO_4$ to diphenylparabanic acid (XIV) in 67% yield.



The structure of the hydantoin XII was confirmed by comparison with previously reported spectral data [1].

We consider the mechanistic distinction between the reactions of a carbodiimide and an isocyanate as follows. The primary difference surely would be in the stability of the negative charge developed on the nitrogen atom by the fission of the N—Fe bond of the intermediate VII. The charge would be distributed into phenyl rings by the strong resonance effect in the case of the carbodiimide. On the contrary, the charge on the nitrogen would be stabilized by the electron-withdrawing carbonyl group in the reaction of the isocyanate, and therefore the attack of the nitrogen at the acetylenic carbon would become predominant (Scheme 2).

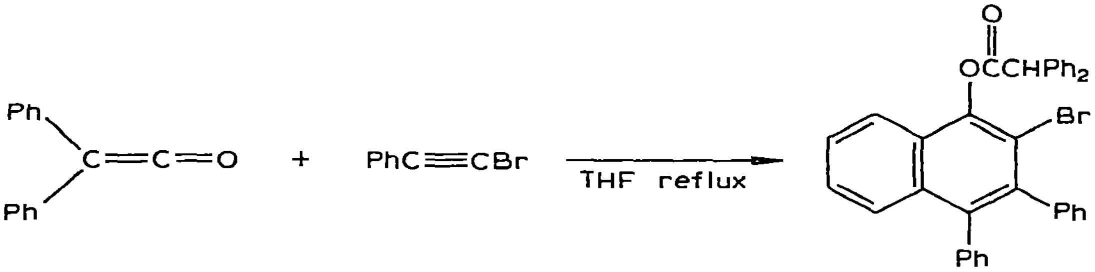
SCHEME 2



In the reaction with the isocyanate, the slow rate of the insertion of the isocyanate into the C—Fe bond of the intermediate VII led to the major coupling reaction of itself, and the diacetylene VI was produced in a high yield.

Reaction with diphenylketene

In the presence of iron pentacarbonyl, the reaction of phenylbromoacetylene with diphenylketene gave 2-bromo-3,4-diphenyl-1-diphenylacetoxynaphthalene (XV) in 22% yield together with the diacetylene VI. In this reaction, no adduct formed by insertion of diphenylketene into the acetylide complex VII was obtained.



(XV)

A similar naphthalene derivative is obtained from the reaction of phenylacetylene with diphenylketene without catalyst [4]. This non-catalytic reaction is carried out under mild conditions and the naphthalene is produced in high yield.

From these results, the reaction of the ketene with the acetylene would be predominant over the formation of the acetylide complex VII.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected.

Infrared spectra were recorded on Nujol mulls of solids with a Jasco IR-E spectrophotometer. Proton magnetic resonance spectra were taken on a Jeol LNM-3H-60 spectrometer with TMS as the internal standard. Mass spectra were taken with a Hitachi RMU-6E spectrometer.

All reactions were carried out under nitrogen in four-necked flasks with stirrers. Chromatographic separations were carried out using activated alumina columns.

Materials

Commercial iron pentacarbonyl was used without further purification. Commercial phenyl isocyanate was used after distillation. Diphenylcarbodiimide, di-*p*-tolylcarbodiimide and di-*o*-tolylcarbodiimide were prepared by the reported method [5]. Phenylbromoacetylene was prepared from phenylacetylene and sodium hypobromide in the usual way [6].

Reactions of phenylbromoacetylene with carbodiimides

(a). Reaction with diphenylcarbodiimide. A mixture of phenylbromoacetylene (0.025 mol) and iron pentacarbonyl (0.025 mol) in 5 ml of THF was stirred for 30 min at room temperature. Diphenylcarbodiimide (0.025 mol) was added dropwise to the mixture at room temperature and then this mixture was heated at 90-100° for 2 h until evolution of carbon monoxide ceased. The reaction was extracted with 200 ml of benzene, and the benzene layer was

washed twice with 300 ml of water. The benzene solution was dried over Na_2SO_4, concentrated in vacuo, chromatographed and eluted with hexane (fraction 1) and ethyl acetate (fraction 2). From the first fraction, 0.48 g (19%) of diphenylbutadiyne (VI) was obtained and recrystallized (hexane—benzene): m.p. 88-89°; no depression of melting point was observed for the mixture with an authentic sample [7]. From the second fraction, 2.57 g (40%) of 6,7-benzo-3-phenyl-2-phenylimino-5-(α-phenylethynyl)benzylidene-1,2,4,5-tetrahydro-1,3-diazepin-4-one (Va) was obtained and recrystallized (benzene—hexane): pale yellow needles; m.p. 150-151°; IR: 3290 (NH), 1640 (C=O) and 1615 cm^{-1} (C=N); mass spectrum: *m/e* 515 $[M]^+$, 395 $[M - PhN{=}CNHPh]^+$, 202 $[PhC{\equiv}CPhC{=}C]^+$ and 194 $[PhN{=}C{=}NPh]^+$; NMR (DMSO-d_6): δ 7.2 (broad, 1H, NH), 7.6-6.8 (22H, aromatic protons).

Analysis found: C, 83.81; H, 5.15; N, 8.37. $C_{36}H_{25}N_3O$ calcd.: C, 83.86; H, 4.89; N, 8.15%.

(b) Reactions with other carbodiimides. Reactions between carbodiimides (0.025 mol), phenylbromoacetylene (0.025 mol) and iron pentacarbonyl (0.025 mol) were carried out in a similar manner (see Table 1 for reaction times, temperatures and yields). The reaction with di-*p*-tolylcarbodiimide gave 4'-methyl-6,7-benzo-3-*p*-tolyl-2-phenylimino-5-(α-phenylethynyl)benzylidene-1,2,4,5-tetrahydro-1,3-diazepine-4-one (Vb) (1.2 g): yellow needles (from benzene—hexane); m.p. 188-190°; IR: 3290 (NH), 1640 (C=O) and 1615 cm^{-1} (C=N); mass spectrum: *m/e* 558 $[M]^+$, 543 $[M - CH_3]^+$, 467 $[M - CH_3C_6H_4]^+$, 292 $[CH_3C_6H_4C{=}CPhC{\equiv}CPh]^+$ and 222 $[CH_3C_6H_4N{=}C{=}NC_6H_4CH_3]^+$; NMR ($CDCl_3$): δ2.2 (s, 3H, CH_3), 2.15 (s, 6H, 2CH_3) and 6.6-7.4 (m, 20H, NH and aromatic protons).

Analysis found: C, 83.63; H, 5.91; N, 7.25. $C_{39}H_{31}N_3O$ calcd.: C, 83.99; H, 5.60; N, 7.54%.

The reaction with di-*o*-tolylcarbodiimide gave 1'-methyl-6,7-benzo-3-*o*-tolyl-2-*o*-tolylimino-5-(α-phenylethynyl)benzylidene-1,2,4,5-tetrahydro-1,3-diazepine-4-one (Vc) (2.3 g): white needles (from benzene—hexane); m.p. 181-182°; IR: 3290 (NH), 1640 (C=O) and 1615 cm^{-1} (C=N); mass spectrum: *m/e* 543 $[M - CH_3]^+$, 467, 292 and 222; NMR ($CDCl_3$): δ2.6-3.6 (m, 9H, 3CH_3), 6.2-7.4 (m, 19H, aromatic protons) and 8.0 (broad, 1H, NH).

Analysis found: C, 84.14; H, 5.68; N, 7.52. $C_{39}H_{31}N_3O$ calcd.: C, 83.99; H, 5.60; N, 7.54%.

The reaction with dicyclohexylcarbodiimide gave no diazepinone derivative, but diphenylbutadiyne (VI) (88%) was isolated.

Reaction of phenylbromoacetylene with phenyl isocyanate

A mixture of phenylbromoacetylene (0.025 mol) and iron pentacarbonyl (0.025 mol) was stirred at 80° for 10 min. Phenyl isocyanate (0.025 mol) was added dropwise to the mixture, and stirring was continued for 4 h at 80-90° until evolution of carbon monoxide ceased. The reaction mixture was extracted with benzene, concentrated in vacuo, and chromatographed and eluted with hexane (fraction 1) and benzene (fraction 2 and 3). From the first fraction, 1.2 g (48%) of diphenylbutadiyne (VI) was obtained and recrystallized (hexane). From the second fraction, 0.9 g (18%) of 4-(α-phenylethynyl)benzylidene-1,3-diphenylhydantoin (XI) was obtained and recrystallized (benzene—hexane):

pale yellow needles; m.p. 228-230°; IR: 1765 and 1720 $\mathrm{cm^{-1}}$ (C=O); mass spectrum: *m/e* 440 $[M]^+$, 293 $[\mathrm{PhC{\equiv}CPhC{=}C{=}NPh}]^+$ and 190 $[\mathrm{PhC{\equiv}CCPh}]^+$; NMR ($CDCl_3$) δ6.8-7.7 (all aromatic protons).

Analysis found: C, 81.90; H, 4.58: N, 6.36. $C_{30}H_{20}N_2O_2$ calcd.: C, 82.28; H, 4.53; N, 6.33%.

From the third fraction, 0.7 g (8.3%) of 4-benzylidene-1,3-diphenylhydantoin (XII) was obtained and recrystallized (benzene—hexane): white needles; m.p. 198° (lit. [8] 193-194°), the melting point of a mixture of compound XII and an authentic sample was not depressed.

Oxidation of XI. Potassium permanganate (0.17 g) was added at room temperature over 30 min to the hydantoin XI (0.2 g) dissolved in pyridine (10 ml)/water (1 ml). Water (5ml) was added to the reaction mixture, and stirring was continued for 1 h. The solution was made acid to congo red with dilute sulfuric acid and decolorized by sodium bisulfite. The resultant precipitate was recrystallized (benzene—hexane) to give 0.08 g (67%) of diphenylparabanic acid (XIV): white needles; m.p. 210°, no depression of the melting point was observed for a mixture with an authentic sample [1]. IR 1770 and 1735 $\mathrm{cm^{-1}}$ (C=O); mass spectrum *m/e* 266 $[M]^+$ and 119 $[\mathrm{PhNCO}]^+$.

Catalytic reduction of XI. The hydrogenation of the hydantoin XI (150 mg) in 150 ml of absolute EtOH over 10% of palladium on carbon (90 mg) with hydrogen (4 atm.) was undertaken at room temperature over a period of 30 h. After filtering off the catalyst, the solution was evaporated and the residue was recrystallized from ethanol—benzene to afford 72 mg (49%) of 4-(α-phenylethynyl)-benzylidene-1,3-diphenylhydantoin (XIII): pale yellow needles; m.p. 176-178°; IR: 1765 and 1720 (C=O), and 1630 $\mathrm{cm^{-1}}$ (C=C); mass spectrum: *m/e* 444 $[M]^+$ and 353 $[M - \mathrm{PhCH_2}]^+$; NMR ($CDCl_3$): δ3.4-3.7 (m, 2 H, CH_2), 2.6-2.9 (m, 2 H, CH_2).

Analysis found: C, 81.06; H, 5.57; N, 6.43. $C_{30}H_{24}N_2O_2$ calcd.: C, 81.06; H, 5.44, N, 6.30%.

Reaction of phenylbromoacetylene with diphenylketene

A mixture of phenylbromoacetylene (0.01 mol) and iron pentacarbonyl (0.01 mol) in 25 ml THF was stirred at 66° for 30 min. Diphenylketene (0.02 mol) was added dropwise to the solution, and the mixture was heated at 66° for 15 h with stirring. After the evaporation of the solvent, the residue was chromatographed and eluted with hexane (fraction 1) and benzene (fraction 2). From the first fraction, 0.4 g (39%) of diphenylbutadiyne (VI) was obtained. From the second fraction, 1.2 g (22%) of 2-bromo-3,4-diphenyl-1-diphenylacetoxynaphthalene (XV) was obtained, and recrystallized (benzene—hexane): white needles; m.p. 210-212°; IR: 1750 $\mathrm{cm^{-1}}$ (C=O); mass spectrum: *m/e* 569 $[M]^+$, 489 $[M - \mathrm{Br}]^+$ and 375 $[M - \mathrm{Ph_2C{=}C{=}O}]^+$; NMR ($CDCl_3$): δ6.6 (s, 1 H).

Analysis found: C, 76.25; H, 4.49. $C_{36}H_{25}BrO_2$ calcd.: C, 75.92; H, 4.43%.

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