NMR (Varian A60 spectrometer) 144 Hz (S, 6 H), 355 Hz (S, 2 H), 395 Hz (S, 2 H), in Me_2SO-d_6; the 355-Hz band disappears on the addition of D_2O. Triphenylamine was used as obtained from Eastman Chemicals (λ_{max} 298 nm, ϵ 22.3 × 10^3 in CH_3CN). Elemental analyses for the compounds in the experimental section were submitted for review and are in agreement with theoretical values.

Preparation of the π Complexes. Method A. A hot solution of 2.5 × 10^{-3} mol of the pyrylium salt in 20 ml of acetonitrile was added to a hot solution of 2.5 × 10^{-3} mol of V in 30 ml of acetonitrile. On cooling, the complex separates in pure form. It may be crystallized from acetonitrile.

Method B. A solid mixture of 2.5 × 10^{-3} M quantities of the pyrylium salt and V was placed in the extraction thimble of a Soxhlet extractor and extracted overnight with ethanol. On cooling, the ethanolic extract deposited the complex in good crystalline form. This method was used if method A was not successful.

4-(2-Methylphenyl)-2,6-diphenylpyrylium Perchlorate. A mixture of 12 g of o-tolylaldehyde and 18 g of acetophenone in 50 ml of BF_3 etherate was heated for 2 h on the steam bath, cooled, diluted with ether, and chilled and the solid was collected. Crystallization of the crude product from acetic acid gave 8 g, mp 230–231 °C, of the fluoroborate. Four grams of the fluoroborate was dissolved in acetonitrile and 3 ml of 70% perchloric acid was added to give 3.5 g of the perchlorate salt, mp 264–265 °C. Also prepared in a similar manner are:

4-(3-Methylphenyl)-2,6-diphenylpyrylium Fluoroborate: mp 253–254 °C from acetonitrile; λ, nm (ϵ × 10^{-3}), 253 (18.3), 273 (17.5), 362 (22.2), 397 (18.1) in CH_3CN.

4-(4-Methylphenyl)-2,6-diphenylpyrylium Perchlorate: mp 291–292 °C; λ, nm (ϵ × 10^{-3}), 235 (17.2) 274 (19.0) 378 (30.4) 390 (29.8) 440 (12.0) in CH_3CN.

2,4,6-Triphenylpyrylium TCNQ–TCNQ Complex. A. A solution of 0.44 g of 2,4,6-triphenylpyrylium iodide in 20 ml of acetonitrile was added to a solution of 0.41 g (2 equiv) of TCNQ in 30 ml of acetonitrile. The complex separated immediately in pure condition, mp 297 °C, yield, 0.6 g (83%). Crystallization from acetonitrile did not change the melting point.

B. A solution of 1.0 g of 1,3,5-triphenylpentene-1,5-dione in 30 ml of acetonitrile and 1.26 g of TCNQ (2 equiv) was heated at reflux for 1 h. After cooling, 1.2 g (58%) of product was collected. Resistivity 4.2 ohm/cm (*11*).

5-Phenacyl-3-phenylpyrazoleazine. A mixture of 3 g of 2,6-diphenylpyrone, 1 ml of hydrazine, and 50 ml of ethanol was heated to reflux for 4 h. After standing overnight, the white solid that had separated was collected and recrystallized from ethanol and then from benzene: mp 168 °C; yield, 72%.

5-Phenacyl-3-phenylpyrazole Hydrazone. A mixture of 2.0 g of 4-(4-dicyanomethylene)-2,6-diphenyl-4*H*-pyran, 10 ml of ethanol, and 5 ml of 64% hydrazine was refluxed for 2 h. Water was added and the mixture was acidified with acetic acid. The product was collected and crystallized from acetic acid to give 1.5 g of the azine: mp 233 °C.

A 5–10% solution of III in a solution of hydroxypropylcellulose (high molecular weight) in dimethylformamide was whirl coated on a polyethylene terephthalate support. After drying, an electronic spectrum was obtained showing peaks at 362 and 430 nm and a broad band centered at 580 nm.

Literature Cited

(1) Ainsworth, C., Jones, R. G., *J. Am. Chem. Soc.*, **76**, 3172 (1954).
(2) Balaban, A. T., Mocanu, M., Simon, Z., *Tetrahedron*, **20**, 119 (1964).
(3) Beaumont, T. G., Davis, K. M. C., *J. Chem. Soc. B*, 575 (1969).
(4) Beaumont, T. G., Davis, K. M. C., *Nature (London)*, **225**, 632 (1970).
(5) Costa, L., Grum, F., Paine, D. J., *Appl. Opt.*, **8**, 1149 (1969).
(6) Feldman, M., Jackson, J. A., *Tetrahedron Lett.*, 797 (1966).
(7) Feldman, M., Winstein, S., *Tetrahedron Lett.*, 853 (1962).
(8) Feldman, M., Winstein, S., *Theor. Chim. Acta*, **10**, 86 (1968).
(9) Foster, R., "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969.
(10) Kato, H., Ogawa, T., Ohta, M., *Bull. Chem. Soc. Jpn.*, **33**, 1468 (1960).
(11) Klanderman, B. H., Hoesterey, D. C., *J. Chem. Phys.*, **51**, 377 (1969).
(12) Ledwith, A., Woods, H. J., *J. Chem. Soc. C*, 1422 (1970).
(13) LeGoff, E., LaCount, R. B., *J. Am. Chem. Soc.*, **85**, 1354 (1963).
(14) Robertson, E. M., Van Deusen, W. P., Minsk, L. M., *J. Appl. Polym. Sci.*, **2**, 308 (1959).
(15) Sakanoue, S., Kai, Y., Yasuoka, N., Kasai, N., Kakudo, M., Mikawa, H., *Chem. Commun.*, 176 (1969).
(16) Van Allan, J. A., Natale, C. C., Rauner, F. J. (to Eastman Kodak Co.), U.S. Patent 3 250 615 (1966).
(17) Van Allan, J. A., Reynolds, G. A., *J. Org. Chem.*, **33**, 4418 (1968).
(18) Verhoeven, J. W., Dirkz, I. P., de Boer, Th. J., *Tetrahedron*, **25**, 3395 (1969).
(19) Weiss, R., Gompper, R., *Tetrahedron Lett.*, 481 (1970).
(20) White, B. G., *Trans. Faraday Soc.*, **85**, 2000 (1969).
(21) Wizinger, R., Ulrich, P., *Helv. Chim. Acta*, **39**, 207 (1956).
(22) Yasuba, H., Imai, T., Okamoto, K., Kusabayashi, S., Mikawa, H., *Bull. Chem. Soc. Jpn.*, **43**, 3101 (1970).

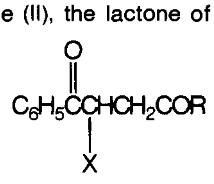
Received for review March 11, 1976. Accepted August 9, 1976.

Structure of the Diazonium Coupling Products of γ-Phenyl-$\Delta^{\beta,\gamma}$-butenolide

Samir A. Khattab,* Sami A. Shawali, and Ahmed M. Farag
Department of Chemistry, Faculty of Science, University of Cairo, Giza, A. R. Egypt

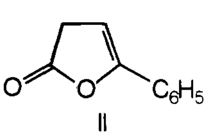
On spectral evidence, the diazonium coupling products of γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide are shown to exist essentially as α-arylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolides. This conclusion is supported by the synthesis of their *N*-methyl derivatives and also by their rearrangement in acid and alkaline media into 1,5-diarylpyrazole-3-carboxylic acids.

Whereas much research has been directed to the study of the structurally similar 4-arylazoisoxazoline-5-ones (*5, 6, 20*), 4-arylazooxazoline-5-ones (*2, 18*), and 4-arylazopyrazolin-5-ones (*11, 13, 16, 19, 22*), only a very little attention has been paid to α-arylazo-γ-phenyl-$\Delta^{\beta,\gamma}$-butanolides. Only four diazonium coupling products (III i, ii, xii, xiii) of γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (II), the lactone of β-benzoylpropionic acid (I), were



$$C_6H_5\overset{O}{\overset{\|}{C}}\underset{X}{\underset{|}{C}H}CH_2COR$$

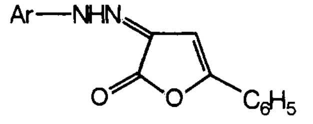
I, R = OH; X = H
a, R = OCH_3; X = H
b, R = OC_2H_5; X = H
c, R = OH; X = Br
d, R = OH; X = Cl



II

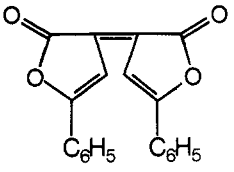
synthesized but they were not proved to be arylazo or arylhydrazono derivatives (*7, 15*). Also no spectroscopic data were reported on any one of them.

By virtue of structural relationships, the diazonium coupling products of II are of expected bacteriostatic, fungistatic, tuberculostatic, and trichomonostatic effects (*4, 17, 26*). For the aim of elucidation of their structure, testing some of their physiological activities, and in continuation of the previous work of one of us (*15*), the present investigation undertakes the synthesis of a series of new diazonium coupling products of butenolide II. Arenediazonium salts and *N*-nitrosoacylarylamines (*25*) are now found to couple smoothly with the active methylene group of II to yield the colored coupling products IIIi–xxx, without the formation of *cis*-dilactone, IV, as a by-product (*15*). Treatment of some of these products, III, with methyl iodide, in acetone, in the presence of potassium carbonate gave the corresponding *N*-methylarylhydrazone derivatives Va–f.

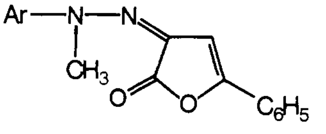


III

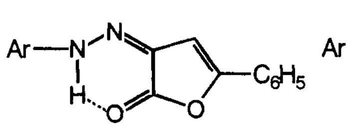
i, Ar = C_6H_5
ii, Ar = C_6H_4-CH_3-*p*
iii, Ar = C_6H_4-CH_3-*m*
iv, Ar = C_6H_4-CH_3-*o*
v, Ar = C_6H_4-OCH_3-*p*
vi, Ar = C_6H_4-OCH_3-*m*
vii, Ar = C_6H_4-OCH_3-*o*
viii, Ar = C_6H_4-OC_2H_5-*p*
ix, Ar = C_6H_4-OC_2H_5-*o*
x, Ar = C_6H_4-Br-*p*
xi, Ar = C_6H_4-Br-*m*
xii, Ar = C_6H_4-Cl-*p*
xiii, Ar = C_6H_4-Cl-*m*
xiv, Ar = C_6H_4-Cl-*o*
xv, Ar = C_6H_4-NO_2-*p*
xvi, Ar = C_6H_4-NO_2-*m*
xvii, Ar = C_6H_4-NO_2-*o*
xviii, Ar = C_6H_4-COOH-*p*
xix, Ar = C_6H_4-COOH-*m*
xx, Ar = C_6H_4-COOH-*o*
xxi, Ar = $C_{10}H_7$-α
xxii, Ar = $C_{10}H_7$-β
xxiii, Ar = C_6H_4-OH-*p*
xxiv, Ar = C_6H_4-SO_3H-*p*
xxv, Ar = 3-Cl-2-$CH_3C_6H_3$
xxvi, Ar = 4-CH_3-2-$NO_2C_6H_3$
xxvii, Ar = 4-CH_3-3-$NO_2C_6H_3$
xxviii, Ar = 2-CH_3-5-$NO_2C_6H_3$
xxix, Ar = 4-NO_2-2-$OCH_3C_6H_3$
xxx, Ar = 5-NO_2-2-$OCH_3C_6H_3$



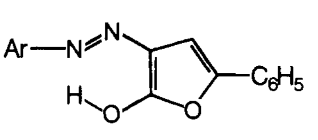
IV



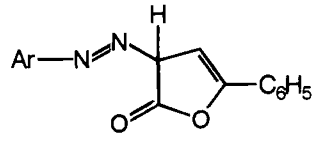
Va, Ar = C_6H_5
b, Ar = C_6H_4-CH_3-*p*
c, Ar = C_6H_4-OCH_3-*p*
d, Ar = C_6H_4-OC_2H_5-*p*
e, Ar = C_6H_4-Br-*m*
f, Ar = C_6H_3-(CH_3-*p*)(NO_2-*o*)



A

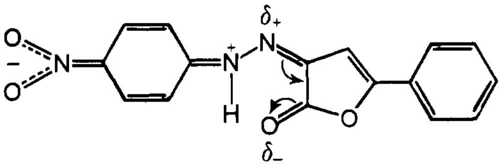


B



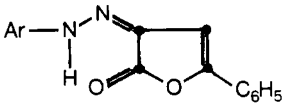
C

The diazonium coupling products IIIi–xxx could have either the keto–hydrazone structure A or the hydroxy–azo structure B or the azoketo structure C. In order to elucidate the actual structure of these products, their IR, UV, and NMR spectra together with the spectra of their *N*-methyl derivatives, V, are now investigated. IR spectra (KBr) of the coupling products III revealed in each case a weak NH band in the 3300–3200 cm^{-1} region, and a strong band at 1760 cm^{-1} assignable to the lactone >C=O group. The presence of both the NH and >C=O bands is in accord with structure A and incompatible with the hydroxyazo structure B. That the >C=O bands are markedly lower in frequencies than that of the parent lactone II (1786 cm^{-1}) (*23*), excludes the possibility of the azo–keto structure C. The latter requires the >C=O of the starting butenolide and of its azo derivative to be almost at the some frequencies. The downward shift of the >C=O stretch together with that of NH can be rationalized in terms of the keto–hydrazone structure A. In the latter, the increased degree of conjugation of the >C=O with C=N double bond and the possible intramolecular hydrogen bonding between the >C=O and the hydrazone NH results in reducing the force constant of the >C=O group and thus leads to lowering of its stretching frequency. This rationalization is substantiated by the IR spectra of the *N*-methyl derivatives Va–e, which are incapable of forming an intramolecular hydrogen bonding, showed their >C=O bands near 1770 cm^{-1}, and showed no NH bands. The fact that the coupling products III show evidence for intramolecular hydrogen bonding is in favor of hydrazone structure A, since compounds with structure C would not possess this property. The electronic absorption spectra of the coupling products III are also compatible with the assigned hydrazone structure A and are similar to those of typical hydrazones rather than azo compounds (*24*). The data of the spectra of 17 of these products, in ethanol, are included in Table I. Also the spectra of α-phenylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (IIIi) and α-(*N*-methyl)-*p*-methoxyphenylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (Vc) each in a series of different solvents showed that they are little affected by the polarity of the solvent (*3*). The relatively small differences observed in λ_{max} are probably caused by solute–solvent interactions (*9*). Furthermore, the similarity found between the spectra of III and their *N*-methyl derivatives provides an additional evidence for the assigned hydrazone structure A. The characteristic absorption band (Table I) with λ_{max} ranging between 420 and 447 nm, for the compounds studied, is undoubtedly assignable to the two possible chromophoric systems ArNHN=CC=O and ArNH–N=CCH=CPh. The data (Table I) indicate that the position of this band seems to be slightly affected by the nature of the substituent present. However, the hypsochromic effect observed for λ_{max} of the *p*-nitro derivative IIIxv suggests a decrease in the stability of the possible excited state D. The NMR spectra of compounds IIIi and IIIii and their *N*-methyl derivatives Va and Vb, respectively, are now studied. Compound IIIi exhibits a multiplet in the region δ 7.0–8.0 ppm. Its *N*-methyl derivative V_a shows two signals in its spectrum, the singlet at δ 3.80 (3 H) and a multiplet at δ 7.2–8.4 (11 H). The singlet at δ 3.8 ppm is undoubtedly due to the N–CH_3 group. Similarly, the spectrum of



D

Table I. α-Arylhydrazono- γ-phenyl- $\Delta^{\beta,\gamma}$-butenolides IIIi–xxx



Compd no.	Mp,[a] °C	Yield, %	Color with concn H_2SO_4	Formula	Anal.%, calcd (found)			Ethanol λ_{max}, nm	Log ϵ
					C	H	N		
IIIi	227 dec	60	Violet	$C_{16}H_{12}N_2O_2$	72.73 (72.45)	4.54 (4.63)	10.61 (10.53)	426	4.68
ii	222 dec	65	Dark brown	$C_{17}H_{14}N_2O_2$	73.36 (73.68)	5.07 (5.11)	10.07 (10.20)	428	4.63
iii	217 dec	68	Deep violet	$C_{17}H_{14}N_2O_2$	73.36 (73.00)	5.07 (5.10)		430	4.62
iv	147–148	58	Violet	$C_{17}H_{14}N_2O_2$	73.36 (73.60)	5.07 (5.11)	10.07 (9.80)	426	4.52
v	223 dec	64	Violet-red	$C_{17}H_{14}N_2O_3$	69.37 (69.00)	4.80 (4.80)	9.52 (9.20)		
vi	208–209 dec	71	Reddish brown	$C_{17}H_{14}N_2O_3$	69.37 (69.12)	4.80 (4.91)	9.52 (9.60)	428	4.49
vii	155	66	Bluish green	$C_{17}H_{14}N_2O_3$	69.37 (69.50)	4.80 (4.90)		442	4.56
viii	214 dec	75	Violet	$C_{18}H_{16}N_2O_3$	70.11 (70.00)	5.23 (5.30)	9.09 (9.20)	442	4.59
ix	142–143	68	Bluish green	$C_{18}H_{16}N_2O_3$	70.11 (70.30)	5.23 (5.30)	9.09 (8.90)	447	4.63
x	255 dec	63	Deep violet	$C_{16}H_{11}BrN_2O_2$[b]			8.16 (8.36)	426	4.63
xi	239 dec	61	Pink	$C_{16}H_{11}BrN_2O_2$[c]	55.99 (55.80)	3.26 (3.40)		420	4.71
xii	252 dec	65	Deep violet	$C_{16}H_{11}ClN_2O_2$[d]	64.32 (64.57)	3.68 (3.77)	9.38 (9.60)	426	4.65
xiii	238 dec	59	Deep violet	$C_{16}H_{11}ClN_2O_2$[e]	64.32 (64.37)	3.68 (3.84)	9.38 (9.10)	424	4.39
xiv	165	55	Violet-red	$C_{16}H_{11}ClN_2O_2$[f]	64.32 (64.10)	3.68 (3.80)	9.38 (9.20)	426	4.60
xv	291 dec	69	Deep violet	$C_{16}H_{11}N_3O_4$			13.59 (13.60)	380	4.21
xvi	254 dec	64	Red	$C_{16}H_{11}N_3O_4$	62.13 (62.40)	3.59 (3.20)	13.59 (13.20)	420	4.60
xvii	198 dec	60	Deep violet	$C_{16}H_{11}N_3O_4$	62.13 (61.99)	3.59 (3.60)	13.59 (13.55)		
xviii	296–297 dec	74	Pink	$C_{17}H_{12}N_2O_4$	66.23 (65.92)	3.92 (3.94)	9.09 (9.20)		
xix	254–255 dec	61	Pink	$C_{17}H_{12}N_2O_4$	66.23 (66.20)	3.92 (4.01)	9.09 (9.20)		
xx	236–237 dec	65	Violet-brown	$C_{17}H_{12}N_2O_4$	66.23 (66.30)	3.92 (4.00)	9.09 (8.89)	438	4.70
xxi	235 dec	53	Bluish green	$C_{20}H_{14}N_2O_2$	76.42 (76.14)	4.49 (4.49)	8.91 (8.72)		
xxii	268–269 dec	60	Violet-red	$C_{20}H_{14}N_2O_2$	76.42 (76.20)	4.49 (4.50)	8.91 (8.80)		
xxiii	232 dec	51	Violet-red	$C_{16}H_{12}N_2O_3$	68.56 (68.70)	4.32 (4.40)			
xxiv	311–312 dec	60	Pink	$C_{16}H_{12}N_2O_5S$[g]	55.82 (55.62)	3.51 (3.50)		428	4.63
xxv	180	53	Pink	$C_{17}H_{13}ClN_2O_2$[h]	65.28 (65.15)	4.19 (4.22)			
xxvi	211–212 dec	55	Deep violet	$C_{17}H_{13}N_3O_4$	63.15 (63.26)	4.05 (4.00)	13.00 (12.80)		
xxvii	241–242 dec	52	Deep violet	$C_{17}H_{13}N_3O_4$	63.15 (63.40)	4.05 (3.90)	13.00 (12.91)		
xxviii	247 dec	53	Violet-red	$C_{17}H_{13}N_3O_4$	63.15 (63.10)	4.05 (3.90)	13.00 (12.89)		
xxix	247 dec	50	Pink	$C_{17}H_{13}N_3O_5$	60.17 (60.07)	3.86 (3.75)			
xxx	260–261 dec	48	Violet-blue	$C_{17}H_{13}N_3O_5$	60.17 (60.19)	3.86 (3.92)	12.39 (12.30)		

[a] Melting points are uncorrected. [b] Calcd: Br, 23.29. Found: 23.20. [c] Calcd: Br, 23.29. Found: 23.50. [d] Calcd: Cl, 11.89. Found: 11.57. [e] Calcd: Cl, 11.89. Found: 12.12. [f] Calcd: Cl, 11.89. Found: 11.80. [g] Calcd: S, 9.31. Found: 9.50. [h] Calcd: Cl, 11.34. Found: 11.54.

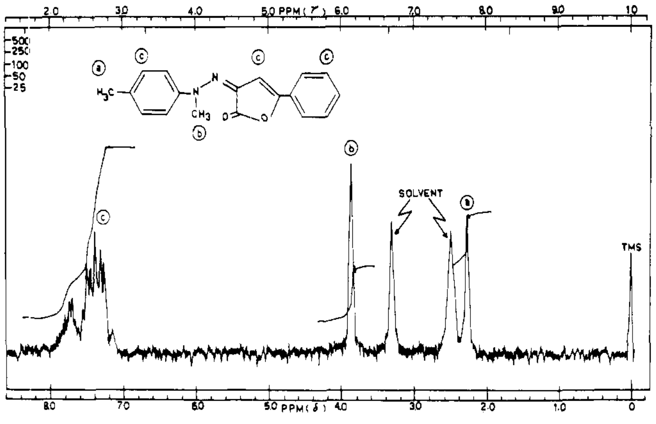
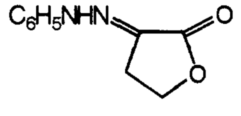


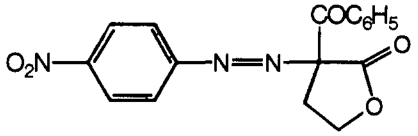
Figure 1. NMR spectrum of α-(N-methyl)-p-tolylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide in Me_2SO.

IIIi showed two signals: a multiplet at δ 7.0–8.0 (11 H, aromatic, 4 CH and hydrazone NH) and a singlet at 2.26 (3 H; $ArCH_3$) ppm. The spectrum of its N-methyl derivative Vb (Figure 1) exhibited two singlets at δ 2.26 and 3.81 ppm assignable to the para CH_3 and the N-CH_3 groups, respectively, and an aromatic proton multiplet at δ 7.0–8.0 ppm. The ratio of the integrals of these three signals is 3:3:10. The results indicate that the assigned structure A for diazonium coupling products III is correct.

Whereas 3-phenylhydrazonobutyrolactone (VI) and 3-arylazo-3-benzoylbutyrolactone (VII) were reported (*12*, *14*) to be stable towards acids and alkali, α-phenylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolide (IIIi) when treated with alcoholic acid or alkali underwent rearrangement to 1,5-diphenylpyrazole-3-carboxylic acid (VIIIa) (*7*, *15*).

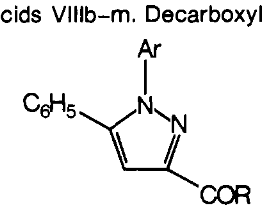


VI

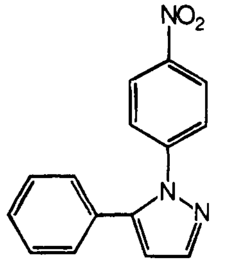


VII

Now, refluxing a number of the colored arylhydrazones III with hydrochloric acid–acetic acid mixture or methanolic potassium hydroxide affords the corresponding colorless 1,5-diarylpyrazole-3-carboxylic acids VIIIb–m. Decarboxylation of 1,5-diarylpyrazole-3-carboxylic acids, VIII, yields the corresponding 1,5-diarylpyrazoles. Thus the decarboxylation of 1-(p-nitrophenyl)-5-phenylpyrazole-3-carboxylic acid (VIIIk), taken as an example, gives 1-(p-nitrophenyl)-5-phenylpyrazole (IX). Hence, this rearrangement constitutes a possible route for the synthesis of new 1,5-disubstituted pyrazoles. Moreover, the ethyl esters VIIIn–r, now obtained from the corresponding acids VIII, react with hydrazine hydrate, in the presence or absence of solvent, to yield 1,5-diarylpyrazole-3-carboxylic acid hydrazides VIIIs–v. These hydrazides are of expected antilepral activity (*8*).



VIIIa, Ar = C_6H_5 R = OH
b, Ar = C_6H_4-CH_3-p; R = OH
c, Ar = C_6H_4-CH_3-m; R = OH
d, Ar = C_6H_4-OCH_3-p; R = OH
e, Ar = C_6H_4-OCH_3-m; R = OH
f, Ar = C_6H_4-OCH_3-o; R = OH
g, Ar = C_6H_4-OC_2H_5-p; R = OH
h, Ar = C_6H_4-OC_2H_5-o; R = OH
i, Ar = C_6H_4-Br-p; R = OH
j, Ar = C_6H_4-Cl-p; R = OH
k, Ar = C_6H_4-NO_2-p; R = OH
l, Ar = C_6H_4-NO_2-m; R = OH
m, Ar = $C_{10}H_7$-β; R = OH
n, Ar = C_6H_4-CH_3-p; R = OC_2H_5
o, Ar = C_6H_4-OCH_3-p; R = OC_2H_5
p, Ar = C_6H_4-Br-p; R = OC_2H_5
q, Ar = C_6H_4-Cl-p; R = OC_2H_5
r, Ar = C_6H_4-NO_2-m; R = OC_2H_5
s, Ar = C_6H_4-CH_3-p; R = $NHNH_2$
t, Ar = C_6H_4-OCH_3-p; R = $NHNH_2$
u, Ar = C_6H_4-Br-p; R = $NHNH_2$
v, Ar = C_6H_4-Cl-p; R = $NHNH_2$



IX

Experimental Section

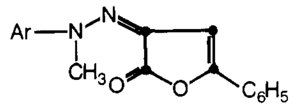
IR spectra were determined on a Unicam SP 1000 infrared spectrophotometer using KBr pellets (1%), electronic absorption spectra were obtained in ethanol (about 10^{-5} M) on a Unicam SP 8000 spectrophotometer. The ethanolic solutions contained 3% DMF by volume to effect complete dissolution. Spectra of compounds IIIi and Vc were also determined in DMF, dioxane, EtOH, Me_2SO, ACOH, and cyclohexane. Because of the poor solubility in $CDCl_3$, the NMR spectra of the compounds investigated were obtained in Me_2SO-d_6 on a Varian A60-T NMR spectrophotometer using Me_4Si as an internal reference.

Synthesis of α-Arylhydrazono-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolides IIII–xxx (Table I). γ-Phenyl-$\Delta^{\beta,\gamma}$-butenolide (II) was prepared (*21*) by heating β-benzoylpropionic acid in acetic anhydride containing a small amount of concentrated sulfuric acid.

(A) Coupling of II with Diazonium Salts. General Procedure. A solution of butenolide II (1.6 g) in ethanol (90%, 150 ml) was stirred with sodium acetate (3.0 g) and the mixture was then chilled in ice to 0–5 °C. A cold solution (0–5 °C) of the diazonium salt was added dropwise while stirring. When the addition was complete (45 min), stirring was continued for half an hour and then left to stand overnight in a refrigerator. The crude product which precipitated as dark colored solid (orange to brown) was collected and washed thoroughly with water and alcohol. It was then recrystallized from glacial acetic acid.

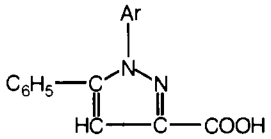
(B) Coupling of II with Nitrosoacylarylamines. General Procedure. To a solution of II (0.01 mol) in acetone (40 ml) was added the appropriate nitrosoacylarylamine (0.01 mol) prepared by nitrosation of acylarylamines (*10*). The reaction mixture was slightly warmed and shaken to effect complete dissolution of reactants and then left to stand overnight at room temperature. The crude diazonium coupling product precipitated was collected, washed with alcohol, and recrystallized from glacial acetic acid.

Table II. α-(*N*-Methyl)arylhydrazone-γ-phenyl-$\Delta^{\beta,\gamma}$-butenolides (Va–f)



Compd no.	Mp, °C	Yield, %	Formula	Anal.%, calcd (found) C	H	N	Br
Va	208	82	$C_{17}H_{14}N_2O_2$	73.36	5.07	10.07	
				(73.04)	(5.10)	(10.02)	
b	211–212	85	$C_{18}H_{16}N_2O_2$	73.95	5.52	9.58	
				(73.90)	(5.60)	(9.70)	
c	200	83	$C_{18}H_{16}N_2O_3$	70.11	5.23	9.09	
				(70.23)	(5.40)	(8.80)	
d	189	84	$C_{19}H_{18}N_2O_3$	70.79	5.63	8.69	
				(70.90)	(5.61)	(8.80)	
e	238	88	$C_{17}H_{13}BrN_2O_2$	57.14	3.67		22.36
				(57.30)	(3.78)		(22.30)
f	196	82	$C_{18}H_{15}N_3O_4$	64.09	4.48	12.46	
				(63.90)	(4.20)	(12.35)	

Table III. 1,5-Diarylpyrazole-3-carboxylic Acids (VIIIb–m)



Compd no.	MP, °C	Yield, %	Formula	Anal. %, calcd (found) C	H	N	Br	Cl
VIIIb	194–195	74	$C_{17}H_{14}N_2O_2$	73.36	5.07	10.07		
				(73.60)	(5.10)	(10.20)		
c	137–138	68	$C_{17}H_{14}N_2O_2$			10.07		
						(10.00)		
d	169–170	72	$C_{17}H_{14}N_2O_3$	69.37	4.80	9.52		
				(69.58)	(4.90)	(9.32)		
e	165–166	70	$C_{17}H_{14}N_2O_3$	69.37	4.80			
				(69.17)	(4.65)			
f	129–130	73	$C_{17}H_{14}N_2O_3$			9.52		
						(9.70)		
g	178	71	$C_{18}H_{16}N_2O_3$	70.11	5.23	9.09		
				(69.90)	(5.15)	(9.30)		
h	119–120	66	$C_{18}H_{16}N_2O_3$			9.09		
						(9.10)		
i	116–118	73	$C_{16}H_{11}BrN_2O_2$	55.99	3.26		23.29	
	dec			(55.65)	(3.32)		(23.40)	
j	180–182	78	$C_{16}H_{11}ClN_2O_2$	64.32	3.71			11.87
	dec			(64.50)	(3.80)			(11.70)
k	137–138	74	$C_{16}H_{11}N_3O_4$	62.13	3.59	13.59		
	dec			(62.40)	(3.70)	(13.32)		
l	225	69	$C_{16}H_{11}N_3O_4$	62.13	3.59	13.59		
				(62.00)	(3.61)	(13.62)		
m	223–224	62	$C_{20}H_{14}N_2O_2$	76.42	4.49	8.91		
				(76.60)	(4.51)	(8.80)		

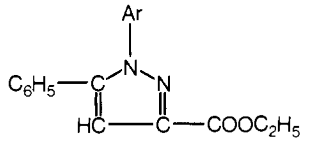
In procedures A and B, the mother liquors, after filtration of the diazonium coupling products III, on concentration afforded no *cis*-dilactone IV (*15*).

The arylhydrazones IIIi–xxx are sparingly soluble in most organic solvents, insoluble in ether and slightly soluble in ethanol and xylene. They are crystalline, have sharp melting points (with decomposition), and are deeply colored. Compounds IIIii, iii, x, xviii, xix, xxiv, and xxv are orange; IIIiv, vii, viii, ix, xi, xx, and xxix are brownish orange; IIIi, xii, xiii, and xxvii are yellowish brown; IIIv, vi, xiv, xv, xvi, xxii, xxiii, and xxviii are brown; IIIxvii, xxi, and xxx are red; and IIIxxvi is lustrous violet and turns into brick-red powder on crushing.

Synthesis of N-Methyl Derivatives of III (Table II). General Procedure. A mixture of III (0.01 mol), potassium carbonate (0.01 mol), and methyl iodide (0.01 mol) was refluxed in acetone (60 ml) for 8 h. The reaction mixture was filtered while hot and the filtrate was concentrated, cooled, and then diluted with water. The yellow solid that precipitated was collected, washed with water, and recrystallized from glacial acetic acid.

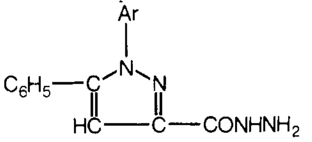
Rearrangement of III. (a) In Acid Medium. General Procedure. The appropriate arylhydrazone III (0.01 mol) was treated with a mixture of glacial acetic acid (60 ml) and hydrochloric acid (6 M, 70 ml). The reaction mixture was refluxed for 30 h then filtered. The filtrate was allowed to cool and was then poured

Table IV. 1,5-Diaryl-3-carbethoxypyrazoles (VIIIn–r)



Compd no.	Mp, °C	Yield, %	Formula	Anal. %, calcd (found) C	H	N	Br	Cl
VIIIn	85	82	$C_{19}H_{18}N_2O_2$	74.49 (74.16)	5.92 (5.80)	9.15 (9.10)		
o	103	85	$C_{19}H_{18}N_2O_3$	70.79 (70.64)	5.63 (5.70)	8.69 (8.83)		
p	81–82	79	$C_{18}H_{13}BrN_2O_2$				21.53 (21.40)	
q	79–80	83	$C_{18}H_{15}ClN_2O_2$					10.79 (10.70)
r	101–102	80	$C_{18}H_{15}N_3O_4$	64.09 (63.90)	4.48 (4.61)	12.46 (12.18)		

Table V. 1,5-Diarylpyrazole-3-carboxylic Acid Hydrazides (VIIIs–v)



Compd no.	Mp, °C	Yield, %	Formula	Anal. %, calcd (found) C	H	N	Br	Cl
VIIIs	149–150	65	$C_{17}H_{16}N_4O$	69.84 (69.90)	5.52 (5.60)	19.17 (19.26)		
t	163–164	61	$C_{17}H_{16}N_4O_2$	66.22 (66.45)	5.23 (5.12)	18.17 (18.30)		
u	167–168	66	$C_{16}H_{13}BrN_4O$	53.79 (54.01)	3.66 (3.52)		22.37 (22.50)	
v	181–182	63	$C_{16}H_{13}ClN_4O$					11.34 (11.15)

into ice water. The solid product that precipitated was collected by filtration, washed with water, and recrystallized from aqueous ethanol (1:1).

The 1,5-diarylpyrazole-3-carboxylic acids VIIIa–m so obtained, were all colorless or almost colorless and were soluble in sodium carbonate (with effervescence) and in sodium hydroxide (10%) (Table III).

(b) In Alkaline Medium. General Procedure. The appropriate compound III (0.005 mol) was dissolved in 60 ml of methanol containing 5 ml of aqueous KOH (20%). After stirring for 30 min at room temperature, the reaction mixture was left to stand overnight. The pale yellow solution was cooled in ice and then acidified with dilute hydrochloric acid. The crystalline solid so obtained was collected, washed with water, and recrystallized from aqueous ethanol (1:1) and found to be the corresponding 1,5-diarylpyrazole-3-carboxylic acid VIII; identical with that obtained from rearrangement in acid medium (melting point and mixture melting point determinations).

Decarboxylation of VIIIk. VIIIk (1.7 g) was heated above its melting point (at 150 °C) in an oil bath until the decarboxylation started. Heating was continued at a lower temperature (138–140 °C) until the evolution of CO_2 had ceased. The pale yellow resinous residue was extracted twice with cyclohexane (40 ml). On evaporation of the solvent, 0.6 g of crude material was obtained. Recrystallization from ethanol gave colorless prisms identified as IX, mp 117–118°, yield, ca. 40%. Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.80; H, 4.30; N, 15.61. The melting point was undepressed when admixed with an authentic sample (*1*). IR spectrum showed no (C═O) band of -COOH group (1710 cm^{-1} in VIIIk).

Synthesis of 1,5-Diaryl-3-carbethoxypyrazoles VIIIn–r. General Procedure. To the appropriate acid VIII (0.005 mol) was added absolute ethanol (30 ml) and concentrated sulfuric acid (0.5 ml) and the reaction mixture was refluxed on a boiling water bath for 8 h. The reaction mixture was allowed to cool and then was poured into ice-cold sodium carbonate solution (100 ml, 0.5%) and the solid so obtained was collected by filtration, washed with water, and recrystallized from aqueous ethanol (1:1). The ethyl esters VIIIn–r, so obtained, were all colorless or almost colorless (Table IV).

Synthesis of 1,5-Diarylpyrazole-3-carboxylic Acid Hydrazides VIIIs–v. Method a. The appropriate ester VIII (0.005 mol) was heated with hydrazine hydrate (85%, 8 ml) on a boiling-water bath for half an hour, then absolute ethanol (30 ml) was added to the reaction mixture which was then refluxed for 3 h. It was allowed to cool and then poured into water. The precipitated hydrazide was collected, washed with water, and recrystallized from aqueous ethanol (1:1).

Method b. To the appropriate ester (0.005 mol) was added hydrazine hydrate (85%, 9 ml), the reaction mixture was then allowed to stand at room temperature for 1 week. The precipitated hydrazide was collected, washed with water, and recrystallized from aqueous ethanol (1:1).

All the hydrazides VIIIs–v, so obtained, were colorless (Table V).

Literature Cited

(1) Auwers, K. V., Mauss, H., *Justus Liebigs Ann. Chem.*, **452**, 204 (1927).
(2) Browne, E. J., Polya, J. B., *J. Chem. Soc.*, 575 (1962).
(3) Burawoy, A., Salem, A. G., Thompson, A. R., *J. Chem. Soc.*, 4793 (1952).
(4) *Chem. Abstr.*, **59**, 6413*c* (1963), and *ibid.*, **68**, 87 286*g* (1968).
(5) Cum, G., Lo Vecchio, G., Aversa, M. C., Crisafulli, M., *Gazz. Chim. Ital.*, **97** (3), 346 (1967).
(6) Cum, G., Lo Vecchio, G., Aversa, M. C., *Atti Accad. Peloritana Pericolanti, Cl. Sci. Fis., Mat. Nat.*, **49**, 151 (1966); *Chem. Abstr.*, **69**, 43 836 (1968).
(7) Dieckmann, W., *Ber.*, **47**, 1435 (1914).
(8) Gardner, E. W., Lee, J., *J. Org. Chem.*, **26**, 1514 (1961).
(9) Gillam, A. E., Stern, E. S., "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Edward Arnold Publishers, London, 1957, p 302.
(10) Hickinbottom, W. J., "Reactions of Organic Compounds", Wiley, New York, N.Y., 1962, p 336.
(11) Jones, R., Ryan, A. J., Sternhall, S., Wright, S. E., *Tetrahedron*, **19**, 1497 (1963).
(12) Kletz, L., Lapworth, A., *J. Chem. Soc.*, 1262 (1915).
(13) Knorr, L., *Ber.*, **29**, 249 (1896).
(14) Korte, F., Wusten, F., *Chem. Ber.*, **96**, 2841 (1963).
(15) Mustafa, A., Khattab, S., Asker, W., *Can. J. Chem.*, **41**, 1813 (1963).
(16) Rothenburg, R. V., *Ber.*, **26**, 1722 (1893).
(17) Sakurai, K., Hiroichi, M., Jun, A., *Yakugaku Zasshi*, **88** (7), 919 (1968); *Chem. Abstr.*, **69**, 94792*j* (1968).
(18) Sawdey, G. W., *J. Am. Chem. Soc.*, **79**, 1955 (1957).
(19) Snavely, F. A., Trahanovesky, W. S., Suydam, F. H., *J. Org. Chem.*, **27**, 994 (1962).
(20) Summers, L. A., Freeman, P. F. H., Shieldes, D. J., *J. Chem. Soc.*, 3312 (1965).
(21) Thiele, J., Salzberger, N., *Justus Liebigs Ann. Chem.*, **319**, 196 (1901).
(22) Toda, S., *J. Chem. Soc. Jpn.*, **80**, 402 (1959).
(23) Wiley, P. F., Weaver, O., *J. Am. Chem. Soc.*, **78**, 808 (1956).
(24) Yao, H. C., Resnick, P., *J. Am. Chem. Soc.*, **84**, 3514 (1962).
(25) Zollinger, H., "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds", Interscience, New York, N.Y., 1961, pp 153, 231.
(26) Zsolnai, T., *Biochem. Pharmacol.*, **14**, (9), 1325 (1965); *Chem. Abstr.*, **63**, 15467d (1965).

Received for review April 27, 1976. Accepted September 28, 1976.

Synthesis and Electronic Spectra of Substituted Bis(hexaphenylbenzenes)

James A. Harvey and Michael A. Ogliaruso*
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

The syntheses of 5 disubstituted hexaphenylbenzenes and 27 tetrasubstituted bis(hexaphenylbenzenes) are reported, and their ultraviolet spectra are discussed.

In two previous papers (*10, 11*) the synthesis and electronic spectra of a number of bis(hexaphenylbenzenes) (BHPB) were reported and discussed in terms of existing information. The conclusions reached were that the main contributor to the electronic spectra for this class of compounds was either the angle between the outer rings and the central ring, the ridigity of the molecule's structure, or a combination of the two (*11*). In an effort to more fully interpret the electronic spectra for these compounds a series of substituted BHPB has been synthesized and their electronic spectra observed.

Results and Discussion

Synthesis. The route chosen to prepare the substituted BHPB is the same as that previously reported (*11*) for the preparation of the unsubstituted BHPB, namely Diels–Alder addition of a series of bis(tetracyclones) with substituted diphenylacetylenes followed by the evolution of carbon monoxide. The substituted diphenylacetylene dienophiles used were all prepared by literature procedures. Preparation of the substituted BHPB was accomplished by allowing the bis(tetracyclones) to react with an excess of the substituted diphenylacetylene at 270–280 °C in a Carius tube sealed under an atmosphere of nitrogen and placed in a Woods' metal bath. All reactions gave good yields of the desired substituted BHPB products, except for the reactions using 4,4′-dinitrodiphenylacetylene (**2**, R = NO_2) with methylene (**6**, Y = CH_2), ether (**6**, Y = O), and sulfide (**6**, Y = S) bis(tetracyclones) which afforded only low melting solids and intractable tars.

The initial product isolated from the reaction of 4,4′-dichlorodiphenylacetylene (**2**, R = Cl) with the sulfur bis(tetracyclone) (**6**, Y = S) was a white solid which softened at 200 °C and appeared to melt from 300 to 310 °C. Heating this solid at 375 °C for 3 min afforded the desired product, bis[2′,5′,6′-triphenyl-3,4′-di(*p*-dichlorophenyl)biphenylyl] sulfide (**7**, R = Cl, Y = S). Although no attempts were made to isolate either the mono- or dicarbonyl adducts from the Diels–Alder addition of the substituted diphenylacetylenes with the bis(tetracyclones), it appears that inadvertently one or both of these carbonyl adducts were isolated in the case of the above reaction. This adduct upon heating completely eliminated the carbon monoxide bridge to afford **7** (R = CL, Y = S).

The possibility that the tetrasubstituted octaphenylquinquephenyls (**3** and **5**) may exist as cis,trans rotamers, effectively