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THE REACTIONS OF 5-METHOXYHYDANTOINS WITH CONJUGATED DIENES[1]

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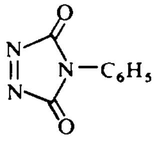
Abstract—5-Methoxyhydantoins **4**, **5** (R = C_7H_7) and **5** (R = C_6H_4Cl) were found to react, thermally or in the presence of an acid catalyst with dienes to give the Diels–Alder adducts **9–19**. The acid catalyzed reactions were found to be more stereospecific than the thermal reactions and in three cases gave the amidoalkylation products **20**, **23**, **24**.

4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE (**1**) is one of the most reactive dienophiles,[2–4] it is much more reactive than its carbon analog N-phenylmaleimide (**2**) in many Diels–Alder additions. In an attempt to prepare the intermediate dienophile 1-phenyl-2,5-imidazolidinedione (**3**), which contains a C=N double bond, we succeeded only in obtaining its methanol addition product—3-phenyl-5-methoxyhydantoin (**4**).



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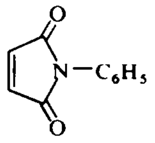

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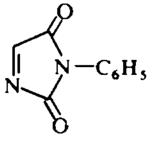

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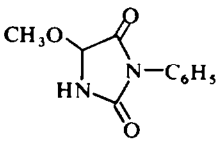

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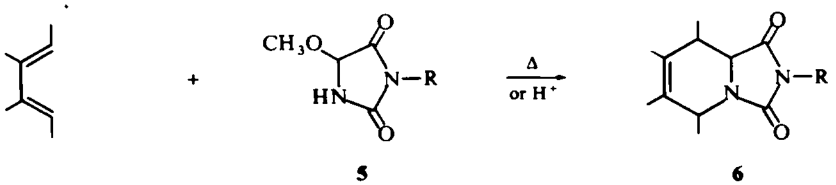
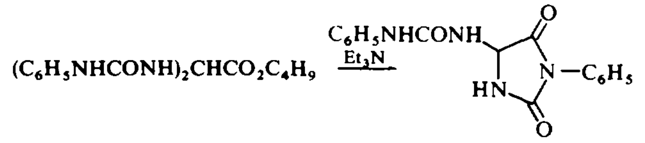
The methoxyhydantoin **4** did, however, react thermally or in the presence of an acid catalyst with conjugated dienes to give Diels–Alder type adducts (**6**, R = C_6H_5):



5 **6**

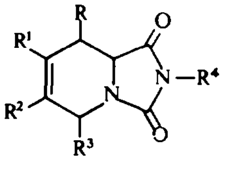
The 3-phenyl-5-methoxyhydantoin (**4**) was prepared by the cyclization of the bisadduct **7** and subsequent treatment of the 3-phenylureidohydantoin (**8**) with hydrogen bromide in acetic acid followed by methanol:



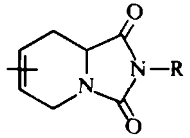
7 **8**

The methoxyhydantoin **4** thus prepared showed a characteristic hydantoin IR spectrum, a CO doublet at 1790 and 1725 cm^{-1} and an NH absorption at 3440 cm^{-1}. Its NMR spectrum showed singlets at δ 3·45 (3H) and 7·42 (5H) and doublets at δ 5·17 (1H) and 7·25 (1H). Attempts to eliminate methanol from **4**, thermally or in the presence of an acid catalyst, led to the formation of polar products which are probably a mixture of polymers (dimers and trimers).[5,6] The methoxyhydantoin was thermally stable up to 180°–190°.

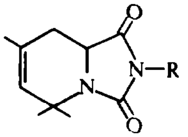
In addition to the 3-phenyl-5-methoxyhydantoin we also used, in the reaction with dienes, 3-benzyl (**5**, $R = C_7H_7$) and 3-*p*-chlorophenyl-5-methoxyhydantoin (**5**, $R = C_6H_4Cl$).[7] The *p*-chlorophenyl derivative is the simplest to prepare and had the advantage of giving crystalline products with all the dienes tried.



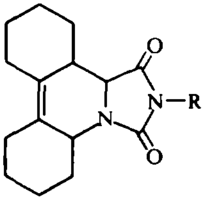
9 a: $R = R^1 = R^2 = R^3 = H$; $R^4 = C_6H_4Cl$
c: $R = R^1 = R^2 = R^3 = H$; $R^4 = C_6H_5$
10 a: $R = R^1 = R^2 = H$; $R^3 = CH_3$; $R^4 = C_6H_4Cl$
c: $R = R^1 = R^2 = H$; $R^3 = CH_3$; $R^4 = C_6H_5$
12 a: $R = R^3 = H$; $R^1 = R^2 = CH_3$; $R^4 = C_6H_4Cl$
c: $R = R^3 = H$; $R^1 = R^2 = CH_3$; $R^4 = C_6H_5$
13 a: $R = R^3 = CH_3$; $R^1 = R^2 = H$; $R^4 = C_6H_4Cl$
c: $R = R^3 = CH_3$; $R^1 = R^2 = H$; $R^4 = C_6H_5$
14 b; $R = R^3 = C_6H_5$; $R^1 = R^2 = H$; $R^4 = C_6H_5CH_2$
16 a; $R = R^1 = R^2 = R^3 = CH_3$; $R^4 = C_6H_4Cl$
b; $R = R^1 = R^2 = R^3 = CH_3$; $R^4 = C_6H_5CH_2$
c; $R = R^1 = R^2 = R^3 = CH_3$; $R^4 = C_6H_5$
17 c; $R = R^3 = CH_3$; $R^1 = R^2 = C_2H_5$; $R^4 = C_6H_5$



11 a: $R = C_6H_4Cl$
c: $R = C_6H_5$



15 a; $R = C_6H_4Cl$
b; $R = C_6H_5CH_2$
c; $R = C_6H_5$

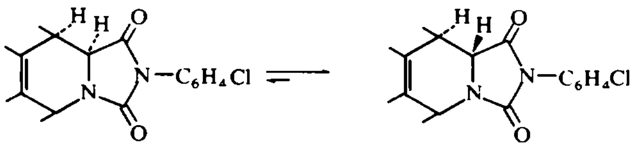


18 a; $R = C_6H_4Cl$
b; $R = C_6H_5CH_2$
c; $R = C_6H_5$

Reacting butadiene, *trans*-piperylene, isoprene, 2,3-dimethylbutadiene, 2,4-hexadiene, 1,4-diphenylbutadiene, 1,2,3,4-tetramethyl butadiene and 1,4-dimethyl-2, 3-diethyl butadiene thermally with 3-phenyl, 3-*p*-chlorophenyl and 3-benzyl-5-methoxyhydantoin gave Diels–Alder adducts (**9–18**) in 16–80% yield. The reactions were carried out in toluene solutions in sealed tubes at 170° for 3 days. The high boiling dienes were also found to react in boiling *p*-xylene but the yields were generally lower. All the adducts obtained with the 3-*p*-chlorophenyl-5-methoxyhydantoin, were crystalline products (**9a–18a**), while most of the benzyl derivatives were oils.

Each of the adducts was identified by its IR and NMR spectra. The imidazopyrimidinones (**9–18**) retained the hydantoin CO doublets at 1790 and 1725 cm^{-1} but lacked the NH absorptions of the starting material at 3400–3500 cm^{-1} in the IR. The main features of their NMR spectra were the protons at the C-5 of the hydantoin system which absorbed at δ 3·5–4·5 ppm. This proton appeared as a quartet (ABX system) in compounds **10** and **15** which supports the structure assigned to them. In compounds **13**, **14**, **16**, **17** and **18** this proton (C-5) appeared as a doublet. In compounds **9**, **11** and **12** they appeared as multiplets.

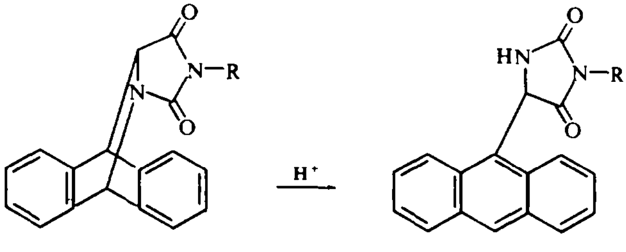
Reacting 1,2,3,4-tetramethylbutadiene with 3-*p*-chlorophenyl-5-methoxyhydantoin in toluene at 170° for 3 days (sealed tube) gave a mixture of two adducts (**16a**) which are according to their NMR spectra a mixture of *cis-trans* isomers:



cis *trans*

The structure assigned to the two stereoisomers is based on the coupling of the C-5 proton of the hydantoin system. One isomer (*cis*) showed a doublet with a coupling constant of 5 cs at δ 4·15 ppm while the other isomer showed a doublet with a coupling constant of 11 cs at δ 3·72 ppm. The same type of isomers were observed in the cases of 2,4-hexadiene (**13**), 1,4-diphenylbutadiene (**14**), 1,4-dimethyl-2,3-diethyl-butadiene (**17**) and 1,1′-bicyclohexenyl (**18**). The ratio of *cis* to *trans* isomers was found to depend on the nature of the diene and the reaction conditions. Thus, 2,4-hexadiene (*t*,*t*) gave thermally only the *trans* isomer (**13a**) while the tetramethylbutadiene afforded, under the same experimental conditions a *cis-trans* ratio of 3:1 (**16a**). The ratio of isomers changed in favour of the *cis* isomers as the reaction temperature was lowered. In boiling *p*-xylene (138°) 1,2,3,4-tetramethyl butadiene gave almost pure *cis* isomer. The isomers with the smaller coupling constants (*cis*) were found to isomerize, thermally or in the presence of a base or acid catalyst, to the isomers with the larger coupling constants (*trans*). The *cis*-adducts from 1,4-diphenylbutadiene (**14a**) was found to isomerize even on an alumina column.

Anthracene reacted with 5-methoxyhydantoins in boiling xylene for three days to give the adducts **19** which isomerized readily to the amidoalkylation product **20** on treatment with acid. It also decomposed on an alumina column. This liability recalls the behaviour of anthracene adducts with 4-phenyl-1,2,4-triazoline-3,5-dione[2] and with azodicarboxylates:[3]

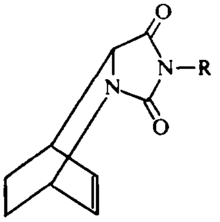


19 **20**

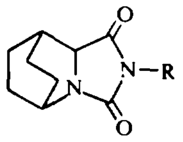
a; $R = C_6H_4Cl(p)$
b; $R = C_6H_5CH_2$

The reactions of the methoxyhydantoins with dienes was found to be strongly acid catalyzed. Thus, reacting 1,2,3,4-tetramethylbutadiene and 1,4-dimethyl-2,3-diethylbutadiene with 3-phenyl-5-methoxyhydantoin in boiling benzene and in the presence of β-naphthalenesulfonic acid for 2 hr afforded Diels–Alder adducts (**16c**; **17c**) in 75 and 74% yield respectively. Only the *cis* isomers were obtained. Under the same experimental conditions 1,1′-bicyclohexenyl afforded a mixture of *cis-trans* isomers in a 1:2 ratio (NMR) and in 76% overall yield (**18**). 2,4-Hexadiene which reacted thermally with 3-*p*-chlorophenyl-5-methoxyhydantoin to give only the *trans* isomer in 53%, was found to react in boiling benzene and in the presence of trifluoroacetic acid to give only the *cis* isomer in 25% yield. This isomer isomerized thermally to the *trans* isomer.

1,3-Cyclohexadiene reacted with the methoxyhydantoin in boiling benzene in the presence of trifluoroacetic acid to give the adducts **21** in 30–33% yield. The thermal reaction with the *p*-chlorophenyl derivative gave **21a** in 75% yield:



21



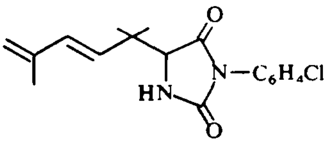
22

a; $R = C_6H_4Cl$
b; $R = C_7H_7$
c; $R = C_6H_5$

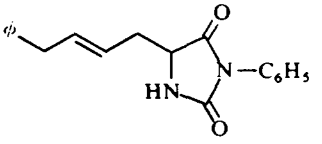
These products are probably the *endo* isomers since catalytic hydrogenation of the double bond of **21b** and **21c** to give compound **22** showed a deshielding effect on the phenyl group of **21c** and on the methylene and the phenyl of **21b** in the NMR spectra.

While there was not a big difference in yields between the thermal and the acid catalyzed reaction with the tetra substituted dienes, there was a difference in yield with the di and mono substituted dienes. The acid catalyzed reactions gave generally a more complex mixture of products with lower yields of the Diels–Alder adducts.

1,1,4,4-Tetramethylbutadiene which is known to be a poor diene reacted with 3-*p*-chlorophenyl-5-methoxyhydantoin in boiling benzene and in the presence of trifluoroacetic acid to give the amidoalkylation product **23** in 64% yield. Butadiene reacted with 3-phenyl-5-methoxyhydantoin, in benzene solution at room temperature and in the presence of boron trifluoride ether complex, to give, in addition to the Diels–Alder type product (**9c**, 10%) the amidoalkylation product **24** (72%).



23



24

The thermal reaction with butadiene was carried out in an autoclave at 170° in benzene solution for 3 days. The yield of **9a** was only 16%.

EXPERIMENTAL

Mps are corrected, IR spectra were measured in $CHCl_3$ and NMR spectra in $CDCl_3$ (unless otherwise indicated).

Carbobutoxymethylenebisphenylurea (7). A solution of N-phenylurea (20·4 g, 0·15 mole) butyl glyoxylate (10·4 g, 0·08 mole) in glacial AcOH (100 ml) containing HBr in AcOH (5 ml, 32%), was left at room temp for 1 hr. The solid mass was filtered off, washed with ether and then triturated with MeOH (500 ml) and filtered again. The triturated product 26·5 g (92%) was pure enough for the cyclization. An analytical sample was obtained by crystallization from BuOH m.p. 250°; IR (KBr): 3350, 1740, 1650, 1610 and 1550–1580 cm^{-1}. (Found: C, 62·62; H, 6·55; N, 14·61. $C_{20}H_{24}N_4O_2$ requires: C, 62·48; H, 6·29; N, 14·58%).

3-*Phenyl-5-phenylureidohydantoin* (8). A suspension of the bisadduct described (38·4 g, 0·1 mole) in MeOH (400 ml) containing Et_3N (4 ml) was refluxed with stirring for 4 hr. The starting material went into soln after 0·5 hr and the product started to precipitate out. The mixture was cooled and the solid product was filtered off and washed with ether. The yield was 30·5 g (98%) and the product used in the next step without further purification. An analytical sample was obtained by crystallization from nitromethane; m.p. 251°; IR (KBr): 3380, 3290, 1790, 1730, 1695, 1610, 1560 and 1510 cm^{-1}. (Found: C, 61·64; H, 4·86; N, 17·83. $C_{16}H_{14}N_4O_3$ requires: C, 61·93; H, 4·55; N, 18·06%).

3-*Phenyl-5-methoxyhydantoin* (4). A mixture of **8** (25·0 g) in HBr in AcOH (250 ml, 32%) was stirred at room temp until all the solid dissolved. The soln was left at room temp for 3 days and then poured into MeOH (400 ml). After 20 min the soln was diluted with EtOAc (2·0 li) washed with water and $NaHCO_3$ aq and dried over $MgSO_4$. The oily residue obtained after the removal of the solvent (27 g) was chromatographed over neutral alumina (270 g). The methoxyhydantoin was eluted with CH_2Cl_2 and crystallized from EtOAc–hexane. The yield was 7·5 g (50%); m.p. 111–112°; IR: 3440, 1790 and 1715 cm^{-1}; NMR: δ 7·42 (s, 5H); 7·25 (d, 1H, broad); 5·17 (d, 1H, J = 2 cs); 3·45 (s, 3H); *m/e* 206. (Found: C, 58·21; H, 5·14; N, 13·76. $C_{10}H_{10}N_2O_3$ requires: C, 58·25; H, 4·89; N, 13·58%).

The thermal reaction of 5-methoxyhydantoin with dienes—General procedure. A mixture of the hydantoin (0·01 mole), the diene (0·04 mole) in toluene (12 ml) in a sealed tube, was heated in an electric oven to 170° for 3 days. The mixture was evaporated *in vacuo* to dryness and the residue chromatographed over neutral alumina (80 g). The products were eluted with benzene and crystallized from EtOAc–hexane. The results are summarized in Table 1.

The reaction with butadiene was carried out in an autoclave at 170° in benzene soln.

Reaction of 3-p-*chlorophenyl-5-methoxyhydantoin with* 1,2,3,4-*tetramethylbutadiene* (**16a**). A refluxing

TABLE 1. THERMAL REACTIONS

Diene	Adduct	M.p. °C	Yield %	Anal. % C		H		N	
Butadiene	**9a**	154	16	59·44	59·73	4·22	4·40	10·66	10·33
t-Piperylene	**10a**	129	61	60·77	60·48	4·74	4·84	10·12	9·94
Isoprene	**11a**	165	46	60·77	61·17	4·78	4·87	10·12	9·86
	11c	120	42	69·40	69·16	5·83	5·79	11·56	11·38
2,3-Dimethylbutadiene	**12a**	217	19	61·97	62·11	5·20	5·17	9·63	9·61
	12c	124	23	70·29	69·86	6·29	6·02	10·93	10·67
2,4-Hexadiene (*t,t*)	**13a**	138[a]	53	61·97	62·03	5·20	5·07	9·63	9·49
	13c	135[a]	46	70·29	70·15	6·29	6·19	10·93	10·74
1,4-Diphenylbutadiene	**14b**	132[a]	28[c]	79·16	79·10	5·62	5·45	7·10	7·37
2,4-Dimethyl-1,3-pentadiene	**15a**	131	79	63·05	63·01	5·62	5·60	9·19	8·92
	15b	oil	63	71·80	71·72	7·09	6·92	9·85	9·74
	15c	108	70	71·09	70·80	6·71	6·65	10·32	10·10
1,2,3,4-Tetramethylbutadiene	**16a**	125[a]	75[c]	64·05	64·22	6·01	6·04	8·79	8·78
	16b	105[b]	70			*d*			
	16c	98[a]	80[f]	71·80	71·88	7·09	7·32	9·85	10·03
1,3-Cyclohexadiene	**21a**	171	75	62·40	62·52	4·54	4·65	9·70	9·49
	21c	145	64	70·85	70·59	5·55	5·56	11·02	10·95
1,1'-Bicyclohexenyl	**18a**	173[a]	80[f]	68·05	68·35	6·19	6·23	7·55	7·29
	18c	148[a]	70[f]	74·97	74·69	7·19	7·11	8·33	8·09
Anthracene	**19a**	228	73	71·50	71·54	3·95	4·05	7·27	7·21
	19b	231	52	78·67	78·41	4·95	5·01	7·65	7·87

[a] *trans* Isomer. [b] *cis* Isomer. [c] Mixture of *cis-trans* isomers. [d] Identical with the product obtained in the acid catalyzed reaction.

TABLE 2. ACID CATALYZED REACTIONS

Diene	Adduct	M.p. °C	Yield %	Anal. %					
				C		H		N	
Butadiene	**9a**	154	15			*c*			
	9c	152	10	68·43	68·63	5·30	5·56	12·27	11·98
2,4-Hexadiene (*t*,*t*)	**13a**	147^a	25	61·97	62·10	5·20	5·15	9·63	9·75
1,4-Diphenylbutadiene	**14b**	146^a	31^b	79·16	78·90	5·62	5·61	7·10	6·86
2,4-Dimethyl-1,3-pentadiene	**15a**	131	41			*c*			
1,2,3,4-Tetramethylbutadiene	**16a**	148^a	72	64·05	63·85	6·01	5·99	8·79	8·77
2,3-Dimethyl-1,4-dimethylbutadiene	**17c**	96^a	74	73·04	72·98	7·74	7·77	8·99	8·94
1,1′-Bicyclohexenyl	**18c**	144^a	76^b	74·97	74·71	7·19	7·15	8·33	8·21
1,3-Cyclohexadiene	**21a**	171	33			*c*			
	21b	125	30	71·62	71·56	6·01	6·07	10·44	10·31
	21c	145	30			*c*			

[a] *cis*-Isomer

[b] Mixture of *cis*-*trans* isomers

[c] Identical with the product obtained in the thermal reaction

mixture of 3-*p*-chlorophenyl-5-methoxyhydantoin (0·6 g) tetramethylbutadiene (1·3 ml) in *p*-xylene for 3 days afforded the *cis* adduct **16a**, 0·37 g (46%); it melted at 138° after crystallization from EtOAc–hezane; IR: 1770 and 1720 cm^{-1}; NMR: δ 7·45 (s, 4H), 4·15 (d, 1H, J = 5 cs); 4·05 (m, 1H), 2·65 (m, 1H), 1·8 – 1·6 (9H), 1·05 (d, 3H, J = 7 cs) (Table 1).

cis-trans-*Isomerization of* **16a**. A soln of *cis* **16a** (0·04 g) in benzene (2 ml) containing β-naphthalenesulfonic acid (0·01 g) was refluxed for 2 hr. The NMR spectrum showed an 8·1 ratio of *cis* to *trans* isomers. after 16 hr reflux the mixture showed a *cis-trans* ratio of 1:2.

b. A soln of the *cis* isomer (0·25 g) in t-BuOH (10 ml) containing KO-Bu-t (0·1 g) was refluxed for 2 hr. The NMR spectrum of the crude product showed a 1:1 ratio of the *cis* to *trans* isomers.

c. A soln of the *cis* isomer (0·1 g) in *p*-xylene (2 ml) was heated in a sealed tube for 3 days at 210°. The NMR spectrum showed a 1:2·5 ratio of the *cis* to *trans* isomers. The TLC of the reaction mixture showed spots of less and more polar by-product.

The *trans* isomer was isolated from the mixture of the acid catalyzed isomerization with hexane. It melted at 125° after crystallization from EtOAc–hexane; IR: 1790 and 1730 cm^{-1}; NMR: δ 7·42 (s, 4H); 4·3 (m, 1H); 3·72 (d, 1H, J = 11 cs); 1·7 (m, 6H) and 1·4 (d, 3H, J = 3 cs).

Reaction with anthracene (**19b**). A soln of 3 benzyl-5-methoxyhydantoin (3 g), anthracene (1·35 g) in *p*-xylene (20 ml) was refluxed for 3 days. The product was precipitated with hexane, triturated once with hexane and then with MeOH in order to remove the less and the more polar by-products or starting materials. Crystallization from EtOAc–hexane afforded 1·2 g (52%) of Diels–Alder adduct; m.p. 231°; IR: 1780 and 1720 cm^{-1}; NMR: δ 7·5–7·0 (m, 11H), 6·7–6·5 (m, 2H), 6·08 (s, 1H), 4·82 (d, 1H, J = 2 cs), 4·4 (s, 2H) and δ 4·13 (d, J = 2 cs).

The adduct (**19b**) was converted to the amidoalkylation product **20b** on treatment with β-naphthalenesulfonic acid in boiling benzene for 15 min. The soln was diluted with EtOAc, washed with water, dried over $MgSO_4$ and taken to dryness. The residue was triturated with ether and crystallized from EtOAc–hexane; m.p. 240° (75%); IR: 3460, 1780 and 1720 cm^{-1}. (Found: C, 79·05; H, 5·06; N, 7·30. $C_{24}H_{18}N_2O_2$ requires: C, 78·67; H, 4·95; N, 7·65%).

The acid catalyzed reaction of 5-methoxyhydantoin with dienes—General procedure. A soln of the hydantoin (0·01 mole), the diene (0·04 mole) and β-naphthalenesulfonic acid (0·3 g) in benzene (35 ml) was refluxed until the disappearance of the hydantoin (2–4 hr, TLC). The residue obtained after the removal of the solvent *in vacuo* was chromatographed over neutral alumina (75 g) and eluted with benzene. It was crystallized from EtOAc–hexane. The results are summarized in Table 2.

The reaction with 2,4-hexadiene. A soln of 3-*p*-chlorophenyl-5-methoxyhydantoin (1·2 g; 0·005 mole), t,t-2,4-hexadiene (2 ml, 0·02 mole), trifluoroacetic acid (1·2 ml) in benzene (24 ml) was refluxed for 18 hr. The residue obtained after the removal of the solvent *in vacuo* was chromatographed over neutral alumina (20 g). The product was eluted with benzene; m.p. 147° after crystallization from EtOAc–hexane; yield 0·340 g (25%); IR: 1780 and 1730 cm^{-1}; NMR: δ 7·40 (s, 4H); 5·75 (m, 2H); 4·30 (m, 1H), 4·15 (d, 1H; J = 5 cs); 2·80 (m, 1H); 1·80 (d, 3H; J = 9 cs), 1·05 (d, 3H; J = 9 cs); *m/e* = 290. (Table 2).

The thermal reaction which was carried out according to the general procedure afforded after chromatography the *trans* isomer (53%) which melted at 138° after crystallization from EtOAc–hexane; IR 1780 and 1720 cm^{-1}; NMR: δ 7·45 (s, 4H); 5·65 (s, 2H); 4·60 (m, 1H); 3·65 (d, 1H; J = 12 cs); 2·5 (m, 1H); 1·40 (d, 3H; J = 3 cs); 1·30 (d, 3H; J = 3 cs); *m/e* = 290. (Table 1).

The *cis* isomer isomerized partly to the *trans* isomer under the conditions of the general procedures for the thermal and acid catalyzed reactions.

Reaction with 1,3-cyclohexadiene (**21c**). A mixture of 3-phenyl-5-methoxyhydantoin (2·06 g, 0·01 mole), 1,3-cyclohexadiene (2 ml, 0·03 mole), trifluoroacetic acid (1 ml) in benzene (20 ml) was refluxed for 24 hr. The residue obtained after the removal of the solvent *in vacuo* was chromatographed over neutral alumina (60 g) and eluted with benzene. The product **21c** (0·82 g, 31%) was crystallized from EtOAc–hexane; IR: 1780 and 1720 cm^{-1}; NMR: δ 7·40 (s, 5H), 4·75 (m, 1H), 4·0 (d, 1H; J = 2 cs), 3·3 (m, 1H), 6·40 (m, 2H) and δ 2·4–1·1 (m, 4H) (Table 2).

The benzyl derivative **21b** was prepared similarly. It was crystallized from EtOAc–hexane (Table 2); IR: 1775 and 1720 cm^{-1}; NMR: δ 7·35 (s, 5H), 6·35 (m, 2H), 4·65 (m, 1H), 4·60 (s, 2H), 3·85 (d, 1H, J = 2 cs), 3·2 (m, 1H) and δ 1·65 (m, 4H).

Reacting 3-*p*-chlorophenyl-5-methoxyhydantoin (2·4 g), 1,3-cyclohexadiene (3·8 ml, 0·04 mole) and trifluoroacetic acid (2 ml) in benzene (45 ml) as described above afforded the product **21a** which was crystallized from EtOAc–hexane (Table 2).

Catalytic hydrogenation of **21**. A mixture of **21c** in EtOAc (25 ml) and 10% Pd/C (0·050 g) was catalytically hydrogenated at atmospheric pressure. The equivalent of H_2 was absorbed within 15 min. The soln was filtered, concentrated under reduced pressure and the residue was crystallized from cyclohexane; m.p. 160°; IR: 1780 and 1720 cm^{-1}; NMR: δ 7·48 (s, 5H), 4·1 (m, 2H), 2·45 (m, 1H), 1·85 (s, 4H) and δ 1·55 (m, 4H); *m/e* = 256. (Found: C, 69·95; H, 6·26; N, 10·56. $C_{15}H_{16}N_2O_2$ requires: C, 70·29; H, 6·29; N, 10·93%).

The benzyl derivative **21b** was hydrogenated similarly to give a product which melted at 120° after crystallization from EtOAc–hexane; IR: 1775 and 1710 cm^{-1}; NMR: δ 7·40 (5H), 4·70 (s, 2H), 3·95 (m, 2H) and δ 2·5–1·0 (m, 9H). (Found: C, 71·40; H, 6·67; N, 10·11. $C_{16}H_{18}N_2O_2$ requires: C, 71·09; H, 6·71; N, 10·36%).

Reaction of 3-phenyl-5-methoxyhydantoin with butadiene in the presence of boron trifluoride etherate. To a suspension of the hydantoin (3 g) in benzene (15 ml) containing excess butadiene (2·25 g) there was added with stirring BF_3–etherate (3 ml). The soln was left at room temp for 24 hr and then was diluted with EtOAc (200 ml). The EtOAc soln was washed with water, $NAHCO_3$ aq and dried over $MgSO_4$. The residue obtained after the removal of the solvent was chromatographed over neutral alumina (100 g). Elution with benzene gave 0·23 g (10%) of **9c**. (Table 2), which was crystallized from EtOAc–hexane; IR: 1775, 1710 and 1600 cm^{-1}; NMR: δ 7·45 (s, 5H), 5·9 (s, 2H), 4·1 (m, 3H), 2·6 (m, 2H); *m/e* = 228.

CH_2Cl_2 eluted the more polar product **24** (3·1 g, 72%). It melted at 110° after crystallization from EtOAc–hexane: IR: 3450, 3250, 1780, 1710 and 1490 cm^{-1}; NMR: δ 7·45 (s, 5H), 7·25 (s, 5H), 6·85 (s, 1H), 5·75 (m, 2H), 4·15 (m, 1H), 3·35 (d, 2H, J = 8 cs), 2·6 (m, 2H); *m/e* = 3·6. (Found: C, 74·23; H, 5·88; N, 9·40. $C_{19}H_{18}N_2O_2$ requires: C, 74·49; H, 5·92; N, 9·15%).

The reaction of 1,1,4,4-*tetramethylbutadiene with* 2-p-*chlorophenyl*-5-*methoxyhydantoin* (**23**). A mixture of the hydantoin (2·4 g), 1,1,4,4-tetramethylbutadiene (3·3 g), trifluoroacetic acid (2·4 ml) in benzene (45 ml) was refluxed for 24 hr. The soln was taken to dryness *in vacuo* and the residue was chromatographed over neutral alumina (80 g). The product was eluted with benzene to give 1·95 g (64%) of a crystalline product. It melted at 143° after crystallization from EtOAc- hexane; IR: 3450, 3250, 1780, 1730, 1610 and 1495 cm^{-1}; NMR: δ 7·35 (d, 4H), 7·15 (m, 1H), 5·9 (q, 2H), 4·95 (s, 2H), 3·9 (s, 1H), 1·75 (s, 3H), 1·30 (s, 3H), 1·22 (s, 3H). (Found: C, 64·34; H, 5·85; N, 8·49. $C_{17}H_{19}N_2O_2Cl$ requires: C, 64·05; H, 6·01; N, 8·79%).

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