The Amidoalkylation of Aromatic Compounds and Olefins with 5-Alkoxyhydantoins (1,2)

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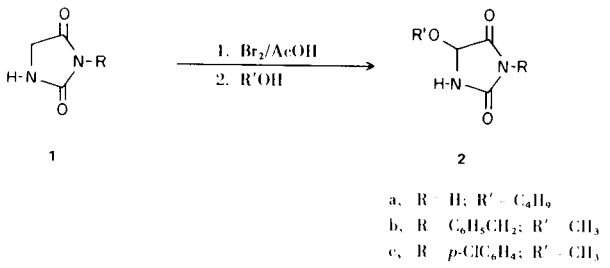
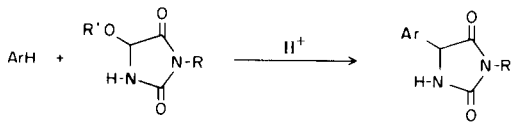
5-Butoxyhydantoin (**2a**), 3-benzyl-5-methoxyhydantoin (**2b**) and 3-*p*-chlorophenyl-5-methoxy hydantoin (**2c**) were found to react, in the presence of an acid catalyst, with aromatic compounds and olefins to give 5-arylhydantoin (3) and 5-alkylhydantoins with an unsaturated side chain. Isomers which differ in the location of the double bond (**4**,**5**,**6**) as well as *cis-trans* isomers were isolated and characterized.

Cyclic acylimines and their methanol addition products, *N*-α-methoxylactams, were found to react, in the presence of an acid catalyst, with active methylene compounds and dienes to give amidoalkylation or Diels-Alder type products (3,4). 5-Methoxyhydantoins which also possess the methoxylactam grouping reacted similarly with dienes to give two types of products (5). The amidoalkylation products, in this case, were 5-substituted hydantoins which are known as synthetic precursors of amino acids. We extended therefore the reactions of the 5-alkoxyhydantoins to aromatic compounds and olefins in order to develop a new synthesis of 5-substituted hydantoins (amino acids) bearing aromatic and unsaturated side chains. The general scope of the amidoalkylations of aromatic compounds and aliphatic compounds containing active methylene or methine groups was reviewed by Zaugg and Martin (6).



1 2

a, R = H; R' = C_4H_9
b, R = $C_6H_5CH_2$; R' = CH_3
c, R = *p*-ClC_6H_4; R' = CH_3



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a, R = H, Ar = C_6H_5
b, R = *p*-ClC_6H_4, Ar = C_6H_5
c, R = H, Ar = p-ClC_6H_4
d, R = H, Ar = CH_3CONH-C_6H_4
e, R = H, Ar = $C_{10}H_7$
f, R = H, Ar = $C_{14}H_9$
g, R = H, Ar = $(CH_3)_2C_6H_3$
h, R = H, Ar = $CH_3C_6H_4$
i, R = $C_6H_5CH_2$, Ar = $CH_3C_6H_4$
j, R = C_6H_5-CH_2, Ar = C_6H_5

The three 5-alkoxyhydantoins which were used in the reactions were prepared by the bromination of the corresponding hydantoin, followed by the action of an alcohol. Thus, bromination of hydantoin (1, R = H) with bromine in glacial acetic acid at 85-95° and subsequent treatment of the reaction mixture with *n*-butanol afforded the 5-*n*-butoxyhydantoin (**2a**) in 53% yield. Similarly prepared were 3-benzyl-5-methoxyhydantoin (**2b**) in 93% yield and 3-*p*-chlorophenyl-5-methoxyhydantoin in 87% yield.

The alkylation of the aromatic compounds, with the above described alkoxyhydantoins, were carried out in concentrated sulfuric acid at room temperature, or in boiling chloroform in the presence of boron trifluoride etherate as the acid catalyst. The sulfuric acid method was especially useful in the cases of the less reactive aromatic compounds. Thus, reacting benzene, chlorobenzene and acetanilide with 5-butoxyhydantoin for 24 hours afforded the corresponding 5-substituted hydantoins **3** in 50-90% yield. Naphthalene and phenanthrene reacted in boiling chloroform and in the presence of boron trifluoride etherate. The 5-tolyl derivative was obtained by refluxing a toluene solution of the 5-butoxyhydantoin for 48 hours in the presence of boron trifluoride.

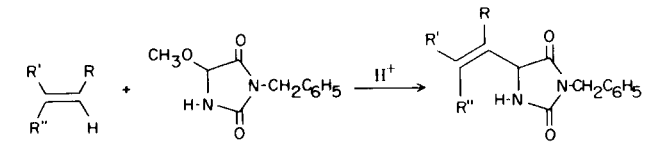
In the case of the monosubstituted benzene derivatives the crude product contained a mixture of *ortho* and *para* isomers. The *para* isomers which predominated were obtained pure on repeated crystallizations. In the case of the tolyl and the acetamido derivatives the products were identified with the authentic hydantoins which were prepared from the *p*-substituted benzaldehyde, potassium cyanide and ammonium carbonate.

Similar results were also obtained with the 3-*p*-chlorophenyl-5-methoxyhydantoin and 3-benzyl-5-methoxy-

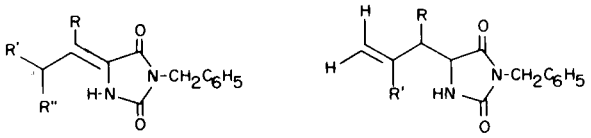
hydantoin. Both were more reactive in the alkylation reactions than the 5-butoxyhydantoin. The 3-benzyl-5-methoxyhydantoin could not be subjected to the concentrated sulfuric acid procedure due to its instability in the concentrated acid. It did however react with toluene or benzene at reflux in the presence of boron trifluoride etherate to give the expected products.

The infrared spectra of the 5-arylhydantoins showed the characteristic hydantoin CO absorptions at 1780 and 1720 cm^{-1} and the NH absorption at 3440 cm^{-1}. The NMR spectra showed the C-5 hydrogen, of the hydantoins at δ 5.10-5.30 ppm.

3-Benzyl-5-methoxyhydantoin was found to react with olefins in boiling benzene and in the presence of naphthalene-2-sulfonic acid, to give one of the isomeric products **4**,**5** or **6**, or a mixture of products.



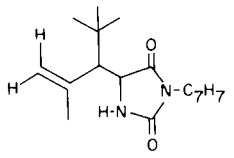
2b **4**



5 **6**

In general, olefins capable of yielding tertiary or benzyl carbonium ion intermediates reacted faster than the mono- or *sym*-disubstituted olefins. Reacting 1,1-diphenylethylene and 1,1-diphenylpropylene with the methoxyhydantoin **2b** for 17 hours afforded the corresponding products **4** (R = H; R′ = R″ = C_6H_5) and **4** (R = CH_3; R′ = R″ = C_6H_5) in 78 and 67% yield. α-Methylstyrene reacted similarly to give a mixture of *cis-trans* isomers (**4**, R = H, R′ = CH_3; R″ = C_6H_5) in 75% yield. β-Methylstyrene, β,β-dimethylstyrene and indene gave under the same experimental conditions a more complex mixture of products. Styrene itself reacted with 3-benzyl-5-methoxyhydantoin in refluxing 1,1,2-trichloroethane to give a *cis-trans* mixture of a product of type **5** (R = R′ = H; R″ = C_6H_5) with the double bond conjugated to the hydantoin carbonyl group. 2-Phenyl-2-butene gave a type **6** (R = CH_3; R′ = C_6H_5) product in 68% yield.

Isobutylene reacted with the 3-chlorophenyl-5-methoxyhydantoin in 1,1,2-trichloroethane solution at 80° in a sealed tube to give a mixture of type **4** and type **5** products. We did not succeed in separating the two isomers but catalytic hydrogenation of the mixture afforded one product, identical with the hydantoin prepared from the amino acid leucine. Reacting isobutylene with the butoxyhydantoin (**2a**) in methylene chloride at room temperature and in the presence of boron trifluoride etherate afforded a different product which possesses an eight carbon side chain (**7**). This product was derived from the dimer of isobutylene. Tetramethylethylene which does not have olefinic hydrogen reacted smoothly with 3-benzyl-5-methoxyhydantoin to give a type **6** product (**8**) in 75% yield. Allyl benzene and 1-octene



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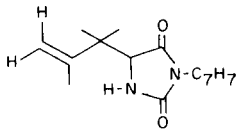

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reacted sluggishly with the alkoxy hydantoin. Tetraphenyl and triphenylethylene as well as 2-methyl-1,1-diphenylpropene failed to react with the methoxyhydantoins under the conditions used.

EXPERIMENTAL

Melting points are corrected, infrared spectra were measured in chloroform solutions and NMR spectra in deuteriochloroform (unless otherwise indicated).

5-Butoxyhydantoin (**2a**).

To a hot solution (90-95°) of hydantoin (20.0 g., 0.20 mole) in glacial acetic acid (80 ml.) there was added, dropwise with stirring, a solution of bromine (35.2 g., 0.22 mole) in glacial acetic acid (20 ml.). The addition was regulated according to the disappearance of the bromine (30 minutes). The heating was continued for an additional 30 minutes and the solution was cooled to 40-50° before *n*-butanol (200 ml.) was added. The reaction mixture was allowed to stand at room temperature overnight, ethyl acetate (600 ml.) was added and the solution was neutralized with powdered sodium carbonate and dried over magnesium sulfate. The residue obtained after removal of the solvent was triturated with petroleum ether and filtered to give 24.5 g. of crude 5-butoxyhydantoin. The product was purified by column chromatography (200 g. neutral alumina), employing 5% methanol in chloroform as eluent. The yield of pure product was 19.0 g. (55%) m.p. 105-106°; ir: 3440, 3260-3140, 1800 and 1750 cm^{-1}; nmr (DMSO d_6); δ 0.8-1.6 (m, 7H), 3.3-3.7 (m, 2H), 5.15 (d, 1H J = 2 cps), 8.46 s, 1H) and 10.70 (s, 1H) ppm.

Anal. Calcd. for $C_7H_{12}N_2O_3$: C, 48.84; H, 6.98; N, 16.28. Found: C, 48.76; H, 6.99; N, 16.50.

3-Benzyl-5-methoxyhydantoin (**2b**).

A hot solution (90-95°) of 3-benzylhydantoin (15.0 g., 0.079 mole) in glacial acetic acid (80 ml.) was brominated with bromine (16.54 g., 0.104 mole) as described above. The acetic acid was removed under reduced pressure and methanol (75 ml.) was added to the residue. The solution was left at room temperature for

20 hours, the solvent was evaporated and the oily residue was purified by chromatography (neutral alumina), employing methylene chloride as the eluent. The yield of the oily product was 15.0 g. (93%); ir: 3450, 3300-3210, 1785 and 1725 cm^{-1}; n.m.r.: δ 3.32 (s, 3H); 4.63 (s, 2H), 5.08 (d, 1H, J = 2 cps) and 7.32 (s, 5H) ppm.

Anal. Calcd. for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.75; H, 5.74; N, 12.42.

3-(*p*-Chlorophenyl)-5-methoxyhydantoin (**2c**).

A hot solution of 3-*p*-chlorophenylhydantoin (10.53 g., 0.05 mole) in acetic acid (100 ml.) was brominated with bromine (3 ml.) in acetic acid (20 ml.) as described above. The solution was cooled to 40° and methanol (400 ml.) was added. After standing at room temperature overnight, the solution was evaporated to dryness and the residue was taken up in ethyl acetate (500 ml.) and water. The organic layer was washed with aqueous sodium bicarbonate, dried and evaporated under reduced pressure. The residue was triturated with ethyl acetate (10 ml.) and filtered to give 10.5 g. (87.5%) of a white solid which was found to be pure enough for the alkylation reactions. An analytical sample was obtained by the crystallization from ethyl acetate; m.p. 176°; ir: 3450, 3280-3240, 1800, 1745 and 1605 cm^{-1}; n.m.r. (acetone d_6): 3.48 (s, 3H), 5.38 (s, 1H), 7.50 (s, 4H) and 8.40 (s, 1H).

Anal. Calcd. for $C_{10}H_9ClN_2O_3$: C, 49.91; H, 3.76; Cl, 14.78; N, 11.64. Found: C, 49.90; H, 3.65; Cl, 15.06; N, 11.54.

5-Phenylhydantoin (**3a**).

To a cooled (0°) solution of 5-butoxyhydantoin (**2a**) (1 g.) in concentrated sulfuric acid (5 ml.) was added excess benzene (2 ml.). The reaction mixture was stirred at room temperature overnight, and was then poured onto crushed ice. The aqueous suspension was continuously extracted overnight with chloroform and the residue obtained after the removal of the solvent was crystallized from 2-propanol-petroleum ether. The yield was 95%, m.p. 180-181° (lit. (7) m.p. 181-183°).

3-*p*-Chlorophenyl-5-phenylhydantoin (**3b**).

3-*p*-Chlorophenyl-5-methoxyhydantoin (**2c**) (6.0 g.) in concentrated sulfuric acid (25 ml.) was treated with benzene (15 ml.) as described above. The aqueous suspension was extracted with ethyl acetate dried and evaporated. The residue was chromatographed over neutral alumina (160 g.) using chloroform as the eluent. The product melted at 177-178° after crystallization from ethyl acetate-hexane, yield 2.5 g. (35%).

Anal. Calcd. for $C_{15}H_{11}ClN_2O_2$: C, 62.83; H, 3.84; Cl, 12.40; N, 9.76. Found: C, 62.70; H, 3.93; Cl, 12.18; N, 9.66.

5-*p*-Chlorophenylhydantoin (**3c**).

A solution of 5-butoxyhydantoin (**2a**) (8.0 g.) in concentrated sulfuric acid (40 ml.) was treated with chlorobenzene (16 ml.) as described above. After pouring onto crushed ice, the product was extracted with ethyl acetate and the solution was washed with aqueous bicarbonate (5%) and dried over magnesium sulfate. The residue was triturated with hexane to give 8.6 g. of crude product. The crude product was a mixture of two isomers (tlc). Two crystallizations from ethyl acetate-hexane gave a pure product, m.p. 142-144°, yield 4.9 g. (50%), ir: 3440, 3220 (broad) 1800 and 1720 cm^{-1}; n.m.r. (DMSO d_6): δ 5.28 (s, 1H), 7.54 (s, 4H).

Anal. Calcd. for $C_9H_7ClN_2O_2$: C, 51.32; H, 3.33; N, 13.30. Found: C, 51.49; H, 3.48; N, 13.19.

5-(*p*-Acetamidophenyl)hydantoin (**3d**).

A solution of 5-butoxyhydantoin (**2a**) (0.86 g., 0.005 mole) in concentrated sulfuric acid was treated with acetanilide (0.67 g., 0.005 mole) as described above. After pouring onto crushed ice the product was filtered, triturated with methanol (10 ml.) and then crystallized from methanol. It melted at 315°, yield 0.70 g. (60%); ir (potassium bromide) 3300, 3100 (broad), 1780, 1720 (broad), 1680, 1610 and 1545 cm^{-1}; m/e = 233.

Anal. Calcd. for $C_9H_7ClN_2O_2$: C, 56.65; H, 4.72; Cl, 16.86; N, 18.03. Found: C, 56.66; H, 4.75; Cl, 16.58; N, 17.92.

This product was identical (mixed m.p., ir) with a product prepared from *p*-acetamidobenzaldehyde, sodium cyanide and ammonium carbonate.

5-1 or 2-Naphthylhydantoin (**3e**).

To a solution of 5-butoxyhydantoin (**2a**) (1.0 g., 0.0058 mole) and boron trifluoride etherate (1 ml.) in chloroform (25 ml.) was added naphthalene (0.74 g., 0.0058 mole). The solution was heated at reflux overnight and the solvent was evaporated to dryness at reduced pressure. The residue was taken up in ethyl acetate and the solution was washed with water, dried over magnesium sulfate and evaporated to dryness. The residue was crystallized from ethanol, m.p. 223-225° (lit. (8) m.p. 225-227°). The yield was 0.90 g. (67%); ir: 3440, 1790, 1745 and 1605 cm^{-1}.

5-(9-Phenanthryl)hydantoin (**3f**).

Similar results were obtained with phenanthrene. The residue was crystallized from ethyl acetate-hexane, m.p. 215-216°, yield 1.19 g. (74%); ir: 3440, 3200 (broad), 1790, 1735 and 1610 cm^{-1}.

Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.91; H, 4.35; N, 10.14. Found: C, 73.57; H, 4.44; N, 9.88.

5-(2,5-Dimethylphenyl)hydantoin (**3g**).

A mixture of 5-butoxyhydantoin (**2a**) (1 g., 0.0058 mole) and boron trifluoride etherate (1 ml.) in *p*-xylene (20 ml.) was refluxed overnight (18 hours). The solvent was removed under reduced pressure and the residue was taken up in ethyl acetate and washed with water. The residue obtained after the removal of the solvent was crystallized from ethyl acetate-hexane, m.p. 186-188°. The yield was 0.82 g. (70.0%); ir: 3455, 3200 (broad), 1785, 1740 and 1610 cm^{-1}; n.m.r. (DMSO d_6): δ 2.25 (s, 3H), 2.33 (s, 3H), 5.40 (s, 1H) and 6.7-7.2 (m, 3H) p.p.m.; m/e 205.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.71; H, 5.88; N, 13.73. Found: C, 64.60; H, 6.22; N, 13.57.

5-*p*-Tolylhydantoin (**3h**).

A mixture of butoxyhydantoin (**2a**) and boron trifluoride etherate in toluene was refluxed for 48 hours and treated as described above. Crystallization from ethyl acetate-hexane afforded a product which melted at 156-158° (lit. (8) m.p. 155°), yield 53%. This product was identical (mixed m.p., ir and n.m.r.) with the 5-tolylhydantoin prepared from *p*-tolualdehyde, potassium cyanide and amonium carbonate.

3-Benzyl-5-(*p*-tolyl)hydantoin (**3i**).

A solution of 3-benzyl-5-methoxyhydantoin (**2b**) (5.62 g., 0.025 mole) in toluene (70 ml.) and boron trifluoride etherate (5.5 ml.) was refluxed for 48 hours. The solution was diluted with ethyl acetate (100 ml.), washed with water, dried over magnesium sulfate and evaporated to dryness, at reduced pressure.

The crude product (6.1 g., 87%) was according to the n.m.r. spectrum, a mixture of the *ortho* and *para* isomers. It showed two peaks at δ 2.35 and two peaks at δ 4.9-5.3 p.p.m. Three crystallizations from ethyl acetate-hexane gave one pure isomer (m.p. 110°) which showed only one peak at δ 2.35 (3H) and peaks at δ 4.65 (s, 2H), 4.95 (d, 1H), δ 6.53 (broad, 1H), 7.17 (s, 4H) and 7.33 (s, 5H) p.p.m.; yield 38%; ir: 3455, 3260 (broad), 1785, 1720 and 1610 cm^{-1}.

Anal. Calcd. for $C_{17}H_{16}N_2O_2$: C, 72.86; H, 5.71; N, 10.00. Found: C, 72.69; H, 5.91; N, 10.04.

3-Benzyl-5-phenylhydantoin (**3j**).

Similar results were obtained with benzene after refluxing for 4 days. The residue was crystallized from ethyl acetate; m.p. 170-172° (lit. (8) m.p. 170-173°), yield 49%.

The Reaction of 3-Benzyl-5-methoxyhydantoin (**2b**) with Olefins.

General Procedure.

A solution of 3-benzyl-5-methoxyhydantoin (1.00 g., 0.0045 mole) and olefin (0.0225 mole) in benzene (10 ml.) containing β-naphthalenesulfonic acid (0.10 g.) was refluxed overnight (18 hours). The reaction mixture was diluted with ethyl acetate (50 ml.), washed with aqueous sodium bicarbonate and water, then dried and evaporated. The residue was purified by trituration, crystallization or column chromatography on neutral alumina.

Reaction with 1,1-Diphenylethylene.

The above general procedure was used and the product (**4**, R = H, R′ = R″ = C_6H_5) was crystallized twice from methanol; m.p. 178°; yield 78%; ir: 3460, 1785, 1725, 1630 and 1610 cm^{-1}; n.m.r.: δ 4.63 (s, 2H), 4.70 (d, 1H), 5.80 (d, 1H, J = 12 cps) and 7.20-7.40 (15H).

Anal. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78.26; H, 5.44; N, 7.61. Found: C, 77.85; H, 5.44; N, 7.54.

Reaction with 1,1-Diphenylpropylene.

The above general procedure was used. The product (**4**, R = CH_3; R′ = R″ = C_6H_5) was crystallized from methanol m.p. 194°, yield 67%; ir: 3450, 1785, 1730 and 1720 cm^{-1}; n.m.r.: δ 1.57 (s, 3H), 4.70 (s, 2H), 4.93 (s, 1H), 6.25 (s, 1H) and 7.30 (m, 15H) p.p.m.

Anal. Calcd. for $C_{25}H_{22}N_2O_2$: C, 78.53; H, 5.76; N, 7.33. Found: C, 78.25; H, 5.52; N, 7.34.

Reaction with α-Methylstyrene.

The crude product was chromatographed over neutral alumina (40.0 g.) and eluted with methylene chloride-benzene (1:9) to give a mixture of *cis-trans* isomers, 1.01 g. (75%), in a ratio of 1:2.5 according to the n.m.r. Trituration with ether afforded the *trans* isomer (32%) which melted at 188° after crystallization from ethyl acetate-petroleum ether; ir: 3465, 3295-3255, 1790, 1735, 1720 and 1650 cm^{-1}; n.m.r.: δ 2.21 (d, 3H, J = 2 cps), 4.64 (s, 2H), 4.92 (d, 1H, J = 10 cps), 5.53 (d, 1H, J = 10 cps), 6.35 (s, 1H) and 7.33 (m, 10H) p.p.m.

Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.37; H, 6.05; N, 9.13.

This product was hydrogenated at 45 psi for 10 hours in the presence of 10% Pd/C (0.10 g.) to give a product which melted at 127° (81%) after crystallization from ethyl acetate-hexane.

β-Methylstyrene and β β-dimethylstyrene afforded under the same experimental conditions more complex mixtures which did not separate on chromatography.

Reaction with Styrene.

A solution of 3-benzyl-5-methoxyhydantoin (1.31 g.), excess styrene (4.0 ml.) and β-naphthalenesulfonic acid (0.20 g.) in 1,1,2-trichloroethane (20 ml.) was refluxed overnight (18 hours). The residue obtained after the removal of the solvent was chromatographed over neutral alumina (60.0 g.). Benzene eluted a mixture of non polar material 0.45 g. (26%), and methylene chloride-benzene (1:4) gave a fraction 0.27 g. (38.5%) which was, according to the n.m.r., a type **5** *cis-trans* mixture. Catalytic hydrogenation afforded 3-benzyl-5-(β-phenylethylidene)hydantoin; m.p. 139-140° after crystallization from ethyl acetate-hexane.

Trituration of the *cis-trans* mixture with ether afforded the less polar isomer (18%), m.p. 174°; ir: 3440, 3210, 1775, 1725, 1695 and 1610 cm^{-1}; n.m.r.: δ 3.52 (d, 2H, J = 8 cps), 4.69 (s, 2H), 6.10 (t, 1H), 7.25-7.30 (10H) and 8.58 (s, 1H) p.p.m.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 73.66; H, 5.38; N, 9.45.

Reaction with 2-Phenyl-2-butene.

The general procedure described above was used. The product (**6**, R = CH_3; R′ = C_6H_5) was crystallized from ethyl acetate-hexane, m.p. 137; yield 68%; ir: 3450, 1780, 1720 and 1630 cm^{-1}; n.m.r.: δ 1.02 (d, 3H: J = 16 cps), 3.50 (m, 1H), 4.00 (m, 1H), 4.68 (s, 2H), 5.13 (s, 1H), 5.37 (s, 1H), 6.28 (s, 1H) and 7.37 (s, 10H).

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 75.00; H, 6.25; N, 8.75. Found: C, 74.96; H, 6.40; N, 9.09.

Reaction with Tetramethylethylene.

The above general procedure was used. The product (**8**) melted at 132° after crystallization from ether-hexane, yield 75%; ir: 3350, 1785, 1730, 1720 and 1645 cm^{-1}; n.m.r.: δ 1.71 (s, 3H), 3.98 (s, 1H), 4.62 (s, 2H), 4.78 (s, 1H), 4.91 (s, 1H), 6.10 (s, 1H) and 7.32 (m, 5H) p.p.m.

Anal. Calcd. for $C_{16}H_{20}N_2O_2$: C, 70.59; H, 7.35; N, 10.29. Found: C, 70.20; H, 7.63; N, 10.54.

Reaction of 3-*p*-Chlorophenyl-5-methoxyhydantoin (**2c**) with Isobutylene.

To a solution of isobutylene in 1,1,2-trichloroethane (40 ml., 20%) there was added 3-*p*-chlorophenyl-5-methoxyhydantoin (2.40 g.) and β-naphthalenesulfonic acid (0.50 g.). The solution was heated in a sealed tube at 80° for 48 hours. The solvent was evaporated and the residue chromatographed over neutral alumina (60 g.). Elution with methylene chloride gave a mixture of two isomers (1.74 g.) which was catalytically hydrogenated in methanol (100 ml.) and in the presence of 10% Pd/C (0.4 g.) at 45 psi. The residue obtained after the removal of the catalyst and the solvent was crystallized from ethyl acetate-hexane to give 0.96 g. (36%) of product which melted at 192-193°. This product was identical (mixed m.p., ir and n.m.r.) with the 3-*p*-chlorophenylhydantoin prepared from *d,l*-leucine and *p*-chlorophenylisocyanate in aqueous sodium hydroxide followed by cyclization of the hydantoic acid in refluxing 20% sulfuric-acetic acid.

Reaction of 5-Butoxyhydantoin (**2a**) with Isobutylene in the Presence of Boron Trifluoride Etherate.

To a solution of isobutylene in methylene chloride (50 ml., 5.0%) there was added 5-butoxyhydantoin (2.00 g., 0.0116 mole) followed by boron trifluoride etherate (2 ml.). The solution was left at room temperature for 3 days. The solvent was removed *in vacuo* and the residue was taken up in ethyl acetate. The organic layer was washed with aqueous bicarbonate and

water, dried and evaporated to dryness. The residue was crystallized twice from ethyl acetate-hexane to give 1.06 g. (43.5%) of a product (**7**) which melted at 176-177°; ir: 3460, 3240-3160, 1785, and 1730; n.m.r. (DMSO d_6): δ 0.90 (s, 9H), 2.05 (s, 3H), 2.3 (m, 1H), 4.2 (q, 1H), 4.83 (s, 1H), 4.97 (s, 1H); m/e = 210.

Anal. Calcd. for $C_{11}H_{18}N_2O_2$: C, 62.82; H, 8.57; N, 13.33. Found: C, 62.68; H, 8.79; N, 13.27.

Reaction of 3-Benzyl-5-methoxyhydantoin (**2b**) with Indene.

A solution of the methoxyhydantoin (1.56 g.), indene (4.0 ml.) and β-naphthalenesulfonic acid (0.2 g.) in 1,1,2-trichloroethane (20 ml.) was refluxed for 18 hours. The solvent was removed *in vacuo* and the residue was triturated with methanol. The insoluble material was filtered and crystallized from methanol (0.78 g., 36%), m.p. 256°. It is, according to the n.m.r., 3-benzyl-5-(1-indenyl)hydantoin, n.m.r.: (pyridine d_5) δ = 4.8-5.2 (m, 1H), 4.95 (s, 2H), 4.31 (t, 1H), 3.91 (t, 1H) p.p.m.

Anal. Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 75.15; H, 5.07; N, 9.01.

The residue obtained after the evaporation of the filtrate was triturated with ether, filtered and crystallized from ethyl acetate-hexane (0.59 g., 27%), m.p. 171-172°; ir: 3455, 1785, 1720 and 1605 cm^{-1}; n.m.r.: 3.36 (s, 1H), 3.48 (s, 1H), 4.48 (s, 1H), 4.65 (s, 2H), 6.78 (s, 1H), 6.88 (s, 1H), 7.30 (m, 9H) p.p.m. The spectra agrees best with 3-benzyl-5-(2-indenyl)hydantoin.

Anal. Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.21. Found: C, 74.69; H, 5.29; N, 8.95.

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