Modified Lossen Rearrangement of Malonohydroxamic Acid. Preparation and Properties of 3-(*p*-Toluenesulfonoxy)hydantoin

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3-(*p*-Toluenesulfonoxy)hydantoin (**2**) was obtained by the reaction of malonohydroxamic acid (**1**) with *p*-toluenesulfonyl chloride. Acid hydrolysis and acid alcoholysis of **2** afforded 5-(*p*-toluenesulfonoxy)hydantoic acid (**3**) and alkyl 5-(*p*-toluenesulfonoxy)hydantoate (**4**), respectively. On treatment with ammonia and amines, methylenediurea and its alkyl derivatives (**5**) were obtained. Compound **2** yielded with aniline also ω-phenylsemicarbazidoacetanilide (**6**). Mechanisms of formation and structure of these compounds were studied. When it was necessary for confirmation of structures, some compounds were prepared in alternatives routes.

It was reported[1] that the rearrangement of phenyl- and benzylmalonohydroxamic acids with *p*-toluenesulfonyl chloride led to formation of 5-phenyl- or 5-benzyl-3-(*p*-toluenesulfonoxy)hydantoin.

In the present work the reaction of malonhydroxamic acid with *p*-toluenesulfonyl chloride resulted in the formation of 3-(*p*-toluenesulfonoxy)hydantoin (**2**). This product is a derivative of the unknown N^3-hydroxyhydantoin and exhibits some interesting properties.

Potassium hydrogen malonohydroxamate was prepared in good yield by reaction of ethyl malonate with excess hydroxylamine in methanol. Although potassium hydroxide was in excess the salt which precipitated was found, by elementary analysis and titration, to consist of pure monopotassium salt.

The reaction of malonohydroxamate with *p*-toluenesulfonyl chloride was carried out in cold aqueous medium. The best yield of 3-(*p*-toluenesulfonoxy)-hydantoin (**2**) was obtained in the presence of 2 moles of *p*-toluenesulfonyl chloride and 3 equiv of alkali (Scheme I).

It was impossible to remove the *p*-toluenesulfonyl group either by acid or by base without fission of the ring. 3-(*p*-Toluenesulfonoxy)hydantoin (**2**) underwent by treatment with alkali a total decomposition. In boiling for a short period in dilute hydrochloric acid it gave 5-(*p*-toluenesulfonoxy)hydantoic acid (**3**). Longer reflux in hydrochloric acid resulted in hydantoin. The capability of hydrochloric acid to cleave the oxygen–nitrogen bond in O,N-disubstituted hydroxylamines was shown in this laboratory;[2] hence, it explains the formation of hydantoin from **3**. The formation of hydantoin from the acid **3** may go through hydantoic acid as an intermediate or the reaction can involve a concerted mechanism in which ring closure takes place simultaneous with splitting of *p*-toluenesulfonic acid.

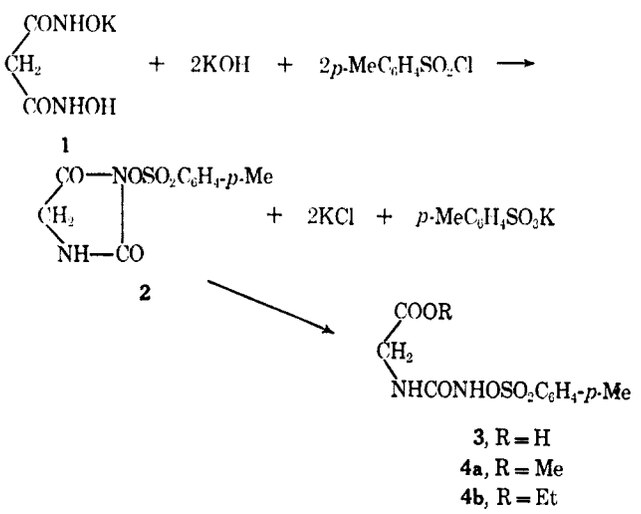
Alcoholysis of 3-(*p*-toluenesulfonoxy)hydantoin (**2**) in the presence of acid (*p*-toluenesulfonic acid) yielded esters of 5-(*p*-toluenesulfonoxy)hydantoic acid. These esters (**4**) could be hydrolyzed to the acid (**3**) or transformed to hydantoin by dilute hydrochloric acid.

Compounds **3** and **4** present a new class of compounds which are derivatives of O-sulfonyl-N-hydroxyurea. Contrary to O-sulfonylhydroxamic acids they are stable compounds, and do not undergo Lossen rearrangement. With amines they yield hydrazine derivatives as will be shown later.

Whereas in acid medium the ring of 3-(*p*-toluenesulfonoxy)hydantoin (**2**) is cleaved between positions 3 and 4, ammonia or aliphatic amines attack it between positions 2 and 3. The reaction in neat amines or concentrated ammonia solution is exothermic and the hydantohydroxamic acid–*p*-toluenesulfonic acid mixed anhydride, which is probably formed and is unstable in these conditions, undergoes further Lossen rearrangement, the end product of which is methylenediurea or its alkylated derivatives **5** (Scheme II).

Methylenediurea derivatives (**5**) are stable compounds and give in mass spectra the molecular ion peaks. It is pertinent to note that the mass spectra consisted of intense *m/e* peaks of monoalkylureas and mono-1-alkyl-2-uretidinones. This indicates a decomposition induced by electron impact which is characteristic for these methylenediurea derivatives.

SCHEME I



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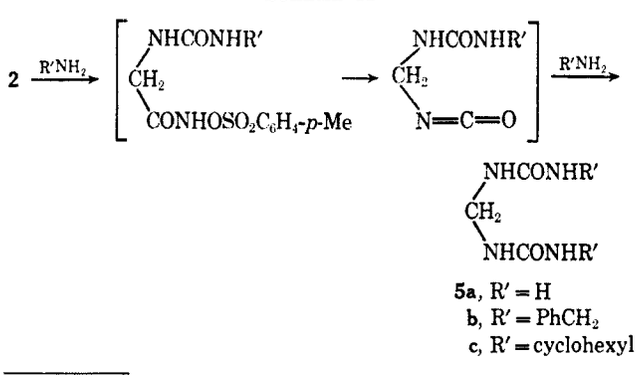
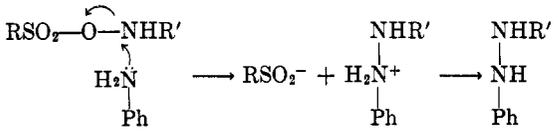


(1) C. D. Hurd and A. G. Prapas, *J. Amer. Chem. Soc.*, **80**, 6053 (1958).

(2) T. Sheradsky, U. Reichman, and M. Frankel, *J. Org. Chem.*, **33**, 3619 (1968).

Upon performing the reaction of 3-(*p*-toluenesulfonoxy)hydantoin (**2**) with aniline in neat aniline a product was obtained, elementary analysis of which was in agreement with methylenebis(3-phenylurea), as would have been expected. But this product differed from methylenebis(3-alkylurea) (**5**) in its spectral features. The infrared spectrum consisted of additional absorption bands around 3040–3270 and around 1700 cm^{-1}. The mass spectrum did not show electron-impact-induced decomposition to monophenylurea and 1-phenyl-2-uretidinone, which was expected in analogy with the aliphatic derivatives; it showed, instead, an intense peak at 108 *m/e*. This fact aroused the idea that the product is a hydrazine derivative. The structure of the product of aminolysis of 3-(*p*-toluenesulfonoxy)hydantoin (**2**) was proved to be ω-phenylsemicarbazidoacetanilide (**6**) by an independent synthesis from glycylanilide and phosgene followed by phenylhydrazine. 5-Phenylhydantoic acid phenylhydrazide, which has also the same elementary composition as methylenebis(3-phenylurea) and ω-phenylsemicarbizidoacetanilide (**6**), was also prepared in order to exclude such a structure for the product which was obtained here.

SCHEME III



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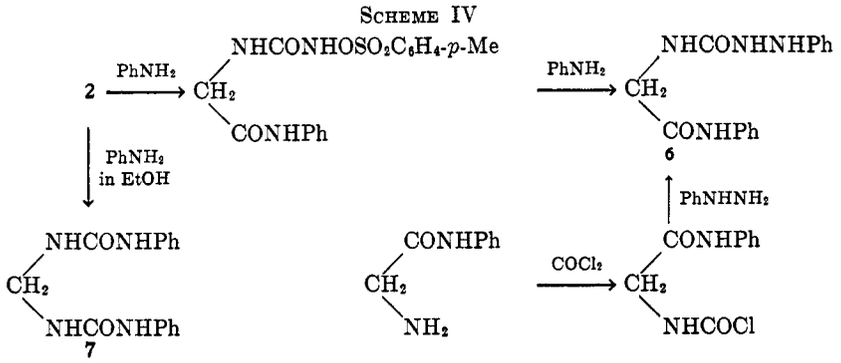
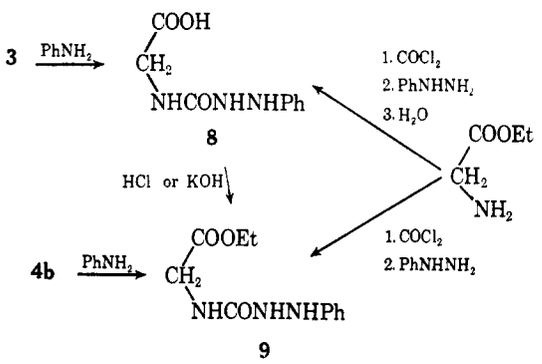


SCHEME V



In conclusion, the formation of **6** by reaction of 3-(*p*-toluenesulfonoxy)hydantoin (**2**) in aniline proceeds through cleavage of the ring system between positions 3 and 4. 5-(*p*-Toluenesulfonoxy)hydantoic anilide is formed, which then gives with aniline ω-phenylsemicarbazidoacetanilide (**6**). A molecule of aniline undergoes a rare kind of N-amination reaction, similar to that which occurs with hydroxylaminesulfonic acid, O-acylhydroxylamines,[3] or 2,4-dinitrophenylhydroxylamine.[4] The *p*-toluenesulfonate anion is a good leaving group and thus enables the heterolytic

$$RSO_2\text{—}\overset{\curvearrowleft}{O}\text{—}NHR' \longrightarrow RSO_2O^- + {}^+NHR'$$

fission of the N–O bond. The positively charged nitrogen attacks the nucleophilic nitrogen of aniline to form compound **6**. Another mechanism which can be proposed is a one-step nucleophilic displacement (Scheme III).

Ring fission of **2** with aniline between positions 2 and 3 also occurred resulting in methylenebis(3-phenylurea) (**7**) (Scheme IV). This product was obtained when the aminolysis was performed in ethanol.

The capability of the *p*-toluenesulfonoxyamino group to aminate aniline was shown also by the reaction of 5-(*p*-toluenesulfonoxy)hydantoic acid (**3**) and its ethyl ester (**4b**) which afforded ω-phenylsemicarbazidoacetic acid (**8**) and ethyl ω-phenylsemicarbazidoacetate (**9**) (Scheme V). The structures of **8** and **9** were also confirmed by independent syntheses from ethyl glycinate. The formation of **8** or **9** from **3** or **4b**, respectively, provides a proof for the course of formation of **6** from 3-(*p*-toluenesulfonoxy)hydantoin (**2**).

Compounds **2**–**7** (except **5a**[5]) were not hitherto described. ω-Phenylsemicarbazidoacetanilide (**6**) was found to consist of two forms which differ from each other in their spectral properties. There are some differences in the infrared spectra in the solid state and in solution. There is also a variation in the nmr spectra in solution provided that the spectrum is run immediately after dissolving the sample. From the nmr large variation, where one of the NH peaks moves from δ 3.4 to 8.0, one can suggest that it is not only a matter of hydrogen bonding but involves a certain kind of tautomerism or isomerism. Different crystalline forms could be excluded by examination of the ir in solution and of the mass spectra of the two forms. The absorption maximum at 1050 cm^{-1} which is present in the ir spectrum of form B in bromoform was absent in the solution of form A, as it is also in Nujol. The mass spectra of both forms were carried out in the same conditions and the remarkably different fragmentation supplied further support for isomerism. The variations

(3) L. A. Carpino, *J. Org. Chem.*, **30**, 321 (1965).
(4) T. Sheradsky, *Tetrahedron Letters*, 1909 (1968).
(5) H. Kadowaki, *Bull. Chem. Soc. Japan*, **11**, 249, 256 (1936).

TABLE I

SPECTRAL DATA OF TWO FORMS OF ω-PHENYLSEMICARBAZIDOACETANILIDE (6)

Ir in $CHBr_3$, cm^{-1}		Mass spectra			Nmr, δ	
			%Σ40			
Form A	Form B	m/e	Form A	Form B	Form A	Form B
3390	3390	284[a]	0.6	3.0	3.40 (s)	
	3300	191	0.5	3.3	4.00 (s)	4.00 (d)
1695	1695	184	0.00	10.2[b]	6.8–7.8[e]	6.8–7.8[e]
1600	1600	176[c]	5.4	0.5		8.00 (s)
1540	1540	151	0.6	3.4	9.14 (s)	9.14 (s)
1500	1500	108	10.2[d]	3.5		
1450	1450	93	7.9	4.5		
	1050	65	7.9	4.5		

[a] Parent peak. [b] Base peak (PhNHNHPh). [c] Phenylhydantoin. [d] Base peak ($PhNHNH_2$). [e] Complex of aromatic hydrogens.

between the two forms are summarized in Table I. From these data one can see that their different fragmentation is a result of different relative conformations of the functional groups. In form A the phenyl group of the anilide moiety is located in such a way that there is no possibility for decomposition to N,N-diphenylhydrazine (*m/e* 184), whereas it is the foremost decomposition in form B. In form B the main fragmentation is to phenylhydrazine and to N-phenylhydantoin (*m/e* 108 and 176, respectively).

Experimental Section

The melting points are uncorrected. Mass spectra were determined in an Atlas CH-4 (70 eV), ionization-cell temperature about 100–130°. Infrared spectra were determined with a Perkin-Elmer Model 257 spectrophotometer.

Potassium Hydrogen Malonohydroxamate (1).—Hydroxylamine hydrochloride (70 g, 1.0 mol) was dissolved in methanol (400 ml) by heating, and the solution cooled to 45°. Potassium hydroxide (85 g, 1.5 mol) was dissolved in methanol (200 ml) and cooled to 25°. The latter solution was introduced to the hydroxylamine hydrochloride solution with shaking and cooling on an ice bath. After 5 min the potassium chloride which precipitated was filtered off, and to the clear solution, ethyl malonate (40 g, 0.25 mol) was added at once. A few minutes later a white precipitate of **1** appeared. After keeping at room temperature for 2 hr the product was collected (33 g, 80%), mp 195°.

Anal. Calcd for $C_3H_5N_2KO_4$: C, 20.92; H, 2.94; N, 16.27; mol wt, 172. Found: C, 20.73; H, 2.82; N, 16.36; mol wt, 170.9 (titration).

3-(*p*-Toluenesulfonoxy)hydantoin (2).—Potassium hydrogen malonohydroxamate (17.2 g, 0.1 mol) was dissolved in water (160 ml), 5 *N* potassium hydroxide (40 ml, 0.2 mol) was added, the solution was cooled in an ice bath, and *p*-toluenesulfonyl chloride (38.1 g, 0.2 mol) was added. The mixture was stirred for 6 hr on ice and then 20 hr at room temperature. The precipitated product was collected and recrystallized from ethanol, mp 175° (19 g, 70%).

Anal. Calcd for $C_{10}H_{10}N_2O_5S$: C, 44.45; H, 3.73; N, 10.37; S, 11.84; mol wt, 270. Found: C, 44.67; H, 3.82; N, 10.38; S, 11.76; mol wt, 270 (mass spectroscopy).

5-(*p*-Toluenesulfonoxy)hydrantoic Acid (3).—3-(*p*-Toluenesulfonoxy)hydantoin (**2**) (2.7 g) was refluxed for 10 min in 2 *N* hydrochloric acid (55 ml), while all the crystals dissolved. Crystals of **3** separated after cooling overnight at 1° (1.5 g, 50%); mp 164°; ir (Nujol), 3650 (NH), 3330 (NH), 3250 (OH), 1750 (C=O), 1680 (C=O), 1540 cm^{-1} (NHC=O); nmr (DMSO-d_6), δ 2.45 (s), 3.68 (d), 7.40–8.10 (aromatic hydrogens), 8.52 (broad peak COO*H*), 10.58 (s, SO_2ONHCO).

Under conditions which exist on determination of mass spectra this compound loses water and gives a considerable ion peak, *m/e* 270 (%Σ40 1.3), corresponding to formation of **2**; additional peaks, *m/e* (%Σ40) 155 (12), 91 (20), 65 (4), 44 (22), 43 (4).

Anal. Calcd for $C_{10}H_{12}N_2O_6S$: C, 41.67; H, 4.20; N, 9.72; S, 11.10. Found: C, 41.62; H, 4.50; N, 9.92; S, 10.80.

Hydantoin from 2, 3, and 4.—3-(*p*-Toluenesulfonoxy)hydantoin (**2**) (2.7 g) was refluxed for 3 hr in 2 *N* hydrochloric acid (55 ml). The solution was evaporated to dryness and the residue was crystallized from ethanol (0.9 g, 79%); mp 229°. The product was identical (by mixture melting point and ir spectra) with commercial hydantoin.

Anal. Calcd for $C_3H_4N_2O_2$: C, 36.01; H, 4.03; N, 27.99. Found: C, 36.32; H, 4.11; N, 28.22.

Hydantoin was obtained in the same manner also from 5-(*p*-toluenesulfonoxy)hydantoic acid (**3**) and from methyl or ethyl 5-(*p*-toluenesulfonoxy)hydantoate (**4**).

Methyl 5-(*p*-Toluenesulfonoxy)hydantoate (4a).—3-(*p*-Toluenesulfonoxy)hydantoin (**2**) (2.7 g) was refluxed in methanol with *p*-toluenesulfonic acid (1.35 g) for 3 hr. On cooling, the ester **4a** precipitated (1.1 g). An additional crop was obtained by evaporation of the methanol to a small volume followed by addition of water and cooling (0.6 g), over-all yield 56%. After recrystallization from methanol the ester (**4a**) melted at 163°; ir (Nujol), 3410 (NH), 3320 (NH), 1750 (C=O), 1700 (C=O), 1550 cm^{-1} (NHC=O); nmr (DMSO-d_6), δ 2.50 (s), 3.52 (s), 3.66 (s), 3.69–3.80 (complex), 7.48–8.08 (complex, aromatic), 10.58 (s, SO_2NHCO); mass spectrum, *m/e* (%Σ40) 302 (1, parent peak), 172 (2), 155 (10), 107 (2), 91 (19), 88 (2), 65 (6.5), 56 (3).

Anal. Calcd for $C_{11}H_{14}N_2O_6S$: C, 43.71; H, 4.67; N, 9.27; S, 10.60; mol wt, 302. Found: C, 43.64; H, 4.74; N, 9.18; S, 10.91; mol wt, 302 (mass spectroscopy).

Ethyl 5-(*p*-toluenesulfonoxy)hydantoate (4b) was obtained by the same procedure as above (**4a**) using ethanol instead of methanol. The ester (**4b**) was separated by evaporation of the ethanol to a small volume followed by addition of water and cooling. Recrystallized from ethanol, it had mp 126° (45% yield). Spectral results are similar to that of ethyl ester **4a**.

Anal. Calcd for $C_{12}H_{16}N_2O_6S$: C, 45.58; H, 5.10; N, 8.86; S, 10.14; mol wt, 316. Found: C, 45.39; H, 4.97; N, 8.58; S, 9.85; mol wt, 316 (mass spectroscopy).

Hydrolysis of 4 to 5-(*p*-Toluenesulfonoxy)hydantoic Acid (3).—Alkyl 5-(*p*-toluenesulfonoxy)hydantoate (**4**) was refluxed for 10 min in 2 *N* hydrochloric acid (0.01 mol of **4** in 55 ml). After keeping overnight at 1° 5-(*p*-toluenesulfonoxy)hydantoic acid (**3**) precipitated and was identical with the product obtained above (by mixture melting point and ir spectra).

Methylenediurea (5a).—3-(*p*-Toluenesulfonoxy)hydantoin (**2**) (2.7 g) was dissolved in concentrated ammonia solution (14 ml). After the exothermic reaction ceased the solution was heated to 60° and cooled overnight at −5°. The precipitated crystals were collected and washed with concentrated ammonia solution (0.93 g, 70%); mp 214° (lit.[5] 218°).

Anal. Calcd for $C_3H_8N_4O_2$: C, 27.27; H, 6.10; N, 42.41. Found: C, 27.61; H, 6.33; N, 41.96.

Methylenebis(3-benzylurea) (5b).—3-(*p*-Toluenesulfonoxy)-hydantoin (**2**) (2.7 g) was introduced into benzylamine (40 ml). The reaction was exothermic but not all the solid was dissolved. The mixture was shaken and heated to 110°, excess water (100 ml) was added, and the mixture was kept for a few minutes at 60°. After cooling to room temperature the product (**5b**) was collected and recrystallized from ethanol (2.2 g, 70%); mp 234°; mass spectrum, *m/e* (%Σ40) 162 (2), 150 (7), 106 (10), 91 (18), 87 (3), 65 (3).

Anal. Calcd for $C_{17}H_{20}N_4O_2$: C, 65.37; H, 6.45; N, 17.94; mol wt, 312. Found: C, 65.39; H, 6.64; N, 18.11; mol wt, 312 (mass spectroscopy).

Methylenebis(3-cyclohexylurea) (5c).—3-(*p*-Toluenesulfonoxy)hydantoin (**2**) (2.7 g) was introduced into cyclohexylamine (40 ml). After the exothermic acid ceased the mixture was heated to 60°, ethanol (100 ml) was added, and the mixture boiled for a few minutes. The solid which was obtained melted at 259° (1.5 g, 50%). The melting point did not change after recrystallization from a large amount of alcohol; mass spectrum, *m/e* (%Σ_{40}) 154 (1.5), 143 (2), 142 (2), 99 (4), 98 (3), 83 (6), 82 (4), 70 (3), 68 (3), 67 (3), 61 (6), 56 (15), 55 (10), 54 (4), 45 (4), 43 (12).

Anal. Calcd for $C_{15}H_{28}N_4O_2$: C, 60.78; H, 9.52; N, 18.90; mol wt, 296. Found: C, 60.68; H, 9.66; N, 19.10; mol wt, 296 (mass spectroscopy).

ω-Phenylsemicarbazidoacetanilide (6). Form A.—3-(*p*-Toluenesulfonoxy)hydantoin (**2**) (2.7 g) was dissolved in aniline (10 ml) and heated for 10 min at 80° (above 100° an exothermic reaction starts with different results). After cooling to room temperature dichloromethane (100 ml) was added and the solution was filtered and kept for a few days at −10°. The solid precipitated (1.2 g, 42%); after washing with water, ethanol, and dichloromethane it melted at 196°.

Anal. Calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71; mol wt, 284. Found: C, 63.50; H, 5.38; N, 19.91; mol wt, 284 (mass spectroscopy).

Form B.—Running the same procedure as above, except that ethanol was used instead of dichloromethane and the product was recrystallized from ethanol, form B was obtained, mp 201°.

Anal. Calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71; mol wt, 284. Found: C, 63.61; H, 5.91; N, 19.51; mol wt, 284 (mass spectroscopy).

The same form could be obtained by heating form A in boiling ethanol for 10 min and cooling. Form B could be transformed back to A by triturating in dichloromethane. The spectral data of the two forms are summarized in Table I.

Methylenebis(3-phenylurea) (7).—Aniline (10 ml) was dissolved in ethanol (60 ml), 3-(*p*-toluenesulfonoxy)hydantoin (**2**) (2.7 g) was added, and the mixture refluxed for 30 min. After keeping overnight at −10° the solid which precipitated was collected and washed with 1 *N* potassium hydroxide, dried, and recrystallized from ethanol (0.7 g, 25%); mp 245°; mass spectrum, *m/e* (%Σ_{40}) 148 (2), 136 (4), 120 (4), 119 (16), 93 (15), 91 (8), 77 (4), 66 (4), 65 (4), 64 (5), 51 (3).

Anal. Calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71; mol wt, 284. Found: C, 63.10; H, 5.95; N, 19.86; mol wt, 284 (mass spectroscopy).

Alternative Preparation of ω-Phenylsemicarbazidoacetanilide (6).—Glycylanilide hydrobromide (1 g) was prepared from carbobenzoxyglycylanilide[6] with hydrogen bromide in acetic acid[7] (mp 200° from acetic acid–ether and satisfactory C, H, N elementary analysis). This hydrobromide was suspended in dry dioxane (25 ml) and phosgene was passed at 40° until the solution was clear (30 min). A stream of nitrogen was bubbled for 30 min, and the solution was filtered and evaporated to dryness *in vacuo*. Phenylhydrazine (1 g) in dichloromethane (20 ml) was added to the residue. The mixture was stirred at room temperature for 3 hr and kept overnight at −10°. The precipitate was collected, washed with a large amount of water, dried in the air, and recrystallized from ethanol (mp 201°) or dichloromethane (mp 192°). The product was identical with that which was obtained from **2** in aniline and also had two forms, identical with those obtained above (by ir and nmr spectra).

Anal. Calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71; mol wt, 284. Found: C, 63.30; H, 5.92; N, 19.71; mol wt, 284 (mass spectroscopy).

Reaction of 5-(*p*-Toluenesulfonoxy)hydantoic Acid (3) with Aniline.—The acid **3** (0.29 g) was heated in aniline (1 ml) for 10 min at 100°, dichloromethane was then added, and the solution was kept 24 hr at −10°. The precipitated ω-phenylsemicarbazidoacetic acid (**8**) (0.1 g, 48%) melted at 205°, and was identical with a sample of ω-phenylsemicarbazidoacetic acid which was prepared independently (see below).

Anal. Calcd for $C_9H_{11}N_3O_3$: C, 51.67; H, 5.30; N, 20.09. Found: C, 51.88; H, 5.34; N, 19.96.

Reaction of Ethyl 5-(*p*-Toluenesulfonoxy)hydantoate (4b) with Aniline.—The ester **4b** (0.32 g) was heated in aniline (1 ml) for 5 min at 100° and cooled to room temperature. Dry ether was added and the solid which precipitated was filtered off. Dry petroleum ether (40–60°) was added to the etheral solution. Ethyl ω-phenylsemicarbazidoacetate (**9**) precipitated on cooling, mp 132° (0.1 g, 42%).

Anal. Calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.83; H, 6.35; N, 18.00.

With a 10-min reflux of this ester (**9**) in 1 *N* hydrochloric acid and cooling, the acid **8** was obtained in 95% yield. By performing the hydrolysis with 5 *N* KOH at room temperature followed by filtration and acidification, 90% of the acid **8** was obtained.

Alternative Preparation of Ethyl ω-Phenylsemicarbazidoacetate (9) and ω-Phenylsemicarbazidoacetic Acid (8).—Ethyl glycinate hydrochloride (2.15 g) was suspended in dioxane (50 ml) and a stream of phosgene was passed at 45° until all the solid dissolved. Dry nitrogen was bubbled for 30 min and the solution evaporated to dryness *in vacuo*. A solution of phenylhydrazine (4.3 g) in dichloromethane (20 ml) was added and the mixture was stirred at 0° for 3 hr and kept overnight at 0°. The solid was collected, washed with a large amount of water, dried in the air, and recrystallized from ethanol (3.8 g, 80%), mp 132°. The product was identical with that which was obtained above from **4b** (by mixture mp and ir spectra).

Anal. Calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.52; H, 6.67; N, 17.98.

This product (2.37 g) was stirred in 5 *N* potassium hydroxide (10 ml) for 15 min. The solution was filtered and acidified with hydrochloric acid. The precipitated ω-phenylsemicarbazidoacetic acid was collected and recrystallized from ethanol (1.9 g, 90%), mp 206°. The product was identical with that which was obtained above from **3** (by mp and ir).

Anal. Calcd for $C_9H_{11}N_3O_3$: C, 51.67; H, 5.30; N, 20.09. Found: C, 51.90; H, 5.60; N, 19.92.

ω-Phenylhydantoyl N-β-Phenylhydrazide.—5-Phenylhydantoic acid (3.56 g) and triethylamine (2.8 ml) were stirred with ethyl chloroformate (2.2 g) in dry toluene (50 ml) at 0° for 3 hr. Phenylhydrazine (2.4 ml) was added, and the mixture was stirred for 1 hr at 10° and kept overnight at 4°. The precipitate was collected, triturated in petroleum ether (40–60°), and washed with 1 *N* hydrochloric acid, with 1 *N* potassium hydroxide, and with water. On recrystallization from ethanol it melted at 244° (2.85 g, 50%). The product differed from compounds **6** or **7** (by mixture melting point and ir spectra).

Anal. Calcd for $C_{15}H_{16}N_4O_2$: C, 63.37; H, 5.67; N, 19.71. Found: C, 63.26; H, 5.96; N, 19.50.

Registry No.—**1**, 38872-90-7; **2**, 18872-91-8; **3**, 18872-92-9; **4a**, 18872-93-0; **4b**, 18872-94-1; **5b**, 18872-95-2; **5c**, 18872-96-3; **6**, 18872-97-4; **7**, 18872-98-5; **8**, 3016-53-3; **9**, 18873-00-2; hydantoic, 461-74-3; ω-phenylhydantoyl N-β-phenylhydrazide, 18873-01-3.

(6) J. R. Vaughan and R. L. Osata, *J. Amer. Chem. Soc.*, **74**, 676 (1952).
(7) D. Ben-Ishai and A. Berger, *J. Org. Chem.*, **17**, 1564 (1952).