

undersirable coupling and side reactions characteristic of difunctional Grignard formation. The triol, *sym*-tris(dimethylhydroxysilyl)benzene (IV), was prepared by careful hydrolysis of I, following the procedure of Merker and Scott, (3). Similar treatment of V failed to give the corresponding pure anisole derivative.

The NMR data, Table II, establish the presence of symmetrical substitution in all cases. A 1,2,3 or 1,2,4 type of substitution would give rise to nonequivalent aromatic protons with a subsequent increase in the number of peaks in the spectrum. The sharp aromatic singlet at low field together with the proton ratios unequivocally point to 1,3,5 substitution for the benzene derivatives and to 2,4,6 substitution for the anisole derivatives. Infra-red spectral analyses were consistent with proposed structures and showed all compounds to be free of siloxane except for a small amount in IV.

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the NMR spectra. Elemental analyses were made by the Analytical Laboratories.

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Isatoic Anhydride

Reactions with Isocyanates, Isothiocyanates, and Schiff's Bases

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The reactions of isatoic anhydride with nucleophiles have been extended to include additional amines, alcohols, and mercaptans which yield respectively substituted *o*-amino benzamides, benzoates and thiobenzoates. The reaction of isatoic anhydride with isocyanates, isothiocyanates and Schiff's base is reported as yielding 2,4-dioxo-; 2-thiono-4-oxo-; and 4-oxo-1,2,3,4-tetrahydroquinazolines. Forty seven compounds of new composition are characterized.

REACTIONS OF ISATOIC ANHYDRIDE with ammonia, primary and secondary amines, amides, primary and secondary alcohols, mercaptans, phenols and thiophenols, and conditions of the reactions have previously been studied (1, 4). The present investigators have extended the reactions of isatoic anhydride to include isocyanates, isothiocyanates, and a Schiff's base forming 2,4-dioxo-1,2,3,4-tetrahydroquinazolines; 2-thiono-4-oxo-1,2,3,4-tetrahydroquinazolines; and 4-oxo-1,2,3,4-tetrahydroquinazoline, respectively.

The reactions of isatoic anhydride with isocyanates and isothiocyanates are carried out under anhydrous conditions using dimethylformamide (DMF) as solvent and catalyst. Upon cooling, the 2,4-dioxo-1,2,3,4-tetrahydroquinazolines and 2-thiono-4-oxo-1,2,3,4-tetrahydroquinazolines separate as crystalline precipitates in yields of 30 to 60% (Figure 1).

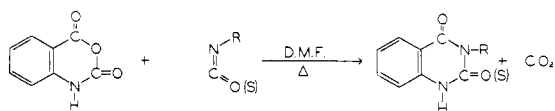


Figure 1. Reactions of isatoic anhydride with isocyanates and isothiocyanates

The nucleophilic nitrogen of the phenyl isocyanate attacks the number four carbon atom of isatoic anhydride, which is followed by loss of CO_2 and ring closure to the 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline. To establish the number three position as the point of substitution of the phenyl group, the 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline was formed by an alternate synthesis through the ψ -phenyl ureidobenzoic acid (2). The physical properties and infrared spectra of the products from the two syntheses were found to be identical (Figure 2).

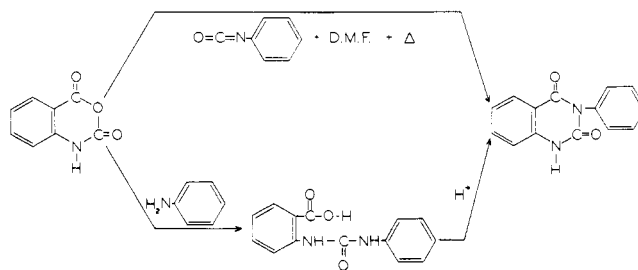


Figure 2. Synthesis of 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline

Table I. Reaction Products of Isatoic Anhydride and Various Nucleophiles
Compounds of New Composition

Reactant	Product M.P. ° C.	%, C		%, H		Salt ^a	M.P. ° C.
		Theor.	Found	Theor.	Found		
Aliphatic alcohol	Anthranilate						
2, 2, 2-Tribromoethanol	59.0-59.5	26.86	26.89	1.99	1.96	HCl	184-7
2-Ethoxyethanol	B.P. 168 (4 mm. Hg)	63.16	63.03	7.1	7.32	TNB	64-6
2-Propynol	Col. liq.	56.74	56.64	4.7	4.60	HCl	176-7
3- <i>n</i> -Hexenol	B.P. 130 (8 mm. Hg)	71.23	71.38	7.76	7.95	HCl	133-5
3- <i>n</i> -Hexynol	B.P. 160 (5 mm. Hg)	71.89	71.98	6.91	7.05	HCl	153-5
Dodecanol	42-3	74.74	74.88	10.16	10.36		
Tetradecanol	46-7	75.76	75.57	10.62	10.47	Pic.	62-4
Hexadecanol	45-6	76.45	76.18	10.78	10.75	Pic.	72-6
Benzyl alcohol	B.P. 206 (7 mm. Hg)	63.76	63.57	5.31	5.36	HCl	170
<i>m</i> -Nitrobenzyl alcohol	89-90	61.76	62.08	4.41	4.32	HCl	171-171.5
Ethyl lactate	27.5-28.5	60.76	60.60	6.33	6.50	Pic.	88-9
Cholesterol	140-1	82.42	82.69	10.3	10.41		
Ergosterol	160-1	81.40	81.57	9.8	9.93	HCl	153-5
Phenols	Anthranilate						
<i>p</i> -Bromophenol	80-81.5	53.42	53.37	3.42	3.13	HCl	175-9
2, 4, 6-Tribromophenol	120-1	34.66	34.87	1.78	1.71	HCl	169-71
<i>o</i> -Chlorophenol	37-41	63.03	63.49	4.04	3.93	HCl	159-62
<i>p</i> -Chlorophenol	80.5-81.5	63.03	63.24	4.04	4.04	HCl	156-9
<i>m</i> -Cresol	71-2	74.01	73.81	5.73	5.94	TNB	95-7
<i>o</i> -Cresol	61-2	74.01	74.21	5.73	5.56	HCl	138-40
α -Phenyl- <i>p</i> -Cresol	96-97.5	79.21	79.03	5.61	5.58	Pic.	117-9
<i>p</i> - <i>tert</i> . Amylphenol	103-5	76.33	76.55	7.43	7.53	Pic.	115-6
<i>o</i> -Ethoxyphenol	69.0-69.5	70.03	70.29	5.83	5.83	TNB	97-9
<i>p</i> (1, 1, 3, 3-Tetramethyl-butyl) phenol	126-7	77.54	77.39	8.32	8.53	HCl	155-160
<i>m</i> -(<i>n</i> -Pentadecyl) phenol	61.5-63.0	79.43	79.39	9.69	9.58	HCl	102-4
<i>p</i> -Benzyloxyphenol	B.P. 121 (8 mm. Hg)	75.23	74.99	5.33	5.15	Pic.	113-6
2-Methyl-5-isopropyl-phenol	B.P. 220-2	75.83	75.61	7.06	7.13	Pic.	80-2
3-Pyridol	75-6	67.29	67.40	4.67	4.38		
Mercaptan	Thioanthranilate						
<i>n</i> -Propanethiol	B.P. 138-43 (3 mm. Hg)	61.54	61.77	6.67	6.56	TNB	75-6
2-Propanethiol	B.P. 158-60 (10 mm. Hg)	61.54	61.75	6.67	6.64	Pic.	84-8
<i>n</i> -Butanethiol	B.P. 176-8 (8 mm. Hg)	63.16	63.09	7.18	6.95	HCl	162-4
<i>n</i> -Pentanethiol	B.P. 212-4 (22 mm. Hg)	64.57	64.40	7.62	7.68	HCl	157-9
<i>n</i> -Heptanethiol	17	66.93	67.13	8.37	8.24	HCl	147-150
<i>p</i> -Chlorothiophenol	114-6	59.25	59.32	3.79	3.64	HCl	145-8
Phenylmethanethiol	B.P. 215-9 (5 mm. Hg)	69.14	69.14	5.35	5.35	Pic.	84-6
2-Naphthanethiol	112-3	73.25	73.41	4.67	4.77	Pic.	132-4
Amine	Anthranilamide						
Pyrrolidine	237-9	69.47	69.81	7.36	7.35		
<i>o</i> -Toluidine	109.5-110.5	74.34	74.54	6.20	6.31	HCl	203-5
<i>p</i> -Toluidine	149-150	74.34	74.31	6.20	6.18	Pic.	202-3
2, 4-Dimethoxyaniline	95.0-95.5	66.18	65.91	5.88	5.65	Pic.	170-1
<i>m</i> -Trifluoromethylaniline	128-131	60.00	60.25	3.93	3.78		
2-Methoxyaniline	103-5	69.42	69.60	5.78	6.01	Pic.	176-8
4-Ethoxyaniline	120-3	70.31	69.85	6.25	6.03	Pic.	160-2
Piperazine	206-7	66.67	66.25	6.19	6.17	Pic.	214
Miscellaneous							Product
2,4-Pentanedione	258-9	71.64	71.83	5.49	5.69		2-Methyl-3-acetyl-4-oxo-3, 4-dihydroquinoline
Methyl isothiocyanate	265-6	56.25	56.18	4.17	4.09		2-Thiono-3-methyl-4-oxo-1, 2, 3, 4-tetrahydroquinazoline
<i>p</i> -Bromophenyl isocyanate	316-317.5	53.00	52.91	2.84	2.88		2,4-Dioxo-3-(<i>p</i> -bromophenyl)-1, 2, 3, 4-tetrahydroquinazoline
6-Nitroisatoic anhydride and Benzalaniline	232-3	69.57	69.66	4.35	4.36		2,3-Diphenyl-4-oxo-6-nitro-1, 2, 3, 4-tetrahydroquinazoline

^a Pic. = picric acid; TNB = 1, 3, 5-trinitrobenzene; HCl = hydrochloric acid.

Phenyl isothiocyanate reacts by the same mechanism to form the 3-phenyl-2-thiono-4-oxo-1,2,3,4-tetrahydroquinazoline.

The reaction of isatoic anhydride with a Schiff's base is found to be analogous to the isocyanate reaction. The nucleophilic nitrogen of benzalaniline attacks the number four carbon atom of isatoic anhydride with subsequent loss of CO₂ and ring closure to form 2,3-diphenyl-4-oxo-1,2,3,4-tetrahydroquinazoline. This product was also prepared by the alternate synthesis through *o*-aminobenzanilide as shown below. The physical properties and

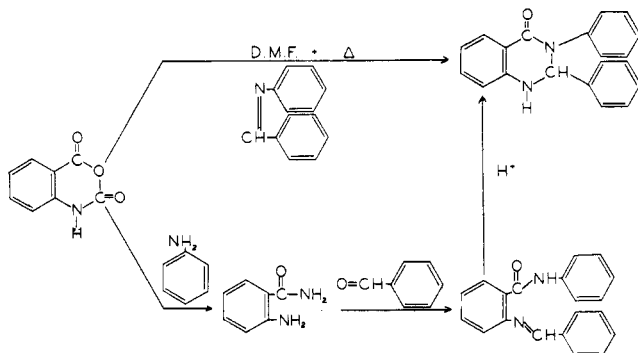


Figure 3. Synthesis of 2,3-diphenyl-4-oxo-1,2,3,4-tetrahydroquinazoline

infrared spectra of the products from the two syntheses were found to be identical (Figure 3).

The established reactions of isatoic anhydride with amines, alcohols, and mercaptans have been extended to enlarge the number of derivatives of isatoic anhydride to facilitate the use of the anhydride as a reagent in organic qualitative analysis or the identification of common nucleophiles. All compounds of new composition appear in Table I.

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The synthesis of new compounds was conducted by a team of undergraduates, Carol D. Bond, Barbara M. Gattiker, F.H. Genter, F.D. Vastine, and C.G. Wade.

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Nitration of Cyclic Sulfites

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IN CONNECTION with another study it became necessary to prepare a series of cyclic sulfites, several of which have not been previously reported. The sulfites were prepared from the corresponding diols by treatment with thionyl chloride, using standard methods (2). The sulfites

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and their physical properties are listed in Table I. The diols were all known compounds.

In the course of working with the sulfites it was found that treatment with common nitrating agents gave the dinitrates of the corresponding diols. In particular, three of the sulfites were cleaved with acetyl nitrate. This represents a new and potentially useful method for the

Table I. Properties of Cyclic Sulfites and Dinitrates

-R-	M.P. ^a	Max. (IR), μ	Yield	Sulfites Nitrating Agent	Analyses							
					Found, %				Calculated, %			
					% C	% H	% S	% N	% C	% H	% S	% N
-CH ₂ CCl ₂ CCl ₂ CH ₂ -	59-60°	8.17 μ	74		17.6	2.09	11.6	...	17.5	1.47	11.7	...
-CH ₂ CF ₂ CF ₂ CH ₂ -	21-22°	...	78		23.5	2.25	15.3	...	23.1	1.92	15.4	...
-CH ₂ C(CH ₃) ₂ C(CH ₃) ₂ CH ₂ -	31-32°	8.38 μ	83		50.3	8.42	16.4	...	50.0	8.32	16.6	...
-CH ₂ CCl ₂ CH ₂ -	62-63°	8.40 μ	65		18.6	2.62	16.4	...	18.8	2.09	16.7	...
-CH ₂ CF ₂ CH ₂ -	<i>n</i> _D ²⁰ 1.458		51		22.3	2.79	...	...	22.7	2.53	...	...
- <i>o</i> -C ₆ H ₄ (CH ₂) ₂ =	36-37°	8.48 μ	57		52.1	4.41	17.8	...	52.1	4.38	17.4	...
-(C ₆ H ₅) ₂ C=	190-191°	8.38 μ	62		61.8	3.84	13.4	...	62.0	3.46	13.8	...
-[<i>o</i> -C ₆ H ₄ (CH ₂) ₂ NO ₂]	132-133°	8.47 μ	42	MA ^c	42.2	3.29	13.7	...	41.9	3.09	13.9	...
-O ₂ NC ₆ H ₄ -C ₂ -C ₆ H ₄ NO ₂	226-228°	6.53 μ										
-C ₆ H ₁₀ (CH ₂) ₂ =	226-228°	8.27 μ	48	AN ^c	44.7	2.07	...	8.55	44.7	1.87	...	8.68
-CH ₂ CCl ₂ CCl ₂ CH ₂ -	<i>n</i> _D ²⁰ 1.4927	8.49 μ	...		50.1	7.18	...	...	50.5	7.42	16.9	...
-CH ₂ CCl ₂ CCl ₂ CH ₂ -	70-71°	6.02 μ	81	AN ^c	15.4	1.27	...	8.53	15.1	1.25	...	8.78
-CH ₂ CF ₂ CF ₂ CH ₂ -	<i>n</i> _D ²⁰ 1.3930	6.00 μ	58	MA ^c	19.5	1.64	...	...	19.1	1.58	...	...
-CH ₂ C(CH ₃) ₂ C(CH ₃) ₂ CH ₂ -	95-96°	6.12 μ	66	AN ^c	40.7	6.68	...	11.9	40.6	6.78	...	11.8
-CH ₂ CCl ₂ CH ₂ -	<i>n</i> _D ²⁰ 1.4766	6.04 μ	73	AN ^c	15.8	1.37	...	11.8	15.3	1.70	...	11.8
-CH ₂ CF ₂ CH ₂ -	<i>n</i> _D ²⁰ 1.4016	6.03 μ	52	MA ^c	18.4	1.98	...	...	17.8	1.98	...	...

^a The melting points are corrected. ^b Sulfite band obscured by CF absorption. ^c MA = Mixed acid; AN = Acetyl nitrate.