nmr ($CDCl_3$) δ 0.88 (m, 6, CH_2CH_3), 1.50 (m, 4, CH_2CH_3), 2.33 (s, 3, NCH_3), 2.63 (broad s, 2, $ArCH_2C$), 3.85 (broad s, 2, $ArCH_2N$), and 7.07 (m, 4, ArH); mass spectrum *m/e* 203 (parent ion).

The cyclohexanesulfamate salt of 3,3-diethyl-1,2,3,4-tetrahydro-2-methylisoquinoline was prepared and recrystallized from Me_2CO–*i*-PrOAc, mp 132–133°.

Anal. Calcd for $C_{20}H_{34}N_2O_3S$: C, 62.79; H, 8.96; N, 7.32; S, 8.38. Found: C, 62.69; H, 8.93; N, 7.20; S, 8.52.

Registry No.—**1a**, 26322-39-4; **2a**, 26278-47-7; **2b**, 21868-91-7; **2c**, 21868-89-3; **2d**, 21868-90-6; **2e**, 20141-85-9; **3a**, 26278-52-4; **3b**, 26278-53-5; **3c**, 26278-54-6; **3c** HCl, 26278-55-7; **3d**, 26278-56-8; **3e**, 26278-57-9; **3f**, 26278-58-0; **3g**, 26278-59-1; **4a**, 26278-60-4; **4b**, 26278-61-5; **5b**, 26278-62-6; **5d**, 26278-63-7; **6**, 24097-54-9; **8a**, 26278-65-9; **8b**, 26278-66-0; **8c**, 26278-74-0; 1-(1,2-diphenylethyl)-urea, 26278-75-1; 3,3-diethyl-1,2,3,4-tetrahydro-2-methylisoquinoline, 26278-76-2; 3,3-diethyl-1,2,3,4-tetrahydro-2-methylisoquinoline cyclohexanesulfamate salt, 26278-77-3.

Acid-Catalyzed Cyclodehydration of Hydroxyamides. II.[1] γ-Hydroxyamides

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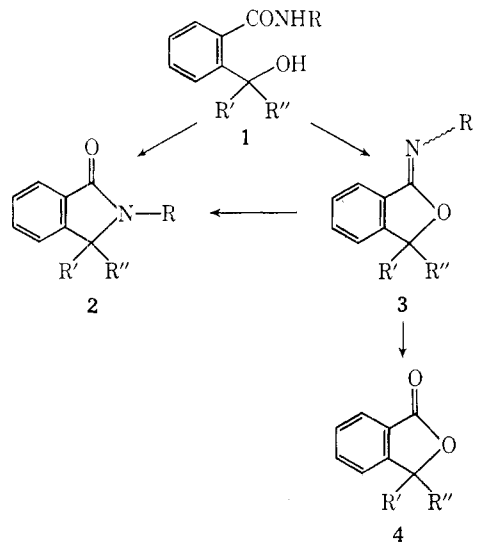
Received May 4, 1970

The H_2SO_4-catalyzed cyclodehydration of certain γ-hydroxyamides first described by Hauser, *et al.*,[2a] has been reexamined. The primary products have been found to be N-substituted phthalanimines instead of the isomeric phthalimidines. The course of the cyclization has been examined as a function of structure.

Following an earlier report[2b] on the acid-catalyzed cyclization of δ-hydroxyamides, Hauser, *et al.*,[2a] presented evidence for the formation of phthalimidines by cyclodehydration of γ-hydroxyamides. However, when we repeated the acid-catalyzed cyclizations of **1a–d** (Scheme I), the products were imino ethers which,

SCHEME I



Compd	R	R′	R″
a	CH_3	C_6H_5	H
b	CH_3	C_6H_5	C_6H_5
c	CH_3	$-(CH_2)_5-$	
d	C_6H_5	C_6H_5	C_6H_5

with the exception of **3d**, had physical properties in essential agreement with the "γ-lactams" of Hauser (Table I). The lability of **3d** (giving **2d**, see below) may account for **2d** being the only material isolated by these investigators.

TABLE I

CYCLODEHYDRATION OF γ-HYDROXYAMIDES[a]

γ-Hydroxy-amide	Acid	Product (% yield)	Mp, °C	Lit. mp or bp, °C (mm)[b]
1a	H_2SO_4	**3a** (59)	141.5–143.5	145.5–146.5
1b	H_2SO_4	**3b** (89)[c]	149–150[d]	153–153.5
		2b (11)[c]		
1b	H_2SO_4	**3b**·H_2SO_4 (86)	142–143[e]	128–129
1c	$HClO_4$	**3c**·$HClO_4$ (27)	226–227	
		4c (58)	80–81	81.5–82.5[f]
		3c (91)[g]	61.5–63.0	145 (3)
1d	H_2SO_4	**3d** (89)[c]	131–132[h]	
		2d (10)[c]	187–188[h]	189–190
		4b (1)[c]	118–119[i]	116–117[f]

[a] All reactions were carried out at 0–5°. [b] For products obtained in ref 2a. [c] Glc analysis of total reaction product. [d] Isolated in 53% yield by crystallization. [e] Sealed tube, strongly dependent on rate of heating. [f] W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **29**, 853 (1964). [g] From **3c**·$HClO_4$. [h] Isolated by column chromatography: **3d**, 62%; **2d**, 7%. [i] Prepared for identification according to reference in footnote *f*.

Before we attempted hydrolysis of the imino ethers, we turned to the syntheses of the anticipated products, the phthalimidines **2a–d** and the phthalides **4a–c**. All of the phthalides were known materials, and the products obtained here had physical properties in accord with published values as well as compatible elemental analyses and parent ions in the mass spectra. Of the phthalimidines, **2a**[3] and **2d**[4] had been prepared before. To provide an additional synthesis for **2a**, we subjected the known[5] 3-hydroxy-2-methyl-3-phenylphthalimidine to hydrogenolysis over palladium.[6] The melting point of the product (101.0–102.5°) was in agreement with that of material obtained by heating 3-phenylphthalide with methylamine at 190–200° (105°).[3] The 3,3-di-

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(1) Part I: D. M. Bailey and C. G. De Grazia, *J. Org. Chem.*, **70**, 4088 (1970).

(2) (a) C. Mao, I. T. Barnish, and C. R. Hauser, *J. Heterocycl. Chem.*, **6**, 475 (1969); (b) *ibid.*, **6**, 83 (1969).

(3) W. Theilacker and W. Schmidt, *Justus Liebigs Ann. Chem.*, **597**, 95 (1955).

(4) O. Fischer and E. Hepp, *Chem. Ber.*, **27**, 2790 (1894).

(5) G. Wittig, G. Closs, and F. Mindermann, *Justus Liebigs Ann. Chem.*, **594**, 89 (1955).

(6) *Cf.* N. Sperber and F. E. Roth, *J. Med. Chem.*, **7**, 453 (1964).

phenylphthalimidine **2d** was prepared by the published procedure.[4] Fortuitously, when 3,3-diphenylphthalide **4b** was mixed with a large excess of methylamine in ethanol at slightly above room temperature, a 92% yield of hydroxyamide **1b** could be isolated by filtration. These mild conditions are in contrast to those used by Hauser, *et al.*,[7] who opened **4b** with potassium amide (65% crude yield) or refluxing 95% hydrazine (unspecified yield).

When phthalide **4b** (or hydroxyamide **1b**) was heated at 170° for 18 hr with a large excess of methylamine, no phthalimidine was produced. If the temperature was raised to 200° and a catalytic amount of methylamine hydrochloride was added, a modest yield of **2b** was obtained after 18 hr.

Compound **2c** was prepared from the known 2′-methylspiro[cyclohexane-1,3′-phthalimidin]-4-one[8] by desulfurization of the corresponding ethylene thioketal derivative over Raney nickel.

A comparison of the physical and spectral properties of the imino ethers and γ-lactams is given in Table II.

TABLE II

SPECTRAL PROPERTIES OF IMINO ETHERS AND γ-LACTAMS

Compd						
Imino ether	γ-Lactam	Infrared[a] C=N	C=O	C-O-C	Nmr[b]	
	2a		1688		NCH_3	2.84
3a		1700		1296, 1078	NCH_3	3.12
	2b		1680		NCH_3	2.87
3b		1700		1295, 1078	NCH_3	3.33
	2c		1670		NCH_3	3.04
3c		1690		1295, 1090	NCH_3	3.20
	2d		1685			
3d		1682		1114, 1074		

[a] In cm^{-1} in $CHCl_3$. [b] In ppm from $(CH_3)_4Si$.

As was also true in the homologous series,[1] the *N*-methyl resonance in the γ-lactams **2a–c** consistently occurs at higher field than the *N*-methyl signal in the corresponding imino ethers **3a–c**. We again take this as evidence in assigning the anti configuration to the *N*-methyl imino ethers.

As in the previous examples,[1] the hydrolyses of the imino ethers were carried out in refluxing 3 *N* HCl for varying periods of time. Analyses of the crude hydrolysates were performed by glc. When the same conditions were applied to the γ-lactams, the starting materials were recovered in essentially quantitative yield. The results of the hydrolysis experiments are compiled in Table III.

To check for the possibility of thermal (Chapman[9]) rearrangement of the imino ethers, compounds **3b** and **3d** were kept at 100° for 1 hr. No lactam could be detected by glc analysis. However, when the samples were heated at 220–245° for the same length of time, conversions to lactams of 33 and 50%, respectively, were observed. Diradical intermediates have been proposed for a similar rearrangement.[10]

Some anomalous results obtained when the nmr spectrum of hydroxyamide **1b** was run in trifluoroacetic acid (TFA) prompted a brief examination of the effect of this acid on cyclodehydration. Compound **1b** dissolved instantly in TFA at 25° without liberation of heat. A glc analysis performed at once (over temperature 230°, duration of run 15 min) indicated that the product consisted of >98% lactam **2b**. However, when the reaction mixture was quenched and the product recrystallized, there was obtained a 74% yield of pure *imino ether* **3b**. That the glc data reflected column thermolysis of the trifluoroacetate salt of **3b** present in the reaction mixture was demonstrable by briefly refluxing a TFA solution of **3b**. The sole product (92.4% yield) was the lactam **2b**. It would appear, therefore, that in certain cases, the use of TFA as a cyclodehydrating agent would be advantageous.

TABLE III

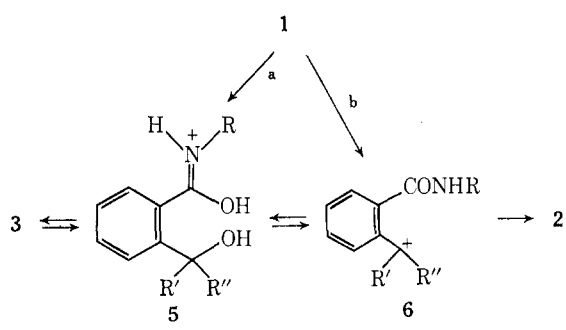
HYDROLYSIS OF IMINO ETHERS IN REFLUXING 3 *N* HCl

Imino ether	Reflux period, hr	Products	% yield[a]
2a	15	**4a**	90
		2a	10
2b	0.75	**4b**	13
		2b	87
2c	2	**4c**	100
2d	1	**4d**	25
		2d	75

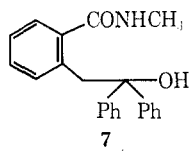
[a] By glc analysis of total crude reaction product.

As was seen earlier,[1] all of the products formed during cyclodehydration can be rationalized on the basis of the initial formation of two types of monocation **5** and **6** (Scheme II).

SCHEME II



Although the reaction pathways are similar to those described for the δ-hydroxyamide case, significant differences exist. The small yield of **2b** (from **1b**) in H_2SO_4 is quantitatively different from the results observed with the next higher homolog **7** which gives roughly equivalent quantities of the corresponding imino ether and lactam.[1] On the basis of arguments

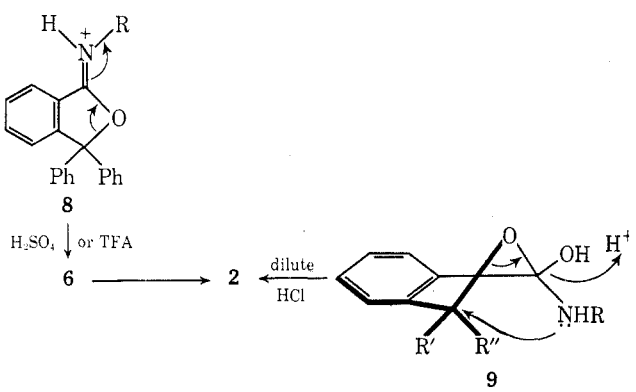


involving the stabilization of carbonium ions, however, **1b** would be expected to produce more lactam than **7** since the latter can form an alkylbenzhydryl carbonium ion while the ion from the former is trityl. This apparent anomaly undoubtedly arises as a consequence of steric crowding in the planar ion **6**, the model of which shows considerable interaction between the

(7) E. M. Levi, C. Mao, and C. R. Hauser, *Can. J. Chem.*, **47**, 3671 (1969).
(8) For a lead reference, see D. M. Collington, D. H. Hey, and C. W. Rees, *J. Chem. Soc. C*, 1017 (1968).
(9) For a comprehensive review, see J. W. Schulenberg and S. Archer, "Organic Reactions," Vol. 14, Wiley, New York, N. Y., Chapter 1.
(10) C. J. M. Stirling, *J. Chem. Soc.*, 255 (1960).

phenyl groups R′ and R″ and the *o*-carboxamide group. With the phenyl groups less able to stabilize the charge in **6**, route b becomes less favored. That route b is, in fact, entirely inoperative in the case of **1b** is demonstrated by observing the effect of H_2SO_4 on each of the products of the cyclodehydration. A pure sample of lactam **2b** was completely inert to the action of H_2SO_4 under the conditions of the cyclodehydration.[11] On the other hand a pure sample of imino ether **3b** was converted by H_2SO_4 at 0–5° into a mixture containing (glc) 89% starting material and 11% lactam **2b**. This corresponds exactly to the ratio of products obtained by cyclodehydrating **1b** (Table I). The logical conclusion to be drawn from these experiments is that lactam **2b** arises (from **3b**) as a consequence of heterolytic cleavage of the protonated imino ether **8** and that in the cyclodehydration of **1b** *this is the exclusive mechanism for the formation of* **2b**. It is probable that a similar heterolytic cleavage occurs when **3b** is heated in TFA (*vide supra*) and when the imino ethers **3a**, **3b**, and **3d** are heated with 3 *N* HCl (Table III).[12] In the latter cases, a concerted rearrangement of the hydrated imino ether **9** cannot be excluded (Scheme III).

SCHEME III



Conclusions

We have demonstrated that the treatment of certain γ-hydroxyamides with concentrated acids produces imino ethers. In cases where sufficient stabilization is afforded the incipient carbonium ions or diradicals, these imino ethers can be made to rearrange, at least partly, to the corresponding lactams. Trifluoroacetic acid has been shown in one case to be an effective solvent and catalyst for cyclodehydration and for rearrangement of imino ethers to lactams.

Experimental Section[1]

γ-Hydroxyamides.—The γ-hydroxyamides **1a–d** were prepared as previously described.[2a] Compound **1b** was obtained as large rhombs from MeCN: mp 183–185° dec (reported mp 164–165° dec); mass spectrum *m/e* 317 (parent ion); ir ($CHCl_3$) 3620 (OH), 3450 (NH), and 1642 cm^{-1} (C=O).

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.40; H, 6.09; N, 4.43.

Preparation of 1b from 3,3-Diphenylphthalide (4b).—A suspension of 3,3-diphenylphthalide[13] in absolute EtOH (50 ml) was saturated with $MeNH_2$. The hot solution was cooled and the resulting solid was washed with *i*-PrOH and dried *in vacuo*. The product (3.6 g, 91.5%), mp 182–184°, was indistinguishable (ir, mixture melting point) from hydroxyamide prepared above.

Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.29; H, 6.04; N, 4.41.

Cyclodehydration of γ-Hydroxyamides in Strong Acids.—The summarized results are found in Table I. The procedure of Hauser, *et al.*,[2a] was modified for glc runs (**1b** and **1d**) as follows. The cold H_2SO_4 reaction mixture was poured in a thin stream into ten times its weight of ice and H_2O. Chloroform (50–100 ml) was added, and the mixture was stirred while excess 35% NaOH was added dropwise. Ice was added as needed to keep $T < 5°$. The organic layer was separated; the aqueous one was extracted once with $CHCl_3$. The combined $CHCl_3$ solutions were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was used for glc analysis, and the products were purified by crystallization or column chromatography on silica gel. In this way were prepared the following compounds (pertinent nmr and ir data are summarized in Table II).

***N*-Methyl-3-phenylphthalanimine (3a)** had mp 141.5–143.5°: mass spectrum *m/e* 223 (parent ion); uv λ_{max}^{EtOH} 237 mμ (ε 11,740), 241 (11,860), 251 sh (7830), 268 (2180), 276 (2660), and 283 (3200).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.59; H, 5.86; N, 6.26.

3,3-Diphenyl-*N*-methylphthalanimine (3b) had mp 149–150°: mass spectrum *m/e* 299 (parent ion); uv λ_{max}^{EtOH} 242 mμ (ε 13,440), 253 sh (9760), 277 (2060), and 283 (2060).

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.99; H, 5.71; N, 4.58.

***N*-Methylspiro[cyclohexane-1,3′-phthalanimine] (3c)** had mp 61.5–63.0°: mass spectrum *m/e* 215 (parent ion); uv λ_{max}^{EtOH} 237 mμ (ε 11,580), 241 (12,200), 251 sh (8300), 267 (2510), 275 (3670), and 283 (4830).

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.76; H, 7.99; N, 6.37.

$HClO_4$ salt had mp 226–227°.

Anal. Calcd for $C_{14}H_{17}NO \cdot HClO_4$: C, 53.25; H, 5.76; N, 4.44. Found: C, 53.18; H, 5.74; N, 4.48.

***N*,3,3-Triphenylphthalanimine (3d)** had mp 131–132°: mass spectrum *m/e* 361 (parent ion); uv λ_{max}^{EtOH} 242 mμ sh (ε 14,040), 252 (10,510), 277 (9020), 287 (10,390), 301 (10,410), 317 (7240), and 333 (2780).

Anal. Calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88. Found: C, 86.55; H, 5.40; N, 3.74.

2-Methyl-3-phenylphthalimidine (2a).—Hydrogenolysis of 3-hydroxy-2-methyl-3-phenylphthalimidine[5] (2.39 g, 0.01 mol) was accomplished in a Parr apparatus at an initial hydrogen pressure of 35 psi gauge using 1 g of 10% Pd on C as catalyst and 100 ml of glacial HOAc as solvent. Uptake was complete in 20 hr. The mixture was heated to 70°, and the catalyst was filtered off. The filtrate was concentrated under reduced pressure. Last traces of acetic acid were removed from the residue by adding toluene and stripping *in vacuo*. The residual gum was dissolved in 20 ml of 1:1 C_6H_{14}–PhH mixture and set aside at ambient temperatures for 3 hr. The precipitated solid was collected by filtration, washed with hexane, and dried *in vacuo*. The product consisted of 1.33 g (60%) of fine needles: mp 101.0–102.5° (reported[3] 105°); mass spectrum *m/e* 223 (parent ion); uv λ_{max}^{EtOH} 216 mμ (ε 23,280), 228 sh (12,600), 243 (5680), 263 sh (3317), 272 sh (2100), and 280 (1340).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.66; H, 5.91; N, 6.12.

2-Methyl-3,3-diphenylphthalimidine (2b).—In a stainless steel autoclave were placed 2.0 g (0.064 mol) of hydroxyamide **1b**, 70 ml of absolute EtOH and 1 ml of concentrated HCl. About 10 g of $MeNH_2$ was run in, and the whole was heated at 200° (internal pressure 2500 psi gauge) for 18 hr. The cooled mixture was concentrated under reduced pressure, and the residue was taken up in H_2O and $CHCl_3$. The organic portion was washed with 2 *N* HCl and H_2O. The dried ($MgSO_4$) $CHCl_3$ solution was stripped *in vacuo*, and the residue (1.64 g) was crystallized from MeCN. The product thus obtained was 0.62 g (33%) of crystals: mp 170.5–171.5°; mass spectrum *m/e* 299 (parent ion); uv λ_{max}^{EtOH} 252 mμ (ε 5310), 263 sh (3950), and 282 sh (1140).

Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.13; H, 5.72; N, 4.66.

2′-Methylspiro[cyclohexane-1,3′-phthalimidine] (2c).—2′-Methylspiro[cyclohexane-1,3′-phthalimidin]-4-one, prepared according to Rees,[3] had mp 193–195° (reported 173–175°). Be-

(11) The 3,4-dihydroisocarbostyril homolog gives a mixture of imino ether and lactam under similar conditions; see ref 1.

(12) In these cases, heterolysis more or less competes with hydrolysis.

(13) J. M. Wilson, *J. Chem. Soc.*, 2297 (1951).

cause of the discrepancy in melting point, the compound was fully characterized: mass spectrum m/e 229 (parent ion); ir ($CHCl_3$) 1680 (γ-lactam C=O) and 1713 cm^{-1} (cyclohexanone C=O); reported 1676 and 1713 cm^{-1}; nmr ($CDCl_3$) δ 1.9 (m, 2, C-H[14]), 2.3-3.1 (m, 6, $-\overset{O}{\overset{\|}{C}}-CH_2-$ and C-H), 3.09 (s, 3, N-CH_3), and 7.60-7.95 (m, 4, ArH).

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.15; H, 6.63; N, 5.99.

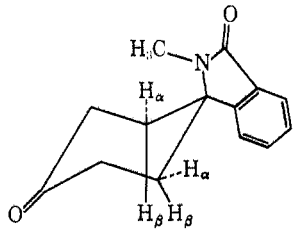
Following the procedure of Fieser,[15] a solution of 2.29 g (0.01 mol) of the above product in 3.2 ml of ethanedithiol was treated with 2.2 ml of $BF_3 \cdot Et_2O$ and the solution was kept at ambient temperature for 1 hr. Ice water and Et_2O were added, and the organic solution was extracted with four 50-ml portions of 10% NaOH. The dried ($MgSO_4$) solvent was removed under reduced pressure, and the residue was crystallized from 15 ml of *i*-PrOAc. The product, 1.94 g (64%), showed biphasic melting. Inserted at 100°, it melted at 161-163°. Inserted at 145°, it melted, resolidified, and melted again at 161-162°. The mother liquors from the above crystallization were stripped to yield 0.65 g of solid, one peak in the glc identical with the major crop: total yield 85%; ir ($CHCl_3$) 1675 cm^{-1} (γ-lactam C=O); nmr ($CDCl_3$) δ 1.17-2.84 (m, 8, four CH_2 groups), 3.07 (s, 3, N-CH_3), 2.38 (m, 4, S-CH_2CH_2-S), and 7.17-8.00 (m, 4, ArH).

Anal. Calcd for $C_{16}H_{19}NOS_2$: C, 62.91; H, 6.27; N, 4.59. Found: C, 62.88; H, 6.27; N, 4.49.

A 0.6-g (0.02 mol) sample of the above thioketal was stirred and refluxed with 3-4 g of Raney nickel in 10 ml of absolute ethanol. After 5 hr, glc analysis indicated that all of the thioketal had been converted to a material with lower retention time. The metal was filtered off and washed with EtOH, and the filtrates were stripped *in vacuo*. The residual oil (0.34 g, 81% crude yield) was homogeneous on glc. Crystallization from heptane gave 0.14 g (33%) of crystals: mp 87-88.5°; mass spectrum m/e 215 (parent ion); uv λ_{max}^{EtOH} 222 mμ (ϵ 9660), 230 (9360), 243 (5870), 269 sh (3090), and 231 (2200); nmr ($CDCl_3$) δ 1.20-2.40 (m, 10, five CH_2 groups), 3.04 (s, 3, N-CH_3), and 7.30-8.00 (m, 4, ArH).

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.94; H, 7.63; N, 6.39.

(14) Assuming the product to have the conformation shown in b in which



b

the phenyl portion of the phthalimidine moiety assumes a more or less equatorial configuration, this multiplet can be assigned to the two equivalent equatorial protons H_α. A model shows these protons to be shielded (relative to the equivalent pair of axial protons H_β) by the positive anisotropic effect of the benzene ring and the amide carbonyl.

(15) L. F. Fieser, *J. Amer. Chem. Soc.*, **76**, 1945 (1954).

Registry No.—**1b**, 23659-57-6; **2a**, 15836-66-5; **2b**, 20141-84-8; **2c**, 23659-74-7; **2c** dithioketal, 23659-74-7; **2d**, 23659-69-0; **3a**, 26278-31-9; **3b**, 26278-32-0; **3b**·H_2SO_4, 26322-31-6; **3c**, 26278-33-1; **3c** $HClO_4$ salt, 26278-34-2; **3d**, 26322-30-5; 2′-methylspiro[cyclohexane-1,3′-phthalimidin]-4-one, 26278-35-3.

The Cycloaddition of Aroyl and Sulfonyl Cyanides with 5,5-Dimethoxy-1,2,3,4-tetrahalocyclopentadienes

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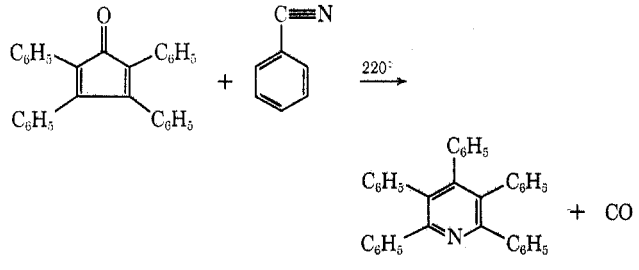
Received April 29, 1970

The cycloaddition of aroyl and sulfonyl cyanides with 5,5-dimethoxy-1,2,3,4-tetrahalocyclopentadienes is facilitated by electron-withdrawing substituents. The sulfonyl cyanides have been shown to be more reactive than the aroyl cyanides providing further evidence that delocalization of the π charge density of the cyano group facilitates the cycloaddition reactions. The effect of solvent on the reaction of benzoyl cyanide and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene is also described.

The dienophilicity of the cyano group is well known and the subject has been reviewed.[2] The first observation of the dienophilic properties of the cyano group was reported by Dilthey[3] who synthesized pentaphenylpyridine from tetracyclone and benzonitrile. An extensive study of the cycloaddition reaction of perhalonitriles, *e.g.*, $CF_3C{\equiv}N$ with butadiene in the gas phase at 350-400°, was carried out by Janz and coworkers.[4] Yields of the pyridines were essentially quantitative. Alder also cited an example of the dienophilic properties of the cyano group in which cyanoformic ester was found to react with butadiene to give 2-picolinic acid ester derivatives.[5] Our interest in this area originated from the literature report[6a] that 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**2a**) would undergo reaction with benzoyl cyanide (**1**) to give a methyl picolinate. This paper describes our results concerning the effect of substituents on the benzoyl cyanide, the effect of solvent on the reaction, and structural proof of the side reaction products. In addition, the reaction is described for a



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