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Chemistry of a Cumulated Double-Bond Compound. X. Reactions of Isocyanates and Carbodiimide with Acetylenic Compounds

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In the reaction of phenyl isocyanate with phenylacetylene in the presence of $Fe(CO)_5$, 4-benzylidene-1,3-diphenylhydantoin (**1a**) was obtained in 85% yield by the addition reaction and hydrogen shift. Oxidation of **1a** gave diphenylparabanic acid. The hydrogen transfer of acetylenic hydrogen was identified with phenylacetylene-1-*d*. The reaction of diphenylcarbodiimide with phenylacetylene in the presence of $Fe(CO)_5$ gave 4-benzylidene-1,3-diphenyl-2,5-bis(phenylimino)imidazolidine and 4-benzylidene-1,3-diphenyl-2-phenyliminoimidazolidin-5-one in 78 and 17% yields, respectively. 1,3,4-Triphenylpyrroline-2,5-dione and 1,3,4-triphenyl-5-phenyliminopyrrolin-2-one were obtained in 42 and 15% yields, respectively, in the reaction using phenyl isocyanate, diphenylacetylene, and $Fe(CO)_5$. In this reaction, hydantoin and imidazolidine were not obtained. Reaction mechanisms are discussed.

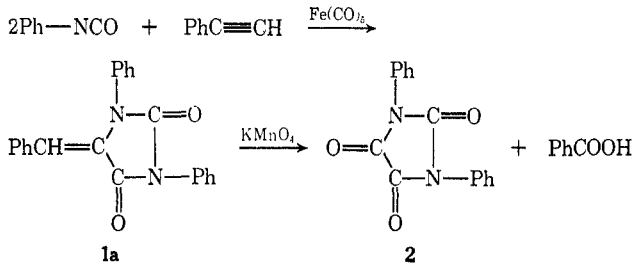
Cycloaddition reactions of heterocumulenes to olefins have been investigated in detail for a long time.[1] On the other hand, the reaction between heterocumulene and acetylenic compound has been dealt with in a few papers,[2-5] but there is no information regarding a reaction between isocyanate (or carbodiimide) and phenylacetylenes without the reaction between metal phenylacetylide and aryl isocyanates.[6-8] It was recognized in our preliminary experiments that isocyanates and carbodiimides were unreactive to acetylenic compounds without a catalyst.

It is well known that acetylenic compounds[9] and heterocumulenes[10-14] form numerous organometallic complexes with metal carbonyls. Consequently, we can expect some reaction between heterocumulenes, such as isocyanates or carbodiimides, and acetylenic compounds in the presence of metal carbonyls *via* metal complex intermediate formation.

In this paper, reactions of isocyanates and carbodiimides with acetylenic compounds in the presence of iron carbonyls are studied and some interesting results are obtained.

Results and Discussion

Reactions with Phenylacetylene.—In the reaction of phenyl isocyanate with phenylacetylene in the presence of iron pentacarbonyl at 150–160°, 4-benzylidene-1,3-diphenylhydantoin (**1a**) was obtained in 85% yield. This product seemed to be formed with 2 mol of phenyl isocyanate and 1 mol of phenylacetylene by an addition reaction and hydrogen shift. The structure of **1a** was confirmed by ir, nmr, and mass spectra, and furthermore, by oxidation of **1a** which gave diphenylparabanic acid (**2**) and benzoic acid.



1a **2**

The ir spectrum of **1a** in a Nujol mull indicated peaks at 1775, 1725, and 1650 cm^{-1}. The former two peaks were assigned to C=O stretching vibration of –CO–NR–CO– group in a five-membered ring and the latter to a C=C stretching vibration. In the mass spectrum of **1a**, the molecular ion was found at *m/e* 340 (calcd for $C_{22}H_{16}N_2O_2$: 340), and the major fragment was found at 193 which corresponded to PhCH=C=NPh resulting from **1a** by losing the –CO–NR–CO– group (calcd for $C_{14}H_{11}N$: 193). The pattern of fragmentation well explained the structure of **1a**.

The hydantoin **1a** had been prepared through different processes,[6-8] and fair agreements between the observed and reported values were obtained by melting point and ir, nmr, and mass spectra.

The hydrogen transfer of the acetylenic hydrogen of phenylacetylene was identified by the following results. The reaction using phenylacetylene-1-*d* in place of phenylacetylene gave 4-(benzylidene-α-*d*)-1,3-diphenylhydantoin (**1'a**) in 60% yield. The melting point of **1'a** was identical with that of hydantoin **1a**, 200°; the mixture melting point of the hydantoin **1a** and **1'a** was not depressed. The ir spectrum of the hydantoin **1'a** was identical with that of hydantoin **1a**

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TABLE I.—REACTION OF PHENYL ISOCYANATE WITH PHENYLACETYLENE

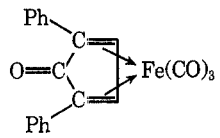
Expt no.	Reactant, mol			Solvent	Temp, °C	Time, hr	Yield, %					
	PhNCO	PhC≡CH	$Fe(CO)_5$				Hydantoin **1a**[a]	Complex **3**[b]	Isocyanurate **4**	Urea **5**[h]	Adduct **6**[a,i]	PhC≡CH[c]
1[d]	0.05	0.025	0.025		160	1.5	85			Trace	Trace	
2[e]	0.025	0.025	0.025		180	4	68	7	7	8	5	
3[e]	0.1	0.05	0.05	THF	67	6	33	Trace	20	34	Trace	50
4[e]	0.06	0.03	*f*	THF	67	6	11	4	69	16		
5[d]	0.05	0.025	*g*		180	6.5	41			24	15	40

[a] Based on PhNCO. [b] Based on PhC≡CH. [c] Unreacted. [d] PhC≡CH was added to the mixture of PhNCO and $Fe(CO)_5$. [e] PhNCO was added to the mixture of PhC≡CH and $Fe(CO)_5$. [f] $Fe_3(CO)_{12}$ (0.01 mol) was used in place of $Fe(CO)_5$. [g] Cu–C≡CPh (5 wt %) was used in place of $Fe(CO)_5$. [h] **5** is N,N′-diphenylurea. [i] **6** is the 3:1 adduct of PhNCO and PhC≡CH.

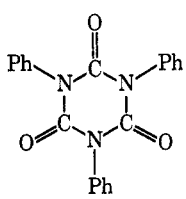
except for the absorption band of the C–D bond; the peak of C–D in-plane deformation of the hydantoin **1′a** appeared at 1250 cm^{-1}, compared with the peak of the hydantoin **1a** (1280 cm^{-1} for C–H). The mass spectrum of the hydantoin **1′a** showed the molecular ion at 341 (calcd for $C_{22}H_{15}DN_2O_2$: 341) and the major fragment corresponding to PhCD=C=NPh at 194 (calcd for $C_{14}H_{10}DN$: 194).

The results of the reaction of phenyl isocyanate and phenylacetylene with and without iron pentacarbonyl at several conditions are summarized in Table I.

In the case of addition of phenyl isocyanate to the mixture of phenylacetylene and iron pentacarbonyl, the yield of the hydantoin **1a** was relatively poor because of formation of stable iron complexes, *i.e.*, 2,5-diphenylcyclopentadienoneiron tricarbonyl (**3**). When the same reaction was carried out in tetrahydrofuran, triphenyl isocyanurate (**4**) was the major product and the yield of the hydantoin **1a** was decreased.



3



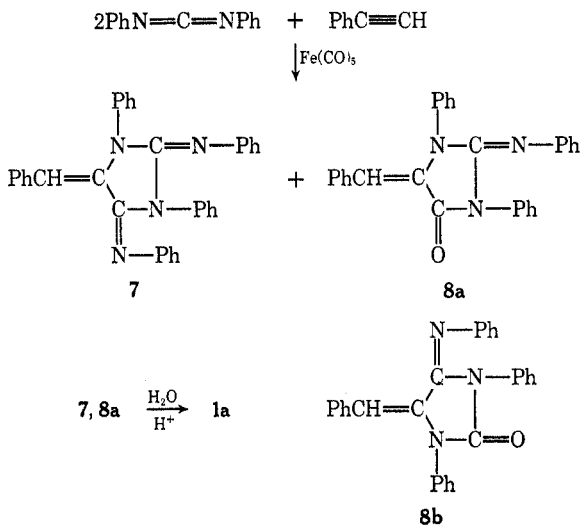
4

The reaction using triiron dodecacarbonyl in place of iron pentacarbonyl gave the hydantoin **1a** in poor yield.

A similar reaction was observed by using 5% (by weight) copper phenylacetylide in place of iron carbonyls; however, the 3:1 adduct **6** of phenyl isocyanate and phenylacetylene was obtained in 15% yield. We could not clarify the structure of the adduct **6**.

The results of the reaction using several isocyanates are shown in Table II. There was no significant difference in the reaction using phenyl isocyanate. *n*-Butyl isocyanate was less reactive and easily formed isocyanurate in 80% yield.

The reaction of diphenylcarbodiimide (2 mol) with phenylacetylene (1 mol) in the presence of iron pentacarbonyl (1 mol) was carried out at 180° for 5 hr, and 4-benzylidene-1,3-diphenyl-2,5-bis(phenylimino)imidazolidine (**7**) and 4-benzylidene-1,3-diphenyl-2-phenyliminoimidazolidin-5-one (**8a**) were obtained in 78 and 17% yields, respectively. The imidazolidines **7** and **8a** were hydrolyzed quantitatively to the hydantoin **1a**. The structure of the imidazolidine **7** was identified by ir and mass spectra and elemental analysis. For the structure of the imidazolidinone, two forms, **8a** and **8b**, were proposed from the infrared spectrum, 1750 (C=O), 1660 (C=N), and 1635 cm^{-1} (C=C). The mass spectrum showed the fragment at 208; this corresponded to $(PhN)_2C{=}NPh$ minus Ph for **8a**. Consequently, the structure of the product was identified as **8a**.



It seemed that the imidazolidine **8a** was formed from phenyl isocyanate, diphenylcarbodiimide, and phenylacetylene. Hence the equimolecular reaction of phenyl isocyanate, diphenylcarbodiimide, phenylacetylene, and iron pentacarbonyl was carried out at 190° for 2 hr. However, the imidazolidine **8a** was not obtained, and the hydantoin **1a**, the imidazolidine **7**, and 5-benzylidene-2,3,4,5-tetrahydro-3-phenyl-1H-1-benzodiazepine-2,4-dione (**11**) were obtained in 82, 67, and 12% yields, respectively.

The reaction mechanism was assumed as shown in Scheme I.

It seemed that the hydrido carbonyl acetylide complex played an important role as an intermediate in the formation of the hydantoins **1a–f** and the imidazolidine **7**. The "doubly σ-bonded" acetylene complex **12** was probably formed at first, and the complex **12** changed readily to the acetylide complex **13** owing to the polarization of the C–H bond of the acetylenic group. A similar conversion has previously been proposed by Meriwether[15] and Collman.[16] Acetylene–iron carbonyl complexes such as **12** had been isolated[17] and termed "doubly σ bonded."[16]

In the second step, R–NCX was inserted into the C–Fe bond of the complex **13**, and the complex **14** was

(15) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **27**, 3930 (1962).
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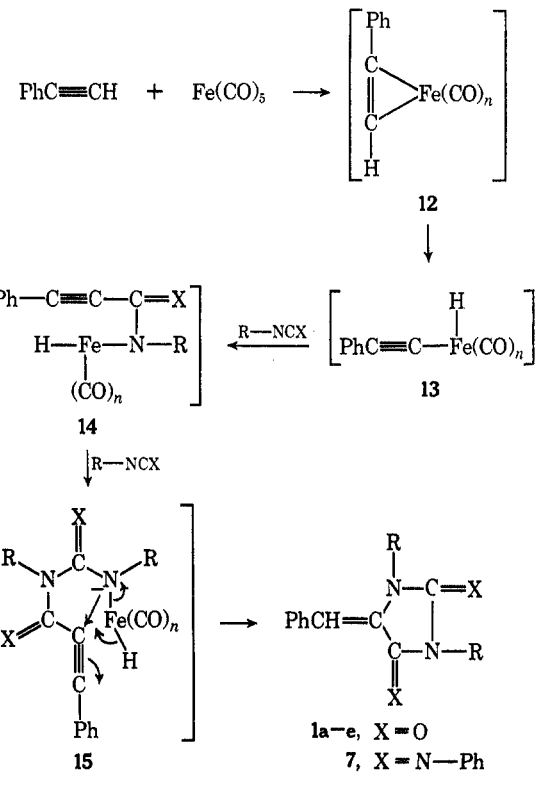
TABLE II.—CHARACTERIZATION DATA ON REACTION PRODUCTS

Compd	X	R	Yield, %	Mp, °C	Hydantoin 1a–f: Ir, cm⁻¹ $\nu_{C=O}$	Ir, cm⁻¹ $\nu_{C=N}$	Ir, cm⁻¹ $\nu_{C=C}$	Imidazolidine 7,8: Formula	Imidazolidine 7,8: Calcd, % C	Imidazolidine 7,8: Calcd, % H	Imidazolidine 7,8: Calcd, % N	Pyrroline 9,10: Obsd, % C	Pyrroline 9,10: Obsd, % H	Pyrroline 9,10: Obsd, % N
1a		Phenyl	85	200	1775, 1725		1650	$C_{22}H_{16}O_2N_2$	77.63	4.74	8.23	77.94	4.78	8.01
1b		*o*-Chlorophenyl	67	147.5	1775, 1730		1650	$C_{22}H_{14}O_2N_2Cl_2$[a]	64.56	3.45	6.85	64.82	3.33	6.56
1c		*o*-Tolyl	38	221	1770, 1725		1650	$C_{24}H_{20}O_2N_2$	78.24	5.47	7.60	78.25	5.16	7.32
1d		α-Naphthyl	33	259–260	1770, 1730		1645	$C_{30}H_{20}O_2N_2$	81.80	4.58	6.30	81.27	4.41	6.20
1e		Cyclohexyl	48		1760, 1710		1650	$C_{22}H_{28}O_2N_2$	74.96	8.01	7.95	75.27	8.29	7.49
1f		*n*-Butyl	7		1760, 1710		1650	$C_{18}H_{24}O_2N_2$	71.97	8.05	9.33	71.83	7.92	9.10
7	N–Ph		78	145		1690, 1660	1635	$C_{34}H_{28}N_4$	83.24	5.34	11.42	83.12	5.29	11.51
8	O		17	195	1750	1660	1635	$C_{28}H_{21}ON_3$	80.94	5.09	10.11	81.37	5.00	10.04
9	O		42[b]	180–181	1770, 1710		1620	$C_{21}H_{15}O_2N$	81.21	4.65	4.31	81.47	4.64	4.40
10	N–Ph		48	157–158	1720	1635	1590	$C_{28}H_{20}ON_2$	83.97	5.03	7.00	83.98	5.03	6.79
11			12	215–216	1760, 1710	*c*	1645	$C_{22}H_{16}O_2N_2$	77.63	4.74	8.23	77.58	4.65	8.14

[a] Cl, %: calcd 17.33, obsd 17.31. [b] Pyrroline 10 was obtained in 15% yield. [c] NH stretching: 3300 cm⁻¹.

SCHEME I

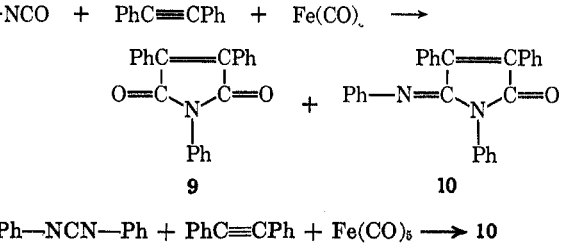


formed consequently. The insertion of an additional R–NCX into the complex **14** led to the complex **15**. The complex **15** was converted into the hydantoins **1a–f** and the imidazolidine **7** by hydrogen transfer and ring closure.

The reaction mechanism as shown above was supported by the result of the reaction between phenyl isocyanate and phenylacetylene with copper phenylacetylide catalyst, in which the hydantoin **1a** was obtained in high yield. There are several reports for the reaction between metal phenylacetylide (metal: Na,[6] $PbEt_3$,[7] $SnEt_3$[8]) and aryl isocyanate (Ar = phenyl, α-naphthyl) resulting in the formation of the hydantoin **1a**.

The reaction path to the imidazolidine **8a** could not be clarified from the results of this experiment.

Reactions with Diphenylacetylene.—In the reaction using diphenylacetylene in place of phenylacetylene, the 2:1 adduct with phenyl isocyanate or diphenylcarbodiimide, corresponding to the hydantoin **1** or the imidazolidine **7**, was not obtained. 1,3,4-Triphenylpyrroline-2,5-dione (**9**) and 1,3,4-triphenyl-5-phenyliminopyrrolin-2-one (**10**) were obtained in 42 and 15% yields, respectively, in the reaction using 2 mol of phenyl isocyanate, 1 mol of diphenylacetylene, and 1 mol of iron pentacarbonyl at 175° for 4 hr. The results are shown in Table II.

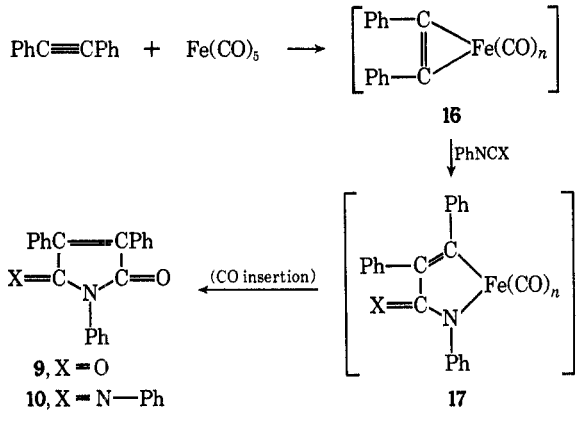


Ph—NCN—Ph + PhC≡CPh + $Fe(CO)_5$ ⟶ **10**

These products were formed by CO insertion and their structures were confirmed by ir and mass spectra and elemental analysis. It could be presumed that the pyrroline **10** may be constructed with diphenylacetylene, carbon monoxide, and diphenylcarbodiimide which was produced *in situ* from phenyl isocyanate under the catalysis of iron pentacarbonyl.[12] The pyrroline **10** was also obtained in 45% yield in the equimolecular reaction using diphenylcarbodiimide, diphenylacetylene, and iron pentacarbonyl at 185° for 2 hr. The pyrroline **10** was hydrolyzed quantitatively to the pyrroline **9** by acid.

The reaction mechanism to produce the pyrrolines **9** and **10** was assumed to proceed as shown in Scheme II.

SCHEME II



The "doubly σ-bonded" acetylene complex **16** was initially formed and was easily added to Ph–NCX across the N=C bond to form the complex **17**. The complex **17** was converted to the pyrrolines **9** and **10** by insertion of CO.

Experimental Section

All melting points were determined on Yanagimoto micro melting point apparatus and are uncorrected.

Infrared spectra were taken with a Jasco IR-E spectrometer. Proton magnetic resonance spectra were taken with a Joel LNM-3H-60 spectrometer in CCl_4 with TMS as the internal standard. Mass spectra were taken with a Hitachi RMU-6E spectrometer.

All reactions were carried out under a nitrogen atmosphere in a 50-ml four-necked flask equipped with a mechanical stirrer, reflux condenser, dropping funnel, and nitrogen inlet. Chromatographic separations were carried out using activated alumina columns.

Materials.—Phenyl isocyanate, *n*-butyl isocyanate, α-naphthyl isocyanate, phenylacetylene, and iron pentacarbonyl were purchased from a commercial source. *o*-Chlorophenyl isocyanate, *o*-tolyl isocyante, and cyclohexyl isocyanate were prepared from the corresponding amines and carbonyl chloride in the usual way.[18] Diphenylacetylene,[19] N,N′-diphenylcarbodiimide,[12] copper phenylacetylide,[20] and triiron dodecacarbonyl[21] were prepared according to previously outlined procedures. Phenylacetylene-1-*d*[15] was prepared in 88.8% isotopic purity by hydrolysis of the Grignard reagent of phenylacetylene with 99.7% deuterium oxide. Tetrahydrofuran was dried by refluxing on sodium wire in the presence of benzophenone.

4-Benzylidene-1,3-diphenylhydantoin (1a).—A mixture of phenyl isocyanate (0.05 mol) and iron pentacarbonyl (0.025 mol) was stirred at 150° for 40 min. Phenylacetylene (0.025 mol) was added dropwise to the mixture, and stirring was continued for 1.5 hr at 150–160°. After removal of carbon monoxide, the reaction mixture was extracted (benzene) and crystallized (benzene) to give 7.5 g of the yellow crystals **1a**. The product was chromatographed (benzene) and recrystallized (benzene) to give the hydantoin **1a** (white crystals): mp 200° (lit.[7] 193–194°); nmr (CCl_4) δ 7.65–6.70 (all protons); ir (Nujol mull) 1775 and 1725 (C=O), 1650 cm^{-1} (C=C); mass spectrum (70 eV) *m/e* 340 (M^+), 193 (PhCH=C=NPh).

The equimolecular reaction of phenyl isocyanate and phenylacetylene was carried out in a similar manner (*vide supra*). The products were chromatographed with benzene (fractions 1–3), benzene–ethyl ether (1:1) (fraction 4), and ethyl ether–ethanol (1:1) (fraction 5). From the first fraction, 0.3 g of π-2,5-diphenylcyclopentadieneiron tricarbonyl (**3**) was obtained and recrystallized (benzene–ethanol), mp 222° dec; the melting point of the mixture of compound **3** and the authentic sample[22] was not depressed. From the second fraction, 2.9 g of the hydantoin **1a** was obtained. From the third fraction, 0.2 g of triphenyl isocyanurate (**4**) was obtained and recrystallized (benzene), mp 294°; no depression of melting point was observed for the mixture with the authentic sample.[23] From the fourth fraction, 0.2 g of adduct **6** (white crystals) was isolated and recrystallized (benzene): mp 165°; ir (Nujol mull) 1775 and 1730 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 459 (M^+), 368 (M − N-C_6H_5), 340 (M − C_6H_5NCO), 249 (M − $C_6H_5NCONC_6H_5$).

Anal. Calcd for $C_{29}H_{21}N_3O_3$: C, 75.80; H, 4.61; N, 9.15. Found: C, 75.50; H, 4.49; N, 9.05.

From the fifth fraction, 0.2 g of N,N′-diphenylurea (**5**) was obtained and recrystallized (ethanol), mp 239°; no depression of melting point was observed for the mixture with the authentic sample.[24]

4-Benzylidene 1,3-Disubstituted Hydantoins (1b–f).—Reactions between isocyanate (0.05 mol), iron pentacarbonyl (0.025 mol), and phenylacetylene (0.025 mol) were carried out at 150–180° for 3 hr in a similar manner (*vide supra*). Isocyanates used were *o*-chlorophenyl, *o*-tolyl, α-naphthyl, cyclohexyl, and *n*-butyl isocyanates. After similar treatments, the following products were obtained by recrystallization or distillation (Table II).

4-Benzylidene-1,3-di-*o*-chlorophenylhydantoin (**1b**): white crystals; mp 147.5°; mass spectrum (70 eV) *m/e* 192 (C_6H_4N=C=CHPh), 227 and 229 (ClC_6H_4N=C=CHPh), 373 and 375 (M − Cl), 408 and 410 (M^+).

4-Benzylidene-1,3-di-*o*-tolylhydantoin (**1c**): white crystals; mp 221°; mass spectrum 368 (M^+), 291 (M − C_6H_5), 277 (M − C_7H_7), 207 (C_6H_5CH=C=$NC_6H_4CH_3$).

4-Benzylidene-1,3-di-α-naphthylhydantoin (**1d**): white crystals; mp 259–260° (lit.[7] 254–256°); mass spectrum 440 (M^+), 363 (M − C_6H_5), 243 (C_6H_5CH=C=$NC_{10}H_7$).

4-Benzylidene-1,3-dicyclohexylhydantoin (**1e**): orange oil; bp 180° (3 mm); mass spectrum 352 (M^+), 270 (M − C_6H_{10}), 199 (C_6H_5CH=C=NC_6H_{11}), 188 (M − $2C_6H_{10}$).

4-Benzylidene-1,3-di-*n*-butylhydantoin (**1f**): orange oil; bp 148° (0.3 mm); mass spectrum 300 (M^+), 243 (M − C_4H_9), 186 (M − $2C_4H_9$), 173 (C_6H_5CH=C=NC_4H_9). In the reaction of *n*-butyl isocyanate, 4.0 g of tri-*n*-butyl isocyanurate was obtained as a by-product in 80% yield, ir 1690 cm^{-1} (C=O); the ir spectrum was identical with that of the authentic sample.

4-Benzylidene-1,3-diphenyl-2,5-bis(phenylimino)imidazolidine (7) and 4-Benzylidene-1,3-diphenyl-2-phenyliminoimidazolidin-5-one (8a).—The reaction using N,N′-diphenylcarbodiimide (0.0366 mol), iron pentacarbonyl (0.0183 mol), and phenylacetylene (0.0183 mol) was carried out in a similar manner as above at 150–180° for 5 hr. The products were extracted (benzene), chromatographed (benzene), and recrystallized (benzene–hexane) to give following compounds.

Imidazolidine **7**: yellow crystals; 7.0 g; mp 145°; mass spectrum 490 (M^+), 296 (M − C_6H_5N=C=NC_6H_5), 193 (C_6H_5-CH=C=NC_6H_5).

Imidazolidine **8a**: yellowish orange crystals; 1.3 g; mp 195°; mass spectrum 415 (M^+), 338 (M − C_6H_5), 296 (M − C_6H_5-NCO), 208 [C_6H_5N=C(NC_6H_5)$_2$ − C_6H_5], 193 (C_6H_5CH=C=NC_6H_5).

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1,3,4-Triphenylpyrroline-2,5-dione (9) and 1,3,4-Triphenyl-5-phenyliminopyrrolin-2-one (10).—The reaction using phenyl isocyanate (0.05 mol), diphenylacetylene (0.025 mol), and iron pentacarbonyl (0.025 mol) was carried out in a similar manner as above at 175° for 4 hr, and the products were extracted (benzene) and chromatographed (benzene, fractions 1–5; ethanol, fraction 6). From the first fraction, 0.1 g of π-tetraphenylcyclobutadieneiron tricarbonyl, $Fe(CO)_3(PhC_2Ph)_2$ (mp 238° dec), and 0.7 g of the binuclear iron carbonyl complex, $Fe_2(CO)_6$-$(PhC_2Ph)_2$ (mp 205° dec), were obtained and recrystallized (benzene–ethanol); no depressions of melting points were observed for each mixture with authentic samples.[22] From the second fraction, 0.2 g of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (mp 220°) was obtained and recrystallized (benzene); no depression of the melting point was observed for the mixture with the authentic sample.[25] From the third fraction, the pyrroline **9** was obtained and recrystallized (benzene–ethanol): yellow needles; 3.3 g; mp 180–181° (lit.[26] 178–179°); mass spectrum (70 eV) *m/e* 325 (M^+), 297 (M − CO), 206 (M − C_6H_5NCO). From the fourth fraction, the pyrroline **10** was obtained and recrystallized (ethanol): orange crystals; 1.5 g; mp 157–158°; mass spectrum (70 eV) *m/e* 400 (M^+), 372 (M − CO), 295 (372 − C_6H_5), 281 (M − C_6H_5NCO), 194 (C_6H_5N=C=NC_6H_5). From the fifth and sixth fractions, 0.1 g of the cyanurate **4** (mp 294°) and 1.0 g of the urea **5** (mp 239°) were obtained; no depression of melting points were observed for the mixture with the authentic samples.[23,24]

The pyrroline **10** was also obtained in 48% yield in the reaction using N,N′-diphenylcarbodiimide (0.0073 mol), diphenylacetylene (0.0073 mol), and iron pentacarbonyl (0.0073 mol) at 185° for 2 hr.

4-(Benzylidene-α-*d*)-1,3-diphenylhydantoin (1′a).—The hydantoin **1′a** was prepared from phenylacetylene-1-*d* in a similar manner to that used to prepare the hydantoin **1a**: white crystals, 60% yield, mp 200°.

Equimolecular Reaction of Phenyl Isocyanate, Diphenylcarbodiimide, Phenylacetylene, and Iron Pentacarbonyl.—A mixture of diphenylcarbodiimide (0.01 mol), phenyl isocyanate (0.01 mol), and iron pentacarbonyl (0.01 mol) was heated to 140° for 30 min. Phenylacetylene was added dropwise to the mixture, and stirring was continued for 2 hr at 140–190°. The products were extracted (benzene), concentrated, and chromatographed (benzene). From the first and second fractions, 1.7 g (67%) of the imidazolidine **7** and 1.4 g (82%) of the hydantoin **1a** were obtained, respectively. From the third fraction, 0.2 g (12%) of the benzodiazepinone **11** was obtained and recrystallized (benzene–ethanol): yellow crystals; mp 215–216° (lit.[6] 202–203°); mass spectrum (70 eV) *m/e* 340 (M^+), 220 (M − PhNCO), 192 [M − CON(Ph)CO].

Acid Hydrolysis of the Imidazolidines 7 and 8a and the Pyrroline 10.—Either **7**, **8a**, or **10** (0.5 g) was dissolved in a mixture of 20 ml of ethanol and 10 ml of water, and concentrated hydrochloric acid (10 ml) was added. After refluxing for 10 min on a steam bath, the reaction mixture was cooled, extracted (ethyl ether), dried ($MgSO_4$), concentrated, and recrystallized (benzene) giving **1a** (from **7** and **8a**) or **9** (from **10**). Hydrolyses were quantitative.

Oxidation of the Hydantoin 1a.—Powdered potassium permanganate (1.3 g) was added over 1 hr to the hydantoin **1a** (1.5 g) dissolved in pyridine (20 ml)–water (2 ml) with vigorous stirring; the temperature was held at 18–20°. Water (10 ml) in limited amounts was added to the reaction mixture with stirring, and stirring was continued for 30 min. The solution was made acid to congo red with dilute sulfuric acid and decolorized by sodium hydrogen sulfite. The precipitate was washed with water (30 ml) and ethyl ether (30 ml) and crystallized (benzene–hexane), giving 1.0 g (85%) of white needles of parabanic acid **2**: mp 210° (lit.[27] 206–207°); ir 1785 and 1740 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 266 (M^+), 119 (C_6H_5NCO).

Anal. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.66; H, 3.79; N, 10.52. Found: C, 67.67; H, 3.79; N, 10.46.

The filtrate was made acid with concentrated hydrochloric acid and extracted with two 100-ml portions of ether. The ethereal extract was dried ($MgSO_4$) and concentrated. Benzoic acid (0.2 g) was obtained by crystallization of the residue with hexane: 37% yield; mp 124°; no depression of melting point was observed for the mixture with the authentic sample.

Registry No.—**1a**, 4514-33-4; **1b**, 24707-10-6; **1c**, 24707-11-7; **1d**, 17858-25-2; **1e**, 24707-13-9; **1f**, 24704-22-1; **2**, 6488-59-1; **7**, 24707-15-1; **8a**, 24707-16-2; **9**, 5191-53-7; **10**, 24707-18-4; **11**, 4514-34-5.

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Mass Spectra of Tetraza-3,6-disilacyclohexanes and Silylhydrazines

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The mass spectra of some silylhydrazines and tetraaza-3,6-disilacyclohexanes are presented. Silicon-containing fragments are the most abundant. Characteristic fragmentation modes are the direct and stepwise loss of free radicals and neutral molecules from the molecular and fragment ions. Hydrogen transfer and skeletal rearrangement processes are observed. Evidence for rearrangements of doubly charged ions has been obtained. Two different types of metastable ions are detected which support many fragmentation modes. High-resolution data are in agreement with the proposed fragmentation processes.

Although the interest in organosilicon chemistry has been steadily increasing in recent years, only a limited amount of information is available concerning the mass spectral fragmentation of organosilicon compounds.[2–7] The mass spectra of trimethylsilyl ethers, amines, and sulfides, derivatives of acids,[8–10] and siloxanes[11–13] have been reported.

The information available in literature on the be-

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