Metal-Catalyzed Synthesis of Cyano Enaminediones from β-Dicarbonyl Compounds and Cyanogen. Identification of Traube's Isomers

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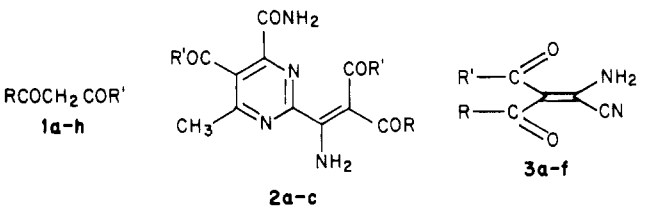
Bis(2,4-pentanedionato)zinc(II) is found to be a mild, efficient, and simple to use catalyst for the additions of a variety of β-dicarbonyls to cyanogen in aprotic solvents. The catalytic system is very selective in the formation of multifunctional cyano enaminediones **3** from β-diketones, β-keto esters, and β-diesters. A rational mechanism for the role of the metal is presented. In the presence of an acid or a base the adducts afford the previously unidentified Traube's isomers. Single-crystal X-ray diffractometry demonstrated that the derivatives of acetylacetone are a 5-methylene lactam and a 5-methylene-2-iminofuran derivative.

In the course of our studies on the activation of cyanogen by metal centers in homogeneous phase,[1-7] we found that β-dicarbonyl compounds **1a–c** (R, R′ as in Table I) react with C_2N_2, in the presence of catalytic amounts of $Ni(acac)_2$ or $Cu(acac)_2$, yielding the fully substituted pyrimidines **2a–c**.[5]



The reaction was proposed to involve the formation of intermediates **3a–c**, whose cyclodimerization gave the isolated pyrimidines.

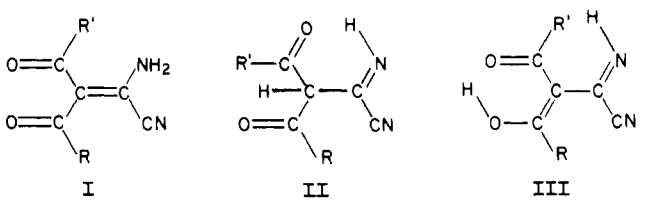
We find that a proper choice of the metal catalyst, i.e., $Zn(acac)_2$, enables the control of the reaction of β-dicarbonyls with cyanogen at the stage of the intermediates that can further dimerize or isomerize to different products.

Results

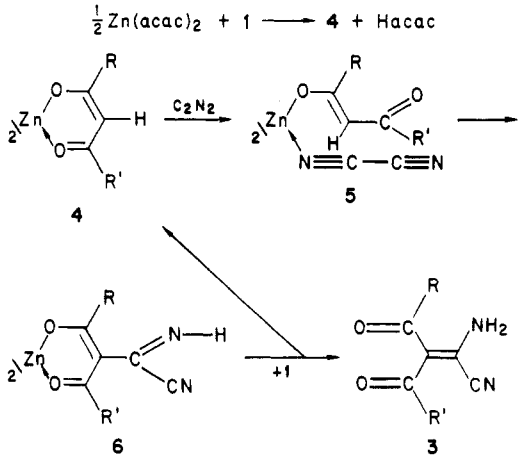
Addition of β-Dicarbonyls to Cyanogen Catalyzed by $Zn(acac)_2$. Addition of catalytic amounts of $Zn(acac)_2$ to solutions of various β-dicarbonyls (hereafter referred to as H-β-dic) in toluene containing C_2N_2 in comparable concentration leads to ready formation of adducts of stoichiometry H-β-dic·C_2N_2. Most of these products precipitate spontaneously as white, crystalline, and very pure materials.

The general reaction conditions, and essential data pertinent to the synthesis are collected in Table I. Yields were moderate to high and were not optimized. TNs reached figures as high as 1350 (R = R′ = CH_3). Adducts of Table I were characterized by elemental analysis, IR, ^1H NMR, and mass spectrometry.

The condensation products can be represented a priori by the tautomeric structures I, II, and III. The spectral



Scheme I



data in solution (Table II) rule out structures II and III and point to structure I.

Spectra in $CDCl_3$ are consistent with nonequivalence of R,R′ protons (**3a,d,f**), thus suggesting a strong hydrogen bond between an amido hydrogen atom and one of the conjugated carbonyl oxygens. In Me_2SO the nonequivalent groups become apparently equivalent and the NH_2 signals become sharper and better defined, thus suggesting hydrogen bond breaking and rotation about the C=C bond in this solvent. IR data in solid phase support structure I, which has been confirmed by an X-ray single-crystal analysis of compound **3d**.[7]

Products **3a–c** had been prepared a long time ago[8] by catalytic action of EtO^- in ethanolic solutions of the carbonyls with C_2N_2. Yields were reported as moderate to fairly good but no choice among the expected tautomeric structures (I–III) was made.

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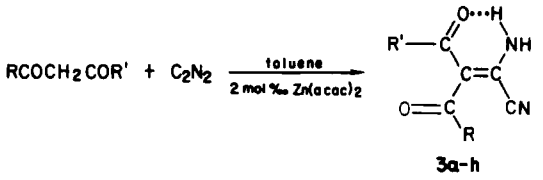
Table I. Addition of Cyanogen to β-Dicarbonyls Catalyzed by 2 mol ‰ $Zn(acac)_2$ in Toluene[a]



3a-h

entry	R	R'	t, h	% yield[b]	TN s[c]	IR (Nujol) ν_{N-H}, $\nu_{C\equiv N}$, $\nu_{C=O}$, $\nu_{C=C}$ cm^{-1}	M^+	base peak	mp, °C
a	Me	Me	8	83	324	3280 (s), 3140 (s), 2230 (w), 1660 (m–s), 1610 (s)	152	$M^+ - 57$	133
b	Me	OEt	20	88	344	3260 (s), 3140 (s), undet,[d] 1715 (s), 1615 (s)	182	$M^+ - 15$	123
c	Me	Ph	20	87	340	3260 (s), 3160 (s), 2240 (w), 1655 (m), 1625 (s)	214	$M^+ - 1$	117
d	CMe_3	CMe_3	150	46	193	3435 (s),[e] 3340 (s),[e] 2235 (m), 1655 (s), 1625 (s)	236	$M^+ - 57$	89
e	Ph	Ph	80	64	267	3350 (s), 3240 (s), undet,[d] 1630 (m), 1590 (s)	276	$M^+ - 1$	165
f	OMe	OMe	150	29	113	3360 (s), 3220 (s), 2230 (w), 1680 (s), 1600 (s)	184	$M^+ - 38$	133
g	Me	CF_3	300	0	0				
h	CMe_3	CF_3	300	0	0				

[a] Temperature: 18–22 °C. Typical concentrations: [catalyst] = 1.2×10^{-3} M, [H-β-dic] = 0.5 M, $[C_2N_2]$ = 0.7 M. Catalyst concentration ranged from 5×10^{-4} to 5×10^{-3} M. [b] Based on the spontaneously precipitated adduct (only 3d was obtained by solvent removal to small volume). [c] Turnover number, i.e., moles of converted substrate/moles of added catalyst. [d] Undetectable; $\nu_{C\equiv N}$ bands in compounds of this type are expected to be weak or even unmeasurably weak (see Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975). [e] There is a third unexpected band of medium intensity at 3230 cm^{-1}. The attribution is uncertain. In CH_2Cl_2 3d exhibits two N–H bands at 3475 and 3380 cm^{-1} (very broad).

Table II. ^1H NMR Data for Adducts 3a–f

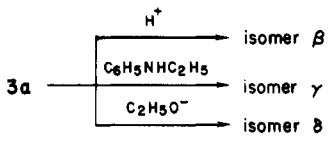
compd	solvent[a]	resonances[b] R	R'	NH_2[c]
3a	A	2.30	2.52	7.52
	B	2.13		9.21
3b	A	2.43	1.45 (t, J = 6 Hz) 4.25 (q, J = 6 Hz)	7.78
	B	2.16	1.13 (t, J = 6 Hz) 4.08 (q, J = 6 Hz)	9.57
3c	A	2.08	7.55 (m)	7.81
	B	1.78	7.41 (m)	9.27
3d	A	1.13	1.19	5.33
	B	0.99		6.68
3e	A	7.26 (m)		7.94
	B	7.31 (m)		9.54
3f	A	3.80	3.82	7.26
	B	3.56		8.57

[a] A: $CDCl_3$; B: Me_2SO-d_6. [b] Values are in ppm from $SiMe_4$. Signals are singlets, unless otherwise stated. [c] Broad singlets.

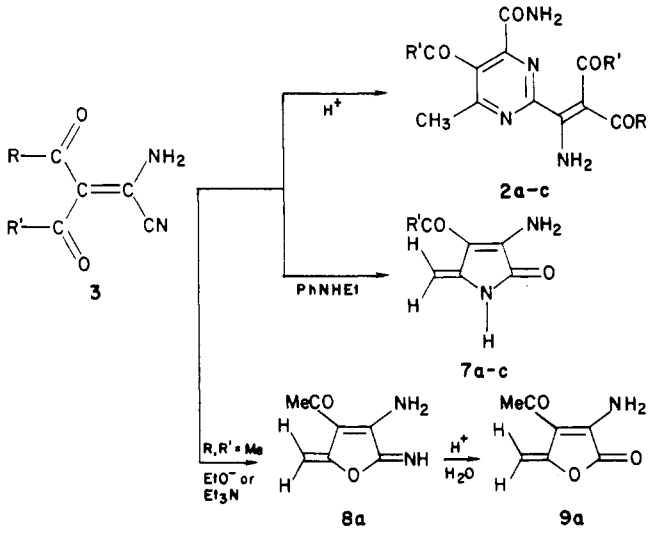
A rational mechanism for the synthesis of the adducts here described can be envisaged on the basis of our previous work.[1-7] We have found[4] that $Zn(acac)_2$ reacts with C_2N_2 in dichloroethane to give the addition compound **6**. We envision the catalysis as proceeding as shown in Scheme I. Thus the electron-rich methine carbon of a coordinated β-carbonyl enolate ligand, **4**, nucleophilically attacks one of the carbon atoms of a metal-coordinated cyanogen, which strongly enhances by this way its electrophilic ability, to afford the cyanoimino β-carbonyl enolato ligand **6**. Protonation with substitution of the coordinated ligand by excess **1** renews the catalyst and releases the product **3**, which accumulates in its more stable tautomeric form. This mechanism closely resembles that proposed for the $Ni(acac)_2$-catalyzed Michael addition of some electrophyles to β-dicarbonyls.[10] The major difference is in the fact that we propose a direct activation of the electrophile upon metal coordination.[11]

Behavior of the H-β-dic·C_2N_2 Adducts in the Presence of an Acid or a Base. Synthesis of Heterocyclic Derivatives. The reactivity of some addition compounds **3** with nucleophiles (such as amonia, amines, hydrogen sulfide, and β-dicarbonyl anions) has been studied by Traube,[8] who demonstrated that these nucleophiles add to the reactive cyano group. Moreover, Traube described the conversion of compound **3a** into three different alleged "isomeric compounds" that he indicated as β, γ, δ "isomers", Scheme II.

Scheme II



Scheme III



We reproduced Traube's conditions[8] and identified the β, γ, δ derivatives of **3a** by physicochemical methods. Moreover, we have taken into account the behavior of the analogous adducts **3b–f** (Scheme III).

In the presence of acetic acid, **3a** gives compound β, i.e., the pyrimidine derivative **2a**, already obtained by us by $Ni(acac)_2$- or $Cu(acac)_2$-catalyzed addition of C_2N_2 to **1a** in dichloromethane. In the same conditions, also compounds **3b,c** give the corresponding pyrimidine **2b,c** in good yields. Such compounds could not be obtained from **3d–f**.

Compound γ resulted upon treatment of **2a** with a weak base. It is a real isomer of **3a**, i.e., a pyrroline derivative

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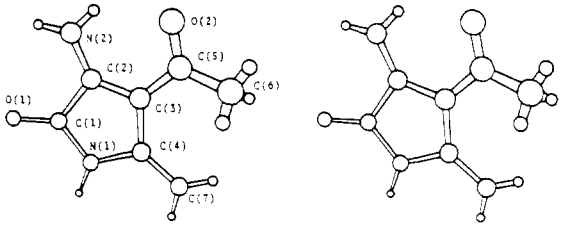

Figure 1. Stereoscopic view of **7a**, showing the numbering scheme adopted.

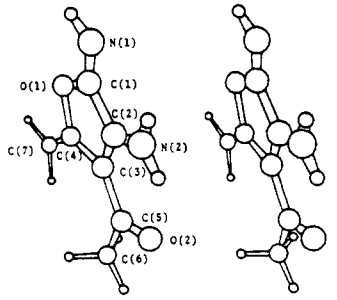

Figure 2. Stereoscopic view of **8a**, showing the numbering scheme adopted.

(**7a**) as shown by ^{1}H NMR spectra and by a single-crystal X-ray analysis. Similarly, **7b,c** have been obtained from **3b,c**.

Compound δ was obtained from **3a** by employing either EtO^- or $(C_2H_5)_3N$ as catalyst and revealed to be again a real isomer, i.e., a furan derivative (**8a**) as shown by X-ray analysis. Attempts to convert adducts **3b,c** into the corresponding furanes failed. No conversion of δ into γ isomer could be achieved by action of $(C_2H_5)_3N$ or $C_6H_5NHC_2H_5$. Isomer **8a** could be transformed into the lactone derivative (**9**) upon mild acid hydrolysis.

Crystal Structure of Traube's Isomers γ and δ (7a and 8a). A stereoscopic view of the molecules, along with selected bond lengths and valence angles are shown in Figure 1 (**7a**), Figure 2 (**8a**), and Tables III (**7a**) and IV (**8a**).

The geometries of two molecules are very similar. Bond lengths are in fact nearly identical, except for a shortening of the C(1)–C(2) and C(3)–C(4) distances (1.476 (5) and 1.451 (5) Å) in isomer **8a** (compared with 1.498 (6) and 1.473 (6) Å), and a slight difference in the C(1)–N(1) and C(1)–O(1) bond lengths. Valence angles compare well, the largest difference being the angle at the heteroatom.

X-ray structures of compounds analogous to γ and δ are not available in the literature; however, the geometric parameters measured fit well with rings displaying some similarities.[12-14]

The calculation of the least-squares planes in **8a** and **7a** show (see supplementary material) that both molecules are strictly planar, i.e., an extended resonance involves rings and substituents (and interatomic distances fit quite well to this situation).

Hydrogen bonds are present in both molecules. In the pyrrole derivative **7a** intramolecular H bonds occur between N(2) and O(2) (2.903 (4) Å), as well as between O(1) and N(2) (2.835 (5) Å). An intermolecular hydrogen bond occurs between O(2) and N(1) (2.835 (5) Å) of different molecules. In the furan derivative **8a** intramolecular H bonds are also present between N(2) and O(2) (2.758 (4) Å) and N(2) and N(1) (2.929 (4) Å), and an intermolecular H bond occurs between N(1) and N(2) (2.983 (3) Å) of related molecules.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for 7a (esd's)

C(1)–C(2)	1.498 (6)	C(1)–C(2)–C(3)	109.1 (4)
C(2)–C(3)	1.374 (6)	C(2)–C(3)–C(4)	107.1 (4)
C(3)–C(4)	1.473 (6)	C(3)–C(4)–N(1)	105.7 (4)
C(4)–N(1)	1.409 (6)	C(4)–N(1)–C(1)	113.0 (4)
C(1)–N(1)	1.347 (6)	N(1)–C(1)–C(2)	105.0 (4)
C(1)–O(1)	1.222 (5)	N(1)–C(1)–O(1)	128.0 (6)
C(2)–N(2)	1.332 (6)	C(2)–C(1)–O(1)	127.0 (6)
C(3)–C(5)	1.433 (6)	C(1)–C(2)–N(2)	119.9 (6)
C(4)–C(7)	1.321 (6)	C(3)–C(2)–N(2)	131.0 (6)
C(5)–O(2)	1.242 (6)	C(2)–C(3)–C(5)	123.0 (6)
C(5)–C(6)	1.499 (6)	C(4)–C(3)–C(5)	129.9 (6)
		C(3)–C(4)–C(7)	132.7 (6)
		N(1)–C(4)–C(7)	121.5 (6)
		C(3)–C(5)–O(2)	119.0 (6)
		C(3)–C(5)–C(6)	121.7 (6)
		C(6)–C(5)–O(2)	119.3 (6)

Table IV. Selected Bond Lenghts (Å) and Bond Angles (deg) for 8a (esd's)

C(1)–C(2)	1.476 (5)	C(1)–C(2)–C(3)	107.6 (4)
C(2)–C(3)	1.381 (5)	C(2)–C(3)–C(4)	107.5 (4)
C(3)–C(4)	1.451 (5)	C(3)–C(4)–O(1)	107.6 (3)
C(4)–O(1)	1.409 (3)	C(4)–O(1)–C(1)	109.5 (3)
C(1)–O(1)	1.361 (3)	O(1)–C(1)–C(2)	107.7 (4)
C(1)–N(1)	1.263 (5)	O(1)–C(1)–N(1)	125.9 (4)
C(2)–N(2)	1.329 (3)	C(2)–O(1)–N(1)	126.4 (4)
C(3)–C(5)	1.455 (5)	C(1)–C(2)–N(2)	121.9 (4)
C(4)–C(7)	1.324 (5)	C(3)–C(2)–N(2)	130.5 (4)
C(5)–O(2)	1.233 (3)	C(2)–C(3)–C(5)	122.1 (4)
C(5)–C(6)	1.501 (5)	C(4)–C(3)–C(5)	130.4 (4)
		C(3)–C(4)–C(7)	135.0 (4)
		O(1)–C(4)–C(7)	117.3 (4)
		C(3)–C(5)–O(2)	119.4 (4)
		C(3)–C(5)–C(6)	120.7 (4)
		C(6)–C(5)–O(2)	119.9 (4)

Discussion and Conclusions

We find that $Zn(acac)_2$ selectively catalyzes the addition of β-dicarbonyls to C_2N_2 to produce cyano enaminediones and blocks the following cyclodimerization to pyrimidines, observed when $Ni(acac)_2$ or $Cu(acac)_2$ are used as catalysts.[6] The main reason for this selectivity has been discussed with specific reference to Hacac and is likely to be due to a relatively scarce stability of the primary addition product of $Zn(acac)_2$ to C_2N_2.[4]

In spite of this feature, the $Zn(acac)_2$ complex system is a very efficient catalyst for the C–C bond formation reactions here described; furthermore, it is superior to EtO^- in that this latter catalyst promotes also subsequent addition of β-dicarbonyls to the reactive C≡N bond of the primary adducts **3**.[8]

It seems worth mentioning that the high selectivity of $Zn(acac)_2$, $Ni(acac)_2$, and $Cu(acac)_2$ as catalysts for the synthesis of adducts **2** and **3** resembles that exhibited by $Ni(acac)_2$ in the Michael addition of dicarbonyls;[10] this fact suggests that these complexes should be convenient catalysts for the addition of any β-carbonyl to C_2N_2 to selectively give adducts of type **2** and **3**.

The chemical behavior of the hexacyclic 5-methylene group (compounds γ and δ), whose presence in natural or synthetic congeners of lactams (**7**) and lactons (**8**) is well-established,[15] has not yet been investigated.

As shown in Scheme IV, nucleophilic addition of a strong base onto the acetyl moiety, followed by ring closure and

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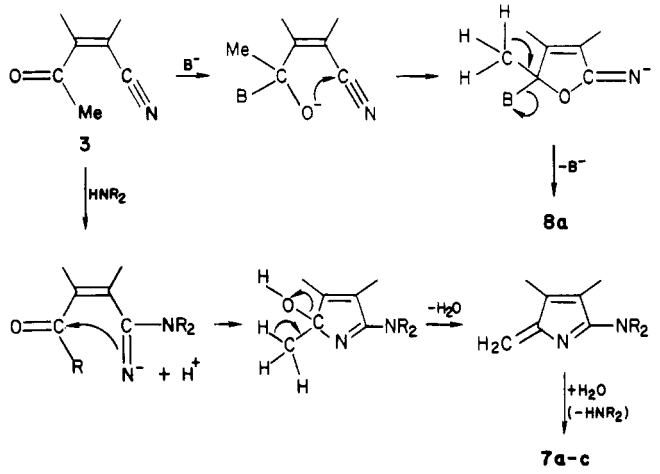
Scheme IV



elimination, appears as a rational path for the formation of the 5-methylenefuran derivative **8a**. Conversely, a nucleophilic addition of a weak base onto the C≡N group, followed by the steps shown, would rationalize the alternative formation of the 5-methylene lactams **7a–c**.

The reasons why the former path is restricted to compound **8a**, whereas the latter leads to compounds **7a–c**, are still open to speculation.

Experimental Section

All reactions involving the dicarbonyls and cyanogen were run in essentially the same manner. The following are exemplary.

Entries 3a–f (Table I). A dry glass one-necked 50-mL cylindrical flask was charged with 25 mL of anhydrous toluene containing ca. 0.8 M C_2N_2 (~20 mmol). The required β-dicarbonyl (~12 mmol) and the solid catalyst were added to give typically 1.2×10^{-3} M solutions. The mixture was stirred for a few minutes and then the solutions were left to stand for the required time. The adducts normally precipitated spontaneously as crystals, which were filtered off, washed with *n*-hexane, and dried in vacuo. In the case of **3d**, the product was obtained by reducing the volume to 5 mL.

Estimate of Selectivity. Selectivity toward adducts **3** was 100%, with the exception of **1d** (70%). In the cases of **1a,b,d,f** the consumption of the substrate was monitored by GLC and the millimoles of isolated adducts were compared with those of the consumed β-dicarbonyl. All adducts, but **3d**, are scarcely soluble in toluene. For **1c** and **1e**, the selectivity was estimated by comparing the amounts of isolated adducts with those of recovered substrate in the mother liquor. For **1g,h** the absence of reactivity was checked by monitoring the IR spectra of the solutions for the required time.

All compounds were characterized by elemental analyses (available as supplementary material), infrared (Table I), ^{1}H NMR (Table II), and mass spectrometry.

Cyclocondensation of 3a–c into the Pyrimidine Derivatives 2a–c. To a stirred suspension of **3a** (152 mg, 1 mmol) in CH_3CN (2 mL) was added acetic acid (0.6 mL, 10 mmol). The resulting solution was stirred at room temperature for 3 h and the separated yellow crystals were filtered off, washed with CH_3CN, and dried in vacuo. The yield was 102 mg (67%); the IR spectrum was identical with that of authentic **2a**.[5] By an identical procedure **3b** gave a solution that was purified by using a silica gel column (ethyl acetate–toluene 1:1). The yield was 64%. The IR was identical with that of authentic **2b**.[5] The pyrimidine **2c** was obtained in 60% yield in 24 h. The IR was identical with that of authentic **2c**.[5] Use of anhydrous acetic acid is necessary in this case to prevent hydrolysis of **3c**.

Reaction of 3a in the Presence of *N*-Ethylaniline: 3-Amino-4-acetyl-5-methylene-Δ^3-pyrrolin-2-one (7a). To a stirred solution of **3a** (152 mg, 1 mmol) in CH_3CN (5 mL) was added *N*-ethylaniline (0.126 mL, 1 mmol). The reaction mixture was kept at room temperature for 12 h and the colorless, separated crystals were filtered off, washed with ether, and dried in vacuo. The yield was 141 mg (91%): mp 212–213 °C (lit. 211 °C);[8] IR (KBr) 3420, 3280, 3200 (NH_2), 1710 (cyclic CO), 1660 (CH_3CO and C=C) cm^{-1}; MS, *m/e* (relative intensities) 152 (M^+) (100), 137 (48), 124 (32), 109 (16), 96 (14), 82 (12), 66 (34), 54 (12), 43 (28), 39 (11); ^{1}H NMR (Me_2SO-d_6) δ 2.32 (CH_3), 4.65, 4.8 (H_2C=, dd, J = 1.2 Hz), 7.6 br (NH_2, exchanges with D_2O), 10.3 (NH, exchanges with D_2O).

Reaction of 3b in the Presence of *N*-Ethylaniline: 3-Amino-4-(ethoxycarbamoyl)-5-methylene-Δ^3-pyrrolin-2-one (7b). The reaction was carried out on 182 mg (1 mmol) of **3b** as reported above for **3a**; the reaction time was 4 h. Product **7b** (31 mg) separated as crystals and a further 97 mg (total yield 65%) was obtained when the reaction mixture was concentrated to dryness and the residue triturated with ether: mp 220–223 °C (lit.[8] 211 °C); IR (KBr) 3320, 3200 (NH_2), 1720 (cyclic CO), 1680 (COR), 1640 (C=C) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) 1.25 (CH_3, t), 4.20 (CH_2, q, J = 8 Hz), 4.6, 5.12 (H_2C=), 7.1 br (NH_2), 10.3 br (NH).

Reaction of 3c in the Presence of *N*-Ethylaniline: 3-Amino-4-benzoyl-5-methylene-Δ^3-pyrrolin-2-one (7c). In the conditions used for **3b** the reaction time was 3 days. The corresponding product **7c** was obtained (yield 47%): mp 196–198 °C; IR (KBr) 3420, 3300 (NH_2), 1740 (cyclic CO), 1650 (CO and C=C) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 3.95, 4.52 (H_2C=), 7.4, 7.8 (C_6H_5 and NH_2), 10.5 (NH).

Compounds **3d–f** were recovered unchanged in the presence of *N*-ethylaniline at ambient temperature for 7–10 days.

Reaction of 3a in the Presence of Triethylamine: 2-Imino-3-amino-4-acetyl-5-methylene-2,5-dihydrofuran (8a). To a stirred suspension of **3a** (152 mg, 1 mmol) in CH_3CN (2 mL) was added triethylamine (0.14 mL, 1 mmol). The resulting solution was stirred at room temperature for 2 h and the separated crystals were filtered off, washed with ether, and dried in vacuo. The yield was 120 mg (79%), mp 167–169 °C (recrystallized from ethanol). This compound is identical with that obtained in ethanol in the presence of EtO^- as catalyst (yield 27%):[8] IR (KBr) 3400, 3200 (NH and NH_2), 1700 (CO), 1660 (C=C) cm^{-1}; MS, *m/e* (relative intensities) 152 (M^+) (100), 137 (18), 125 (28), 124 (14), 108 (12), 95 (11), 82 (13), 66 (60), 43 (80); ^{1}H NMR (Me_2SO-d_6) two species result to be present in a ratio very near to 1:1 2.4 (2 CH_3), 3.6 (m, H_2C=), 7.6 br (1 NH_2), 8.0 br (1 NH_2), 8.7 br (1 NH), 9.3 br (1 NH).

Similar reaction of **3b** and **3c** with triethylamine showed, after 7 days, one decomposition of the reagents. **3d–f** were recovered unchanged after 7 days.

Hydrolysis of the Furan Derivative 8a: Synthesis of 3-Amino-4-acetyl-5-methylenefuran-2(5*H*)-one (9a). To a stirred suspension of the reagent (456 mg, 3 mmol) in water (5 mL) was added 1 N HCl (3 mL, 3 mmol). From the clear solution obtained brown crystals separated, which were filtered off and dried. The yield was 310 mg (67%): mp 144–146 °C (recrystallized from ethanol–water); IR (KBr) 3425, 3300 (NH_2), 1760 (ester CO), 1670 (CH_3CO), 1640 (C=C), 1550 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.37 (CH_3), 4.9, 5.05 (=CH_2, d, J = 3 Hz), 7.8 br (NH_2, exchanges with D_2O).

Molecular Structure Determination by X-ray Crystallographic Techniques. Isomer γ. Crystals were obtained from solutions in acetonitrile. The molecule (M_r 152) crystallizes in space group $P\bar{1}$ with a = 7.898 (5) Å, b = 7.591 (5) Å, c = 7.393 (5) Å, α = 116.9 (1)°, β = 113.9 (1)°, γ = 83.4 (1)°. The cell volume was 360.3 Å^3, Z = 2.

Crystal data were obtained from a single-crystal diffractometric measurements; 1285 intensities up to Θ = 25° were collected on a Philips PW1100 four-cycle diffractometer operating in the Θ – 2Θ scan mode (scan width 1.6°, scan speed 0.04° s^{-1}), with Mo K_α radiation (λ 0.7107 Å), monochromatized by a graphite crystal. During the data collection, two standard reflections were measured every 180 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz polarization effects and converted to an absolute scale by Wilson's method. No absorption correction was applied.

The positional parameters of the non-hydrogen atoms (supplementary material) were determined by direct methods using the SHELX 76 phasing program (Sheldrix, 1976). After a few cycles of full-matrix least-squares refinement, all the H atoms were located in the difference Fourier map and enclosed in the refinement with isotropic thermal parameters. The final R value

for 970 reflections with $I \geq 1.5\sigma(I)$ was 0.060 (R_w = 0.050). The weighing scheme in the last cycle was $w = 2.6[\sigma^2(F) + 0.0003(F)^2]^{-1}$.

Isomer δ. Crystals were obtained from solutions in ethanol. The molecule (M_r 152) crystallizes in space group $P\bar{1}$ with a = 7.811 (5) Å, b = 8.028 (5) Å, c = 6.999 (4) Å, α = 117.5 (1)°, β = 81.2 (1)°, γ = 111.3 (1)°. The cell volume was 326.6 Å^3, Z = 2. Obtainment and treatment of data were similar to those referring to isomer γ. The final R factor for 1157 reflections with $I \geq 1.5\sigma(I)$ was 0.043 (R_w = 0.058).

All calculations for γ and δ isomers were carried out on the IBM 370/158 Computer of the University of Padova.

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Registry No. **1a**, 123-54-6; **1b**, 141-97-9; **1c**, 93-91-4; **1d**, 1118-71-4; **1e**, 120-46-7; **1f**, 108-59-8; **1g**, 367-57-7; **1h**, 22767-90-4; **2a**, 77097-65-5; **2b**, 79593-42-3; **2c**, 79593-43-4; **3a**, 71616-10-9; **3b**, 90281-20-2; **3c**, 90281-23-5; **3d**, 87221-86-1; **3e**, 92220-21-8; **3f**, 90281-22-4; **7a**, 92220-23-0; **7b**, 92220-27-4; **7c**, 92220-26-3; **8a**, 92220-24-1; **9**, 92220-25-2; $C_2H_5O^-$, 16331-64-9; $NC(CH_2)_2CN$, 460-19-5; *N*-ethylaniline, 103-69-5; triethylamine, 121-44-8.

Supplementary Material Available: Analytical data for compounds **3**, **7**, **8**, **9**; tables of X-ray data for compounds including fractional coordinates, thermal parameters, and deviations from the least square plane of the ring (8 pages). Ordering information is given on any current masthead page.

Alkynylaryliodonium Tosylates and Aryl[β-(tosyloxy)vinyl]iodonium Tosylates from Reactions of Terminal Alkynes with [Hydroxy(tosyloxy)iodo]benzene

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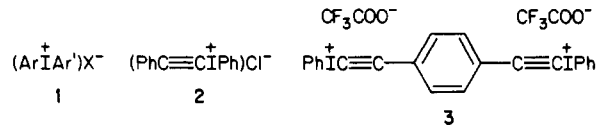
Various terminal alkynes have been found to react with [hydroxy(tosyloxy)iodo]benzene (**4**) in $CHCl_3$ to give either aryl[β-(tosyloxy)vinyl]iodonium tosylates **5** or alkynylaryliodonium tosylates **6** or a mixture of the two. The product composition is subject to steric control. Among the α-branched alkyl groups R in RC≡CH, the isopropyl group seems to define the steric median: those alkynes with R larger than isopropyl (i.e., R = *t*-Bu, *sec*-Bu, cyclohexyl) give only alkynylaryliodonium tosylates while those alkynes with R smaller than isopropyl give only aryl[β-(tosyloxy)vinyl]iodonium tosylates. 3-Methyl-1-butyne and 4-methyl-1-pentyne (β-branching) give a mixture of **5** and **6**. (Trimethylsilyl)acetylene reacts with **4** in a different way; the trimethylsilyl group is cleaved from the alkyne, and phenyl[β-(tosyloxy)vinyl]iodonium tosylate is obtained.

Although the diaryliodonium salts **1** have been known for 90 years and a number of them have been prepared, iodonium salts with an alkynyl ligand bound to the iodine atom are rare.[1] The first example of an alkynyliodonium salt was reported by Beringer and Galton in 1965 who prepared phenyl(phenylethynyl)iodonium chloride (**2**) in



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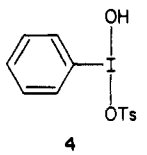

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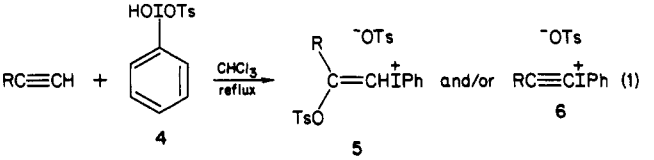
yields of 12–20% by the condensation of lithium phenylacetylide with (dichloroiodo)benzene in ether/hexane at 0–5 °C.[2] The iodonium salt decomposed upon standing for several hours at room temperature into a 1:1 mixture of chlorophenylacetylene and iodobenzene. More recently, the condensation of 1,4-diethynylbenzene with [bis(trifluoroacetoxy)iodo]benzene in dry chloroform to give the alkynyliodonium salt **3** has been reported.[3] In a recent preliminary communication, we described the reactions of several alkenes and several alkynes with [hydroxy(tosyloxy)iodo]benzene (**4**).[4] Particularly relevant is the observation that phenylacetylene and cyclohexylacetylene were converted directly by **4** into the corresponding alkynylphenyliodonium tosylates (60% and 5% yields, respectively).

In this paper, we report the reactions of ten terminal alkynes with [hydroxy(tosyloxy)iodo]benzene and the use of steric bulk in the alkyne to direct a one-step synthesis of alkynylphenyliodonium salts. The treatment of terminal alkynes with **4** in chloroform under reflux affords either phenyl[β-(tosyloxy)vinyl]iodonium tosylates **5** or alkynylphenyliodonium tosylates **6** or a mixture of both (eq 1). For example, 1-pentyne reacted with **4** to give the



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vinyliodonium tosylate **5** (R = *n*-Pr, 58% yield), but when 3,3-dimethyl-1-butyne was the reactant, only the alkynyliodonium tosylate **6** (R = *t*-Bu, 74%) was obtained. 3-

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(4) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324.

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