Addition of 4-Phenyltriazolinedione to Carbonyl Compounds: The Formation of α-Urazolylcarbonyl Compounds

R. Marshall Wilson,* Alvan C. Hengge, Ali Ataei, and Nuanphun Chantarasiri

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

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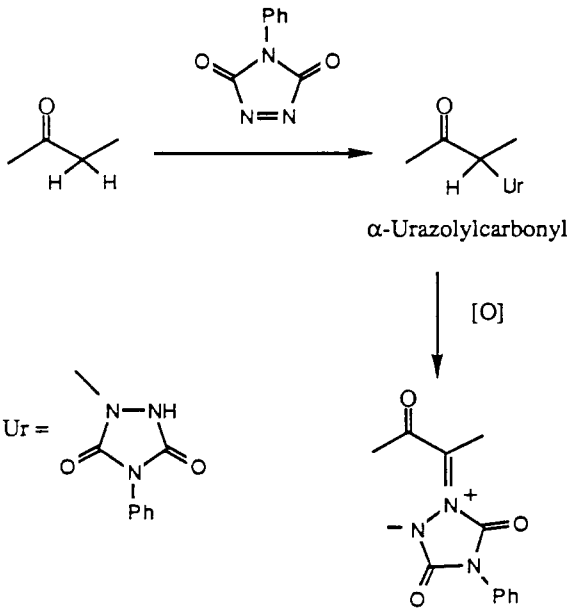
N-Phenyltriazolinedione (PTAD) adds to a variety of carbonyl compounds to form α-urazolylcarbonyl compounds. With highly enolized carbonyl systems, this type of substitution reaction can occur rapidly even in the absence of a catalyst. However, with simple carbonyl systems, the reaction is greatly accelerated by an acid catalyst such as trifluoroacetic acid. Unsymmetrical ketones afford isomeric α- and α′-urazolyl ketones, and the initially formed monourazoles can be further urazolated to the diurazoles through the application of more than 1 equiv of PTAD.

In conjunction with our work on the condensation reactions of triazolinedione ylides with active methylene compounds,[1] we have investigated the addition of 4-phenyltriazolinedione (PTAD) to a number of different functional groups. The N′-substituted *N*-phenylurazoles that typically result from these PTAD addition reactions frequently are easily oxidized to triazolinedione ylides and thus serve as ideal sources for the generation of these unusual ylide species. It is known that PTAD undergoes facile ene reactions with simple olefins to form N′-substituted *N*-phenylurazoles.[2] Similar products also have been observed from the addition of PTAD to enamines[3] and to the carbon–carbon double bond of certain α, β-unsaturated ketones.[4] However, the reaction of PTAD with simple carbonyl compounds has been reported only briefly in the literature,[5] and yet this reaction is quite general and provides an excellent source of substituted urazole precursors for triazolinedione ylide generation as illustrated in Scheme I. In this paper, we report work designed to delineate the scope of this most useful reaction between carbonyl compounds and PTAD.

Since the base-catalyzed addition of carbonyl compounds to diethyl diazodicarboxylate (DEADCAT) has been reported by a number of groups[6] and since DEADCAT, albeit much less reactive than PTAD, does exhibit chemistry similar to that of PTAD, we initially conducted a cursory study of the affect of base upon PTAD addition to carbonyl compounds. Accordingly, the base-catalyzed reaction of dimethyl malonate and dimedone with DEADCAT produced adducts **1** and **2**, respectively, in good yields (Scheme II). DEADCAT does not seem to react rapidly with the enol tautomer of dimedone, since no reaction was observed until a catalytic amount of base was added. ^1H and ^{13}C NMR indicated that **2** exists completely in the enolic form, and yet there does not seem to be a pronounced tendency for **2** to add a second molecule of DEADCAT.

Scheme I



Attempted base-catalyzed addition of dimethyl malonate to PTAD under similar conditions resulted in the rapid decomposition of the PTAD, but no products could be obtained from this reaction. This failure to observe base-catalyzed reaction with PTAD might be due to the known susceptibility of PTAD to decomposition by nucleophiles, which is believed to involve nucleophilic attack at the imide carbonyl followed by ring opening.[7] Alternatively, it might be due to the destruction of the PTAD through an electron-transfer chain process with the amine catalyst or the more powerfully donating enolate species.[8,9] This base-catalyzed approach was not pursued further when it was observed that acid catalysis provided a much simpler and very general method for preparing the desired α-urazolyl carbonyl compounds.

Most simple ketones are unreactive or react only very slowly with PTAD. However, in the presence of catalytic amounts of trifluoroacetic acid, the discharge of the red PTAD color is greatly accelerated. Even so, the time re-

(1) (a) Wilson, R. M.; Hengge, A. C. *Tetrahedron Lett.* **1985**, *26*, 3673. (b) Wilson, R. M.; Hengge, A. C. *J. Org. Chem.* **1987**, *52*, 2699.

(2) Pirkle, W. H.; Stickler, J. C. *Chem. Commun.* **1967**, 760. Ohashi, S.; Leong, K.; Matyjaszewski, K.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 3467. Ohashi, S.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 3472. Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D. *J. Org. Chem.* **1984**, *49*, 2910.

(3) Wamhoff, H.; Wald, K. *Ber. Dtsch. Chem. Ges.* **1977**, *110*, 1716.

(4) Shiloff, J. D.; Hunter, N. R. *Tetrahedron Lett.* **1976**, 3773.

(5) (a) Cookson, R. C.; Gilani, S. S. H.; Stevens, I. D. R. *J. Chem. Soc. C* **1967**, 1905. (b) Williams, A. G.; Butler, G. B. *J. Org. Chem.* **1980**, *45*, 1232.

(6) (a) Huisgen, R.; Jakob, F. *Justus Liebigs Ann. Chem.* **1954**, *590*, 37. (b) Fahr, E.; Lind, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 372, and references therein. (c) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6395. (d) Trimble, L. A.; Vederas, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 6397.

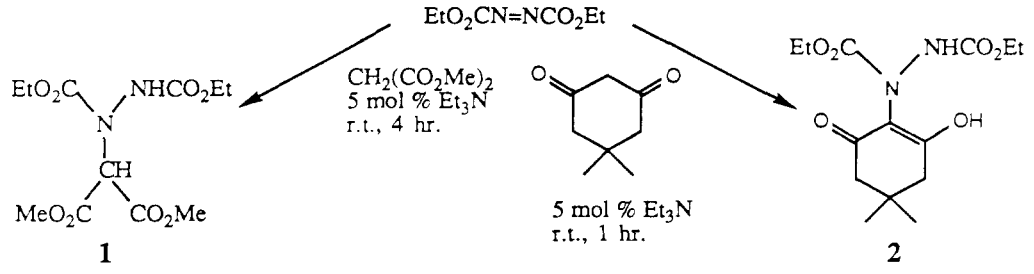
(7) Izydore, R. A.; Johnson, H. E.; Horton, R. T. *J. Org. Chem.* **1985**, *50*, 4589.

(8) PTAD is bleached rapidly in the presence of a catalytic quantity of triethylamine. Similar observations have been reported previously: Dao, L. H.; Mackay, D. *Can. J. Chem.* **1979**, *57*, 2727. See also ref 6a.

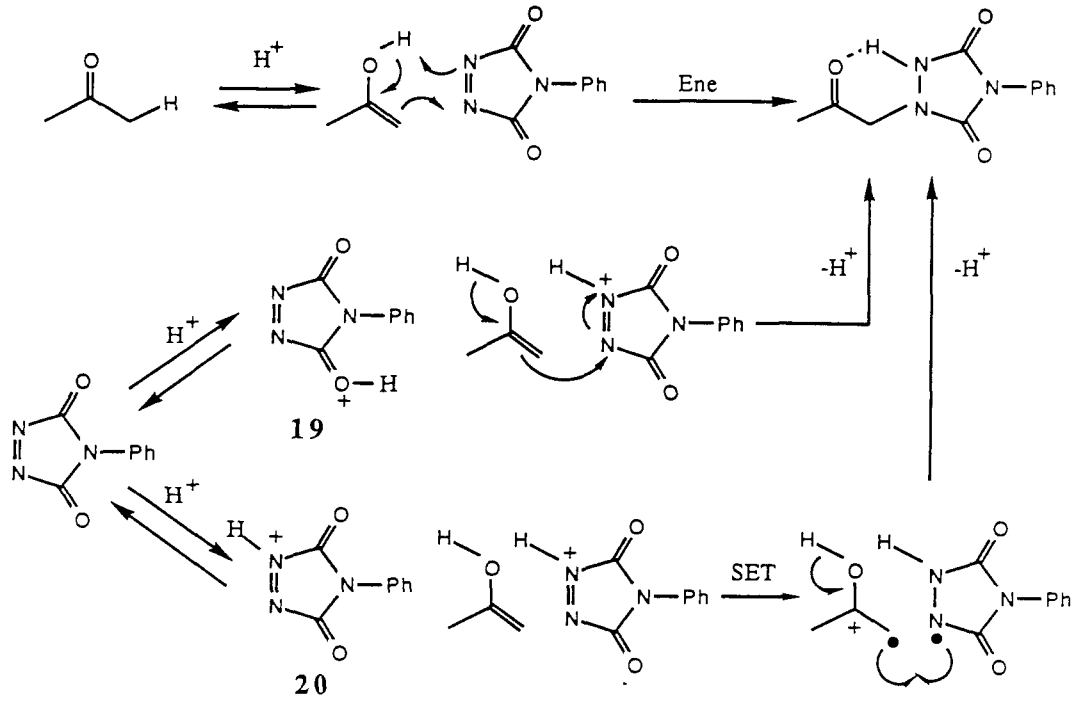
(9) Borhani, D. W.; Greene, F. D. *J. Org. Chem.* **1986**, *51*, 1563.

0022-3263/90/1955-0193$02.50/0

Scheme II



Scheme III



quired for the discharge of the PTAD color is highly variable, requiring from as long as 5 days[10] to as short as 2 min (see Table I), and seems to be dependent upon the enol content of the carbonyl constituent. In all cases studied to date, the major and frequently the only products isolated from these reactions of simple carbonyl compounds are the α-urazolyl carbonyl compounds (Scheme I and Table I). Most of these substances are nicely crystalline and readily characterizable materials. It is significant to note that unsymmetrical ketones such as 2-octanone (entry 3 in Table I) can afford a mixture of the two possible α-urazolyl ketones **5** and **6** and that these two regioisomers are easily separated by routine thick-layer chromatography.

β-Dicarbonyl compounds (entries 9–12 in Table I) are sufficiently reactive that trifluoroacetic acid catalysis is not always necessary.[5b] In fact carbonyl compounds of this class are frequently so reactive that they add a second molecule of PTAD to form mixtures of mono- and diurazolyl adducts. Ethyl acetoacetate (entry 10 in Table I) is an example of such a system. It gives rise to a mixture of the mono- and diurazolyl ketones **13** and **14**, respectively. Formation of the bis-adduct **14** can be completely suppressed by the application of a large excess of ethyl acetoacetate. The proton NMR spectrum of the mono-adduct **13** indicates that this material exists primarily as its enol tautomer. This may account for the propensity of **13** to add a second PTAD molecule even in the presence of substantial amounts of unreacted starting ketone. In contrast, the mono-adduct **15** of dibenzoylmethane seems to be formed much more readily than the bis-adduct **16**, as **15** can be readily isolated free from contamination by **16** through the application of excess diketone and short reaction times. The bis-adduct **16** can be easily prepared by prolonged reaction of PTAD with the mono-adduct **15** (entry 11 in Table I).

Only one case of a simple carboxylic acid derivative was examined, oxindole (entry 6 in Table I), and this readily enolizable derivative was found to form the mono-adduct **9** smoothly.

These PTAD reactions might be most simply interpreted as proceeding through an ene mechanism as shown in Scheme III. If this is the case, then the marked catalytic effect of the trifluoroacetic acid in the reactions of simple ketones might be attributed at least in part to the acid-catalyzed formation of the requisite enol tautomer. However, the very pronounced solvent effect observed in the addition of PTAD to β-diketones is not consistent with an ene mechanism.[5b] Furthermore, in other additions of PTAD to electron-rich systems that do not involve enol intermediates, trifluoroacetic acid is also observed to exert a substantial rate acceleration.[11] Consequently, protonated forms of PTAD such as **19** or **20** probably play an

(10) Since the light-induced polymerization of PTAD is known to occur in solution [Pirkle, W. H.; Stickler, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 7497], all of these reactions were protected from ambient light.

(11) Wilson, R. M.; Dietz, J. G., unpublished results.

Table I. Addition of PTAD to Carbonyl Compounds: Reaction Conditions, Products, and Yields

entry	carbonyl compd	reaction conditions[a]	product (mp, °C)	yield, %
1	cyclohexanone	4 h	**3**[b,c] (165.3–166.8)	80
2[d]	cyclooctanone	13 h	**4**[b] (127.2–128.3)	69
3	2-octanone	3 days	**5**[b] (colorless oil)	36
			6[b] (104.6–105.5)	15
4[d]	4-heptanone	2 days	**7**[b] (146.6–148.8)	29
5[d]	acetophenone	16 h	**8**[b,c] (160.0–161.8)	57
6[d]	oxindole	12 h	**9**[e] (195, dec)	45
7[d]	deoxybenzoin	5 days	**10**[b] (177.0–178.4)	65
8[d]	1,3-diphenyl-2-propanone	4 days	**11**[b] (152.2–153.4)	76
9[d]	dimedone	10 min[f]	**12**[b] (180.6–181.8)	61
10	ethyl acetoacetate	(a) 4 h,[g] (b) 1 h[i]	**13**[b,h] (143.7–144.4)	(a) 42 (b) 86
			14[h] (210.0–211.5)	(a) 24 (b) 0
11	dibenzoylmethane	2 min[j]	**15**[b,d,e,h] (172.0–174.0)	85
	15	6 days[j]	**16**[d,h] (182.0–184.0)	69
12[d]	Meldrum's acid	4 h[j,k]	**17** (180–181)	53

[a] All reactions were conducted at room temperature in dichloromethane using a catalytic amount of trifluoroacetic acid unless noted otherwise. [b] M^+ confirmed by HRMS data ($m/z \leq 0.004$ amu). [c] Reference 16. [d] For detailed experimental procedure and spectroscopic data see paragraph at the end of the paper about supplementary material. [e] Structure consistent with the chemistry of the corresponding ylide, ref 13 and 14. [f] One equivalent of trifluoroacetic acid in chloroform. [g] Three equivalents of ethyl acetoacetate. [h] Reference 5b. [i] Twenty-five equivalents of ethyl acetoacetate. [j] No trifluoroacetic acid added. [k] Chloroform solvent.

active role in these additions. Finally, there is the further possibility that certain of these reactions proceed via electron-transfer mechanisms. PTAD is known to be an excellent electron acceptor,[9,12] and protonated forms of PTAD such as **19** and **20** should be even better electron acceptors. This possibility deserves further careful investigation.

In summary, PTAD undergoes reaction with a wide variety of carbonyl compounds to form α-urazolyl derivatives. In the case of less reactive carbonyl systems, trifluoroacetic acid greatly accelerates these reactions. The α-urazolyl carbonyl compounds described in this work provide the starting materials for the corresponding triazolinedione ylides as illustrated in Scheme I, and these

(12) PTAD has been shown to react with photoenols via an electron-transfer mechanism: Wilson, R. M.; Hannemann, K.; Heineman, W. R.; Kirchhoff, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 4743.

ylides in turn undergo a variety of extremely interesting and useful reactions.[1,13,14]

Experimental Section

Melting points were determined with a Mettler FP2 melting point apparatus using a polarizing microscope and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with either an IBM NR 80-MHz or a Nicolet NT 300-MHz spectrometer. Spectra were recorded in $CDCl_3$ except where noted otherwise, and chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 599 infrared spectrometer and were calibrated with a polystyrene film. High-resolution mass spectra were obtained with a Kratos MS801-DS55 spectrometer, and fast atom bombardment (FAB) mass spectra were obtained with a VG 30-250 mass spectrometer. FAB samples were prepaired by using glycerol as the matrix. Preparative chromatographic separations were conducted by centrifugal chromatography with a Chromatotron using plates coated with E. Merck 60-PF254 silica gel.

PTAD was prepared by a modification of the standard *tert*-butyl hypochlorite method.[1b,15] These modifications consisted of adding *tert*-butyl hypochlorite to a 4-phenylurazole solution over about an hour rather than 20 min while maintaining the temperature at 5 °C rather than room temperature. The material thus obtained was immediately and rapidly sublimed at 95 °C and 10^{-3} mmHg to yield >98% of pure material (lit.[15] 62–64%).

Diethyl [Bis(methoxycarbonyl)methyl]bicarbamate (1). A mixture of dimethyl malonate (578 mg, 4.37 mmol) and DBN (27.3 mg, 0.22 mmol) in 20 mL of dichloromethane was stirred at room temperature for 20 min. To this solution was added diethyl azodicarboxylate (799 mg, 1.106 mmol), and the reaction mixture stirred for 4 h. The crude reaction mixture was filtered through a 1.5 × 3.0 cm plug of flash silica eluting with ethyl acetate to remove polar impurities. The residue was purified by centrifugal chromatography eluting with dichloromethane/ethyl acetate (5:1). Evaporation of solvent afforded pure **1** (1.24 g, 4.05 mmol, 93%) as a pale yellow oil which slowly crystallized, mp 49.0–51.0 °C; IR ($CHCl_3$) 3400, 2990, 1750–1705 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 1.26 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 3.80 (s, 6 H), 4.17 (q, J = 7 Hz, 2 H), 4.23 (q, J = 7 Hz, 2 H), 5.60 (br s, 1 H), 6.94 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.20 (q), 53.06 (q), 62.03 (t), 62.32 (d), 63.59 (t), 155.15 (s), 155.59 (s), 165.93 (s); HRMS, m/z calcd for $C_{11}H_{18}N_2O_8$ (M^+) 306.1063, found 306.1030.

Diethyl (4,4-Dimethyl-2-hydroxy-6-oxo-1-cyclohexen-1-yl)bicarbamate (2). To a solution of dimedone (97.0 mg, 0.693 mmol) in 20 mL of dichloromethane was added 120 mg (0.69 mmol) of diethyl azodicarboxylate followed by a catalytic amount of triethylamine (3 μL, 0.021 mmol). The yellow solution was stirred at room temperature for 1 h, by which time the dimedone had been completely consumed as judged by TLC. The faintly yellow solution was evaporated to dryness and rapidly chromatographed on a short Chromatotron plate eluting with dichloromethane/ethyl acetate (1:1). This compound is sensitive to silica gel and, therefore, chromatography must be conducted rapidly. Evaporation of the solvent gave pure **2** (210 mg, 0.67 mmol, 96%) as an oil which slowly formed colorless crystals, mp 80.0–81.0 °C; IR ($CHCl_3$) 3400, 3280–2750, 1730, 1710, 1660, 1620 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 1.12 (s, 6 H), 1.29 (t, J = 7 Hz, 6 H), 2.28 (s, 2 H), 2.44 (s, 2 H), 4.16 (q, J = 7 Hz, 2 H), 4.25 (q, J = 7 Hz, 2 H), 7.40 (br s, 1 H), 10.50 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.15 (q), 26.23 (q), 29.69 (q), 31.77 (s), 42.21 (t), 50.01 (t), 61.99 (t), 63.18 (t), 117.83 (s), 155.93 (s), 160.22 (s), 173.47 (s), 193.29 (s); UV (CH_3CN) λ_{max} 250 nm (ϵ = 9270); HRMS, m/z calcd for $C_{14}H_{22}N_2O_6$ (M^+) 314.1478, found 314.1489.

2-(4-Phenylurazolyl)cyclohexanone (3). A solution of cyclohexanone (1.4 g, 14.5 mmol) in 2 mL of dichloromethane containing a catalytic amount of trifluoroacetic acid (8 μL, 0.10 mmol) was stirred at room temperature for 30 min. PTAD (91.2 mg, 0.52 mmol) was then added, the flask wrapped in aluminum foil to exclude light, and the solution stirred for 4 h, by which time the red color of the PTAD was discharged completely. The reaction mixture was concentrated under reduced pressure followed by centrifugal chromatography eluting with dichloromethane/ethyl acetate (1:1) to afford 118 mg (0.43 mmol, 83%) of **3** as colorless crystals after recrystallization from dichloromethane/cyclohexane, mp 165.3–166.8 °C (lit.[16] mp 164–165 °C, 66% yield from the trimethylsilyl enol ether of cyclohexanone); IR ($CHCl_3$) 3340, 3010, 2940, 1780, 1710, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.62–1.86 (m, 2 H), 1.97–2.17 (m, 3 H), 2.28–2.46 (m, 2 H), 2.53–2.59 (m, 1 H), 4.77 (dd, J = 12 and 6 Hz, 1 H), 7.36–7.53 (m, 5 H), 9.27 (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.11 (t), 26.37 (t), 30.39 (t), 41.09 (t), 64.16 (d), 125.58 (d), 127.97 (d), 128.93 (d), 131.27 (s), 154.03 (s), 154.18 (s), 204.91 (s); HRMS, m/z calcd for $C_{14}H_{15}N_3O_3$ (M^+) 273.1113, found 273.1086.

3-(4-Phenylurazolyl)-2-octanone (5) and 1-(4-Phenylurazolyl)-2-octanone (6). A solution of 2-octanone (3.27 g, 25.5 mmol) and trifluoroacetic acid (14.7 μL, 0.19 mmol) in 10 mL of dichloromethane was stirred for 20 min. PTAD (501 mg, 2.86 mmol) was added, and the flask wrapped in aluminum foil, and the solution stirred at room temperature for 4 days. The solvent and excess 2-octanone were removed at 55 °C under reduced pressure. Thick-layer chromatography of the residue eluting with dichloromethane/ethyl acetate (6:1) afforded the less polar 3-urazolyl isomer **5** as a colorless oil (306 mg, 1.00 mmol, 36%); IR ($CHCl_3$) 3305, 3000, 2910, 1770, 1700, 1490 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3 H), 1.25–1.40 (m, 6 H), 1.90 (dt, J = 7 and 7 Hz, 2 H), 2.27 (s, 3 H), 4.98 (dd, J = 7 and 7 Hz, 1 H), 7.47–7.50 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.78 (q), 22.25 (t), 25.81 (t), 27.17 (q) 28.16 (t), 30.00 (t), 64.70 (d), 125.56 (d), 128.19 (d), 129.02 (d), 131.03 (s), 153.22 (s), 154.12 (s), 204.99 (s); HRMS, m/z calcd for $C_{16}H_{21}N_3O_3$ (M^+) 303.1582, found 303.1559. The more polar isomer **6** (134 mg, 0.45 mmol, 16%) formed as colorless crystals, mp 104.6–105.5 °C; IR ($CHCl_3$) 3300, 3000, 2920, 1775, 1710, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3 H), 1.26–1.33 (m, 6 H), 1.59 (tt, J = 7.5 and 7.5 Hz, 2 H), 2.42 (t, J = 7.5 Hz, 2 H), 4.39 (s, 2 H), 7.47–7.51 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.94 (q), 22.36 (t), 23.23 (t), 28.66 (t), 31.39 (t), 39.89 (t), 55.20 (t), 125.69 (d), 128.40 (d), 129.17 (d), 131.02 (s), 154.08 (s), 154.19 (s), 203.86 (s); HRMS, m/z calcd for $C_{16}H_{21}N_3O_3$ (M^+) 303.1582, found 303.1595.

Ethyl 2-(4-Phenylurazolyl)-3-oxobutanoate (13) and Ethyl 2,2-Bis(4-phenylurazolyl)-3-oxobutanoate (14). Procedure A. A solution of ethyl 3-oxobutanoate (250 mg, 1.92 mmol) and trifluoroacetic acid (7.7 μL, 0.10 mmol) in 7 mL of dichloromethane was stirred for 15 min. PTAD (105 mg, 0.60 mmol) was added, the flask wrapped in aluminum foil, and the solution stirred for 4 h. A spatula tip of $NaHCO_3$ was added, and the solution was filtered through a 1.0 × 3.0 cm plug of flash silica gel eluting with ethyl acetate and evaporated to dryness. Centrifugal chromatography eluting with dichloromethane afforded recovery of 150 mg of unreacted starting material. Subsequent elution with dichloromethane/ethyl acetate (9:1) gave 74.8 mg (0.25 mmol, 42%) of mono-adduct **13** and 85.1 mg (0.18 mmol, 29.5%) of the bis-adduct **14**.

The slightly more polar mono-adduct **13** formed colorless crystals, mp 143.7–144.4 °C (lit[5b] mp 152–154 °C); IR ($CHCl_3$) 3320, 3300–2700, 1770, 1725–1700, 1650, 1490 cm^{-1}. The proton and carbon NMR spectra indicated the presence of an equilibrium mixture of keto and enol tautomers. Integration of the proton spectrum suggested enolization to be approximately 90% in dilute solution;[5b] ^1H NMR (80 MHz, $CDCl_3$) δ 1.26 (t, J = 7 Hz, 3 H), 2.13 (s, 2.7 H, enol methyl), 2.46 (s, 0.3 H, keto methyl), 4.25 (q, J = 7 Hz, 2 H), 5.28 (s, 0.1 H, keto methine proton), 7.33–7.54 (m, 5 H), 12.47 (br s, 0.9 H, enol O–H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.99 (q), 17.90 (q), 28.99 (q), 61.71 (t), 63.29 (t), 67.55 (d), 101.96 (s), 125.65 (d), 128.49 (d), 129.24 (d), 131.08 (s), 153.08 (s), 153.73 (s), 154.11 (s), 154.64 (s), 164.47 (s), 168.73 (s), 179.75 (s) 197.99 (s); HRMS, m/z calcd for $C_{14}H_{15}N_3O_5$ (M^+) 305.0975, found 305.0993.

The less polar bis-adduct **14** formed colorless crystals, mp 210.0–211.5 °C (lit.[5b] mp 199–202 °C); IR ($CHCl_3$) 3310, 3010, 1790,

(13) Wilson, R. M.; Hengge, A. C. *J. Org. Chem.*, following article in this issue.
(14) Wilson, R. M.; Hengge, A. C.; Ataei, A., unpublished results.
(15) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1971**, *51*, 121.
(16) Moriarty, R. M.; Prakash, I. *Synth. Commun.* **1985**, *15*, 649.

1730, 1500, 1410 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (t, J = 7.2 Hz, 3 H), 2.46 (s, 3 H), 4.46 (q, J = 7.2 Hz, 2 H), 7.37–7.49 (m, 10 H), 7.76 (br s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.58 (q), 25.18 (q), 65.31 (t), 86.07 (s), 126.03 (d), 129.06 (d), 129.38 (d), 130.02 (s), 153.29 (s), 154.73 (s), 162.14 (s), 190.75 (s); mass spectrum, m/z 305 (M^+ – PTAD); MSCI, 481 (MH^+).

Procedure B. A solution of ethyl 3-oxobutanoate (1.99 g, 15.3 mmol) and trifluoroacetic acid (8 μL, 0.11 mmol) in 7 mL of dichloromethane was stirred for 10 min. PTAD (103 mg, 0.59 mmol) in 2 mL of dichloromethane was added, the flask wrapped in aluminum foil, and the reaction stirred for 1 h. Following removal of solvent under reduced pressure, 1.80 g of unreacted starting material was recovered by distillation at room temperature under reduced pressure. Purification as described in the previous section afforded 153.4 mg (0.50 mmol, 86%) of **13**. None of the diurazole adduct **14** was observed in this procedure.

2-(4-Phenylurazolyl)-1,3-diphenyl-1,3-propanedione (15). To a stirred solution of 1,3-diphenyl-1,3-propanedione (2.52 g, 11.23 mmol) in 5 mL of dichloromethane was added PTAD (252 mg, 1.44 mmol) in 5 mL of dichloromethane. The red color of PTAD was discharged within 2 min. The solution was allowed to stand at 5 °C overnight, during which time **15** crystallized from the solution. Recovery of two crops of crystalline product by filtration afforded 490 mg (1.23 mmol, 85%) of **15** as colorless needles, mp 172.0–174.0 °C (lit.[5b] mp 189–191 °C); IR ($CHCl_3$) 3320, 1775, 1720, 1695, 1600, 1500 cm^{-1}. Both keto and enol tautomers are present in the proton and carbon NMR spectra. Therefore, the integration values cited should be taken as relative ratios only; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 0.3 H), 7.18 (d, J = 7.5 Hz, 0.8 H), 7.33–7.54 (m, 10.5 H), 7.65 (dd, J = 7.2 and 7.2 Hz, 1 H), 7.75 (d, J = 7.2 Hz, 1.5 H), 8.01 (d, J = 7.5 Hz, 1.8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.73 (d), 107.98 (s), 124.82 (d), 124.95 (d), 126.24 (d), 126.56 (d), 127.20 (d), 127.53 (d), 127.99 (d), 130.40 (s), 131.09 (d), 133.29 (d), 133.69 (s), 133.88 (s), 149.82 (s), 152.45 (s), 153.62 (s), 190.17 (s), 191.02 (s); HRMS, m/z calcd for $C_{23}H_{17}N_3O_4$ (M^+) 399.1219, found 399.1238.

2,2-Bis(4-phenylurazolyl)-1,3-diphenyl-1,3-propanedione (16). To a stirred solution of 2-(4-phenylurazolyl)-1,3-diphenyl-1,3-propanedione (**15**, 400 mg, 1.0 mmol) in 15 mL of dichloromethane was added PTAD (175 mg, 1.0 mmol) in 7 mL of dichloromethane. The red color of the PTAD was discharged within 6 days. This reaction mixture was allowed to stand at 5 °C overnight, during which time **16** precipitated from the solution. Recrystallization from dichloromethane/ethyl acetate afforded **16** (400 mg, 0.69 mmol, 69%) as colorless plates, mp 182.0–184.0 °C (dec) (lit.[5b] mp 160–162 °C); IR (KBr) 3226, 1695 (vb), 1563, 1369 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 7.3–7.6 (m, 18 H), 8.03 (d, J = 8.1 Hz, 4 H); ^{13}C NMR (75 MHz, acetone-d_6) δ 93.4 (s), 127.5 (s), 129.3 (s), 129.5 (d), 129.9 (d), 130.4 (d), 132.2 (s), 134.6 (d), 135.5 (s), 154.9 (s), 156.8 (s), 186.4 (s); FAB mass spectrum, m/z 575 (MH^+).

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Supplementary Material Available: Experimental procedures and spectroscopic data including infrared spectra, ^{1}H NMR spectra (300 MHz), ^{13}C NMR spectra (75 MHz), mass spectra (HRMS, CI, or FAB) available for compounds **4**, **7–12**, and **17** (6 pages). Ordering information is given on any current masthead page.

Synthesis and Chemistry of Acyltriazolinedione Ylides and Related Intermediates: New Methods for the Preparation of Di- and Tricarbonyl Compounds

R. Marshall Wilson* and Alvan C. Hengge

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

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α-Urazolylcarbonyl compounds can be easily oxidized to the corresponding ylides, and these ylides hydrolyzed to the corresponding carbonyl compounds. In addition these same urazole precursors can be converted to carbonyl compounds via a novel version of the Swern oxidation. These two methods not only are of synthetic value in the preparation of 1,2-dicarbonyl and 1,2,3-tricarbonyl compounds but also serve as useful probes for the formation of triazolinedione ylides and the related urazolium species.

A number of methods for the oxidation of carbonyl compounds with α-methylene groups have been developed for the preparation of 1,2-dicarbonyl compounds. The reagent in the most widespread use for this purpose is SeO_2.[1] However, this reagent frequently affords quite complex reaction mixtures and products contaminated with toxic selenium impurities that are difficult to remove. Dimethyl sulfoxide has been applied in Swern oxidations of α-halo ketones.[2] While this method can provide quite high yields of the diketones, the starting halo ketones are quiet sensitive substances and must be used shortly after their preparation to ensure high overall yields. β-Keto sulfides have been oxidized to 1,2-diketones and their

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