Synthesis of 2-arylmethylidene-5-oxo-1,4-diphenyl-2,5-dihydro-1*H*-pyrazol-2-ium-3-olates

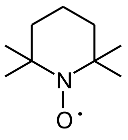
H. Sheibani,[a] J. Lari,[b] M. R. Islami,[a] and K. Saidi[a]★

[a]Department of Chemistry, Shahid Bahonar University of Kerman,
Kerman 76169, Iran.
Fax: +98 341 223 2142. E-mail: saidik@mail.uk.ac.ir
[b]Department of Chemistry, Payam-e Noor University,
Mashhad, Iran

Condensation of several arylhydrazones with chlorocarbonyl phenyl ketene gave 2-(arylmethylidene)-5-oxo-1,4-diphenyl-2,5-dihydro-1*H*-pyrazol-2-ium-3-olates in high yields.

Key words: chlorocarbonyl phenyl ketene, hydrazones, cross-conjugated heterocyclic mesomeric betaines, pyrazole derivatives.

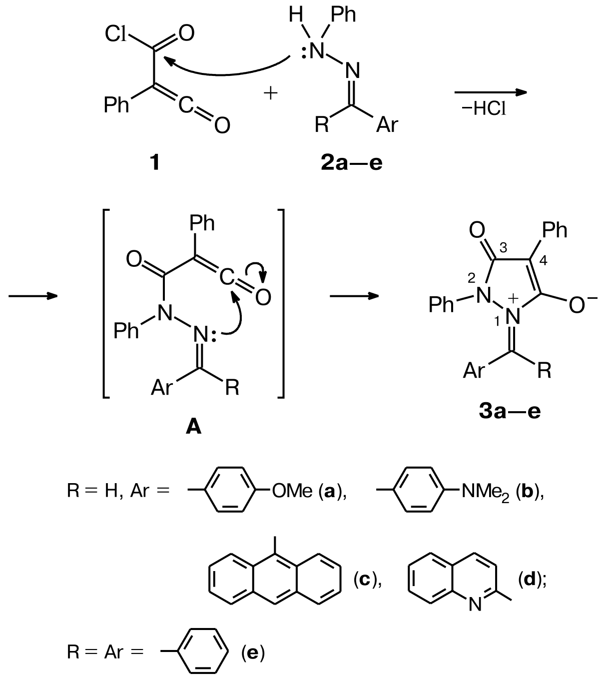
Ketene chemistry was the initial major research interest of Herman Staudinger, who prepared and characterized the first ketene, diphenyl ketene, in 1905 in his attempt to prepare the stable organic radical $Ph_2C^{\bullet}COCl$.[1] Chlorocarbonyl phenyl ketene (**1**) was prepared by dehydrochlorination of phenylmalonyl chloride.[2] This ketene reacts smoothly with carbonyl groups (aldehydes and ketones),[3] oximes,[4] ethoxyacetylene,[5] arylthioamides and thioureas[6] to produce synthetically valuable intermediates. We prepared (bisketenyl)benzenes[7,8] and divinyl ketene[9] and trapped them with stable aminoxyl free radical tetramethylpiperidine 1-oxyl (TEMPO). However, numerous efforts to bring ketene **1** into reaction with TEMPO or deactivated C=N bond (as in *N*-aryltrifluoroacetimidoyl chloride) have been mostly unsuccessful.



TEMPO

Ketene **1** has been found to be a very effective bielectrophile reacting with a variety of nucleophiles under rather mild experimental conditions.[10] The reaction of ketene **1** with arylhydrazones **2** resulting in a new heterocyclic system, *i.e.*, 2-(arylmethylidene-5-oxo-1,4-diphenyl-2,5-dihydro-1*H*-pyrazol-2-ium-3-olates **3**, was discovered in 1980.[11] We reproduced the data[11] for *para*-methoxybenzaldehyde hydrazone (**2a**) and *para*-*N*,*N*-dimethylaminobenzaldehyde hydrazone (**2b**) and obtained compounds **3a** and **3b**, respectively. Ketene **1** reacts readily with hydrazones of 9-anthracenecarboxaldehyde (**2c**), 2-quinolinecarboxaldehyde (**2d**), and benzophenone (**2e**) to form compounds **3c**, **3d**, and **3e**, respectively. The reaction occurs very easily: mixing of the reactants at 0 °C in anhydrous THF results in the immediate formation of a black precipitate, *viz.*, product **3**. Probably, the mechanism of the reaction involves the formation of intermediate **A** (Scheme 1).

Scheme 1



According to the classification by Ollis, Stanforth, and Ramsden,[12] compounds **3** should be regarded as cross-conjugated heterocyclic mesomeric betaines. As already mentioned,[11] these structures have no conjugation between the anionic and cationic delocalized systems of the molecule.

The stability of mesomeric betaines **3** could depend, in principle, on the nature of the aryl group. Electron-releasing groups in the aryl system in the *ortho*- or *para*-positions of the benzene ring could enhance the stability of this five-membered pyrazole system due to

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more efficient delocalization of the positive charge. Electron-withdrawing groups could decrease the stability of this system (*cf.* Refs. 13 and 14). However, all compounds **3** are stable in the solid state and melt without decomposition at high temperatures.

The cyclic structure of all compounds **3** is confirmed by their IR spectra, which do not contain the absorption band of ketene and contain the bands of the carbonyl group. The ^{1}H NMR spectra of compounds **3a—d** (R = H) exhibit one singlet at δ 9.70—12.60, which belongs to the =CH proton. This indicates that only one isomer is formed in the reaction. The ^{13}C NMR and mass spectra also confirm structure **3**.

Experimental

IR spectra (pellets with KBr) were recorded on a Matson 1000 FT spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 spectrometer using DMSO-d_6 as the solvent and Me_4Si as the internal standard. Mass spectra were recorded on a MS-QP2000A Shimadsu spectrometer (EI, 70 eV).

Melting points were determined on a Gallenkamp heating stage and uncorrected. Elemental analysis was carried out using a Heraeus CHN-O-Rapid analyzer.

Commercially available (Merck, Fluka) reagents were used as received, and THF was dried over sodium and distilled prior to use. Chlorocarbonyl phenyl ketene **1** was synthesized using a known procedure.[2]

Synthesis of compounds 3a—e (general procedure). A solution of ketene **1** (1 mmol, 0.18 g) in anhydrous THF (10 mL) was added dropwise to a stirred solution of hydrazone **2** (1 mmol) in anhydrous THF (15 mL) at 0 °C under a nitrogen atmosphere. A black precipitate of product **3** was formed immediately. After the end of the reaction, the precipitate was filtered off and washed with anhydrous THF (50 mL).

2-(4-Methoxyphenylmethylidene)-5-oxo-1,4-diphenyl-2,5-dihydro-1*H*-pyrazol-2-ium-3-olate (3a). Dark red crystal, 82% yield, m.p. 190 °C (*cf.* Ref. 11: m.p. 188—190 °C). ^{1}H NMR, δ: 9.88 (s, 1 H); 7.90—6.92 (m, 14 H); 3.94 (s, 3 H). ^{13}C NMR, δ: 190.91 (N^+=C); 164.69 (C(5)); 154.27 (C(3)); 132.62, 132.05, 130.79, 129.96, 129.64, 129.21, 129.08, 128.73, 128.04, 127.01, 126.91, 123.58, 115.89, 115.30, 114.37, 114.17, 55.85 (OMe). MS, m/z (I_{rel} (%)): 370 $[M]^+$ (40), 252 (75), 118 (100), 90 (85), 51 (50).

2-(4-Dimethylaminophenylmethylidene)-5-oxo-1,4-diphenyl-2,5-dihydro-1*H*-pyrazol-2-ium-3-olate (3b). Brown crystals, 90% yield, m.p. 220 °C (*cf.* Ref. 11: m.p. 222—223 °C). ^{1}H NMR, δ: 9.67 (s, 1 H); 7.91—6.78 (m, 14 H); 3.02 (s, 6 H). ^{13}C NMR, δ: 190.35 (N^+=C); 161.44 (C(5)); 154.64 (C(3)); 138.95, 132.89, 132.02, 129.59, 129.23, 128.40, 127.25, 126.20, 125.07, 125.00, 124.34, 119.71, 119.35, 112.56, 111.60, 89.17 (C(4)); 40.14 (NMe_2). MS, m/z (I_{rel} (%)): 383 $[M]^+$ (20), 238 (55), 222 (50), 147 (37), 118 $[PhCHCO]^+$ (90), 91 $[C_6H_5N]^+$ (100).

2-(9-Anthrylmethylidene)-5-oxo-1,4-diphenyl-2,5-dihydro-1*H*-pyrazol-2-ium-3-olate (3c). Black crystals, 90% yield, m.p. 195 °C. Found (%): C, 81.34; H, 6.05; N, 4.64. $C_{30}H_{20}N_2O_2$. Calculated (%): C, 81.81; H, 6.36; N, 4.54. IR, ν/cm^{-1}: 1780, 1730 (C=O). ^{1}H NMR, δ: 11.44 (s, 1 H); 8.90—7.13 (m, 19 H). ^{13}C NMR, δ: 194.56 (N^+=C); 161.31 (C(5)); 157.04 (C(3)); 138.99, 135.69, 132.92, 131.82, 131.20, 129.70, 129.25, 129.15, 128.43, 126.25, 125.03, 124.81, 124.51, 124.35, 123.91, 119.70, 90.31 (C(4)). MS, m/z (I_{rel} (%)): 440 $[M]^+$ (15), 280 $[C_{21}H_{14}N]^+$ (30), 203 $[C_{14}H_9CN]^+$ (100), 118 $[PhCHCO]^+$ (40), 90 $[PhCH]^+$ (25), 51 $[C_4H_3]^+$ (20).

5-Oxo-1,4-diphenyl-2-(2-quinolylmethylidene)-2,5-dihydro-1*H*-pyrazol-2-ium-3-olate (3d). Red crystals, 70%, m.p. 255 °C. Compound **3d** was not isolated in the individual form. IR, ν/cm^{-1}: 1690, 1670 (C=O). ^{1}H NMR, δ: 12.59 (s, 1 H); 8.80—7.02 (m, 16 H). ^{13}C NMR, δ: 197.06 (N^+=C); 152.01 (C(5)); 143.43 (C(3)); 143.21, 133.92, 129.94, 129.32, 128.65, 127.11, 126.82, 123.11, 120.86, 114.66, 87.34 (C(4)). MS, m/z (I_{rel} (%)): 391 $[M]^+$ (25), 246 $[M - PhC(CO)_2]^+$ (40), 218 (90), 170 (20), 115 (100), 77 $[C_6H_5]^+$ (30).

5-Oxo-1,4-diphenyl-2-(diphenylmethylidene)-2,5-dihydro-1*H*-pyrazol-2-ium-3-olate (3e). Dark green crystals, 85% yield, m.p. 180 °C. Found (%): C, 80.47; H, 4.81; N, 7.06. $C_{28}H_{20}N_2O_2$. Calculated (%): C, 80.76; H, 4.80; N, 6.73. IR, ν/cm^{-1}: 1747, 1696 (C=O). ^{1}H NMR, δ: 7.75—7.10 (m). ^{13}C NMR, δ: 196.31 (N^+=C); 161.5 (C(5)); 138.98, 137.51, 133.17, 132.89, 130.09, 129.25, 129.05, 128.42, 126.24, 125.02, 124.35, 119.69, 89.56 (C(4)). MS, m/z (I_{rel} (%)): 416 $[M]^+$ (10), 339 (18), 252 (72), 118 $[PhCHCO]^+$ (100), 90 $[PhCH]^+$ (55), 77 (75).

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