3 H, C3 $CH_3$), 2.14 (s, 3 H, C2 $CH_3$), 3.29 (d, $J$ = 7.0, 2 H, C4 $CH_2$Ph), 5.58 (t, $J$ = 7.0, 1 H, C4H), 7.04–7.36 (m, 15 H, Ar); mass spectrum, $m/z$ (% base peak) 393 (7.5, $M^+ + 1$), 392 (13.6, $M^+$), 302 (24.7), 301 (100), 105 (85.4), 77 (50.3).

Precise mass calcd for $C_{27}H_{24}N_2O$: 392.189. Found: 392.187.

**Reaction of Phosphorane 23d with Benzylketene (10c). Preparation of 4-Benzyl-6,7-diphenyl-2-methyl-3-(2-propenyl)-4*H*-pyrazolo[5,1-*c*][1,4]oxazine (27i).** Phosphorane **23d** (1.13 g, 2.0 mmol) was reacted as above with 0.60 g (6.0 mmol) of triethylamine and 0.68 g (4.0 mmol) of β-phenylpropionyl chloride. Column chromatography (silica gel, 7:1 *n*-Hex–EtOAc) of the crude reaction product yielded 0.62 g (74%) of **27i** as an oil. Crystallization from hexane–ether afforded a colorless analytical sample: mp 118–120 °C; IR ($CCl_4$) 1642, 1602, 1500, 1450 $cm^{-1}$; $^1H$ NMR δ 2.15 (s, 3 H, C2 $CH_3$), 2.69 and 2.94 (dd, $J_{gem}$ = 16.5, $J_{vic}$ = 6.1, 1 H each, $CH_2CH{=}CH_2$), 3.20 and 3.31 (dd, $J_{gem}$ = 13.6, $J_{vic}$ = 6.6, 1 H each, C4 $CH_2$Ph), 4.97 (dd, $J_{trans}$ = 16.9 and $J$ = 1.7, 1 H, $H_c$), 5.01 (dd, $J_{cis}$ = 10.1 and $J$ = 1.6, 1 H, $H_b$), 5.65 (t, $J$ = 6.6, 1 H, C4H), 5.68 (m, 1 H, $H_a$), 7.07–7.32 (m, 15 H, Ar); mass spectrum, $m/z$ (% base peak) 419 (10.7, $M^+ + 1$), 418 (20.0, $M^+$), 328 (25.3), 327 (100), 105, (34.5), 91 (16.9), 77 (12.2).

Precise mass calcd for $C_{29}H_{26}N_2O$: 418.204. Found: 418.203.

**Reaction of Phosphorane 23e with Benzylketene (10c). Preparation of 3,4-Dibenzyl-6,7-diphenyl-2-methyl-4*H*-pyrazolo[5,1-*c*][1,4]oxazine (27j).** Phosphorane **23e** (1.23 g, 2.0 mmol) was reacted as above with 0.60 g (6.0 mmol) of triethylamine and 0.68 g (4.0 mmol) of β-phenylpropionyl chloride. Column chromatography [silica gel, 7:1 *n*-Hex–EtOAc] of the crude reaction product yielded 0.67 g (72%) of **27j** as an oil. Crystallization from ethanol afforded a colorless analytical sample: mp 138–139 °C; IR (KBr) 1650, 1610, 1500, 1455 $cm^{-1}$; $^1H$ NMR δ 2.15 (s, 3 H, C2 $CH_3$), 3.01 and 3.19 (dd, $J_{gem}$ = 13.6, $J_{vic}$ = 6.8, 1 H each, C4 $CH_2$Ph), 3.29 and 3.55 (d, $J_{gem}$ = 16.4, 1 H each, C3 $CH_2$Ph) 5.41 (t, $J$ = 6.8, 1 H, C4H), 7.05–7.35 (m, 20 H, Ar); mass spectrum, $m/z$ (% base peak) 469 (8.0, $M^+ + 1$), 468 (20.7, $M^+$), 378 (31.9), 377 (100), 105 (18.8), 91 (58.6), 77 (31.9).

Precise mass calcd for $C_{33}H_{28}N_2O$: 468.220. Found: 468.220.

**Acknowledgment.** The generous support of the National Institute of General Medical Sciences (Grant No. GM 276020) is gratefully acknowledged. We would also like to thank Dr. Roger Crecely of the University of Delaware for obtaining and discussing the $^1H$ and $^{13}C$ NMR spectra, reported in this work, with us. Purchase of the Bruker WM 250 spectrometer was supported, in part, by a grant (GM 27616) from the National Institutes of Health.

**Registry No.** **8a**, 89849-20-7; **8b**, 89849-21-8; **8c**, 89849-22-9; **8d**, 89849-23-0; **8e**, 89849-24-1; **8f**, 89849-25-2; **10a**, 463-51-4; **10b**, 3496-32-0; **10c**, 87101-44-8; **23a**, 81724-92-7; **23b**, 89726-08-9; **23c**, 89726-09-0; **23d**, 81724-93-8; **23e**, 81724-94-9; **23f**, 81724-95-0; **24**, 89849-26-3; **27a**, 89849-27-4; **27b**, 89849-28-5; **27c**, 89849-29-6; **27d**, 89849-30-9; **27e**, 89873-79-0; **27f**, 89849-31-0; **27g**, 89849-32-1; **27h**, 89849-33-2; **27i**, 89849-34-3; **27j**, 89849-35-4; PhCHO, 100-52-7; *p*-$O_2NC_6H_4CHO$, 555-16-8; $CH_2O$, 50-00-0.

# Reactions of Azines. 8. Rearrangement of 1-Oxo-3,4,8-triaza-2,4,6,7-octatetraenes to 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones and 4,9-Dihydropyrazolo[5,1-*b*]quinazolines

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*Received October 17, 1983*

Reactions of phosphoranes **1** with isocyanates **2** have given excellent yields of 4,9-dihydropyrazolo[5,1-*b*]-quinazolines **10** and 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13** presumably via the intermediate 1-oxo-3,4,8-triaza-2,4,6,7-octatetraenes **3**. The ratios of the compounds **10** to **13** increased as the bulk of the substituents increase on the phosphoranes **1** and isocyanates **2** and were determined from the $^1H$ NMR data. The ratio of **10** to **13** decreased upon changing the para substituents on the phenyl isocyanate in the following order: $CH_3O$, $CH_3$, H, Cl, $CF_3$, and $NO_2$ (i.e., in order of increasing $\sigma_p$ value). There was a linear relationship between $\sigma_p$ value and the ratio of log [**10**/**13**], $\rho$ = –0.5. The ratios of **10** to **13** in the reaction of α-ethylphosphorane with undistilled isocyanates were almost all the same, 65 ± 2/35 ± 2, and reversed compared to the results observed when freshly distilled isocyanates were used.

In this work we report[1] a new synthesis of 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13** and 4,9-dihydropyrazolo[5,1-*b*]quinazolines **10** based on the thermal rearrangement of 1-oxo-3,4,8-triaza-2,4,6,7-octatetraenes **3**. The antitumor activity of the imidazo[1,2-*b*]pyrazole ring system has received considerable attention during the past few years.[2-4] We have found that 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones may be readily converted into imidazo[1,2-*b*]pyrazoles.[5] The known medicinal activity of fused pyrazoles has also spurred considerable research into the synthesis of imidazo[1,2-*b*]pyrazoles[6-10] as well as the pyrazolo[5,1-*b*]quinazolines.[11-14]

(1) Schweizer, E. E.; Lee, K. J. presented at the 184th National Meeting of the Amercian Chemical Society, Sept 1982.
(2) Shoemaker, D. D.; Ayers, D. C.; D'Anna, M. E.; Cysyk, R. L. *Eur. J. Cancer* **1981**, *17*, 391.
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(5) Schweizer, E. E.; Lee, K. J., unpublished results.
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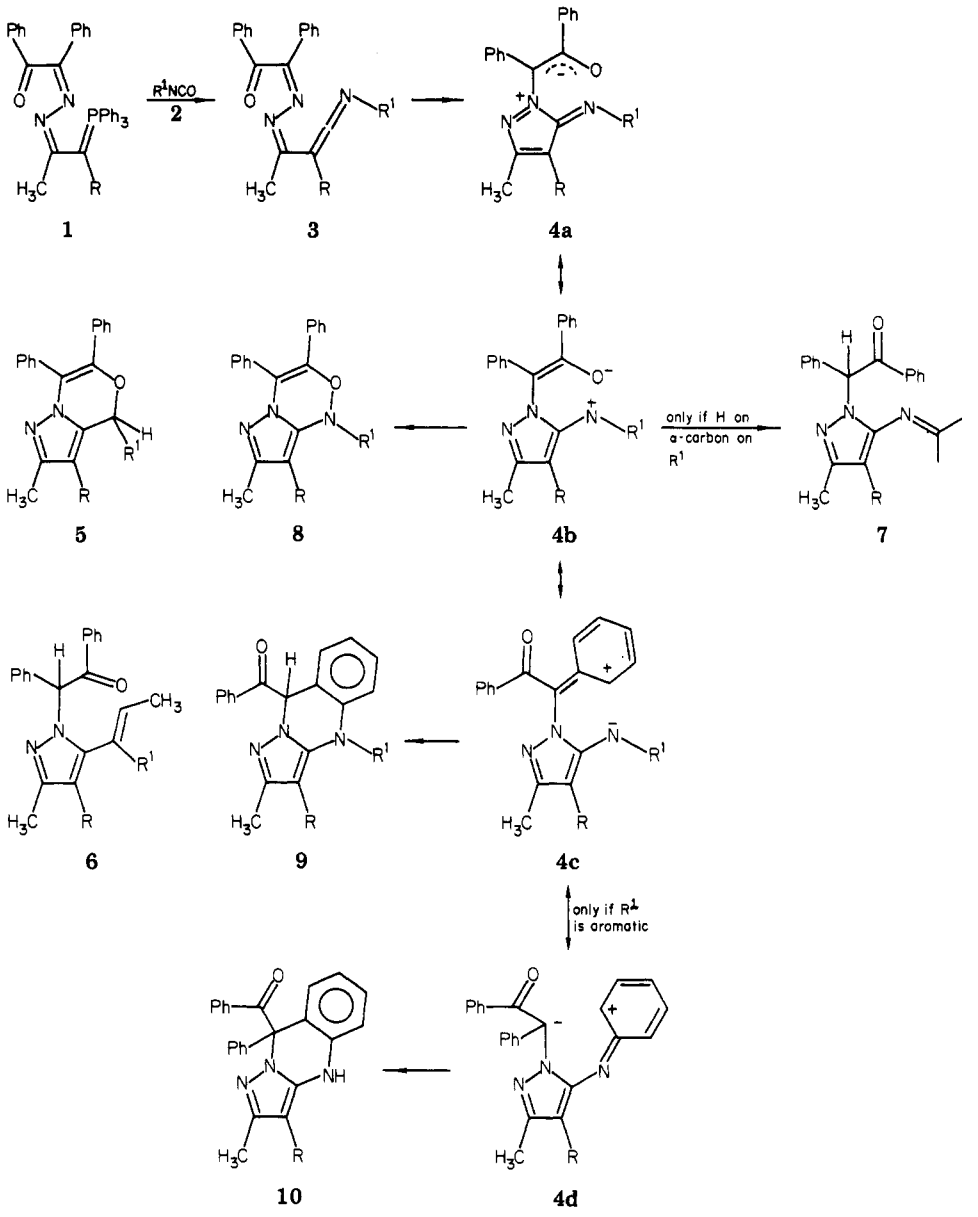
Scheme I




Electrocyclic reactions of azines, $\alpha,\beta$-unsaturated keto azines and allenylic keto azines are well-known in the literature[15] and are reviewed in the accompanying paper.[16]

Staudinger and Meyer[17] showed, in 1920, that phosphoranes without protons on the $\alpha$-carbon atom underwent normal olefination reactions with isocyanates to give ketimines. Our continued interest in the reaction of cumulated azines as synthons for fused pyrazolo ring systems lead us to report our investigations into the reactions of isocyanate **2** with $\alpha$-substituted-phosphoranes **1**.

## Results and Discussion

We anticipated, on the basis of the previous work,[15a,16] that the thermal electrocyclic reactions of keto azine ketimines **3** prepared from the corresponding $\alpha$-substituted-phosphorane **1** and isocyanate **2** would give the resonance-stabilized azomethine imine **4** (Scheme I). The keto azine allenes prepared from $\alpha$-substituted keto azine phosphoranes **1** and monosubstituted ketene, or ketene itself, gave only pyrazolo[5,1-*c*][1,4]oxazines **5**.[16] In contrast, the reaction of ethylphenylketene with **1** (R = H) gives pyrazole **6**, as well as other products related to **8**(**5**), **9**, and **10**.[15a] Thus we expected that **7** and **8** would be the predominant products from the reactions of **1** and **2**, with **9** and **10** being the minor products.

One of the products was indeed the expected 4,9-dihydropyrazolo[5,1-*b*]quinazolines **10**, where $R^1$ is aromatic (with at least one of the ortho positions unblocked), while the other products were 2,3-dihydro-1*H*-imidazo[1,2-*b*]-pyrazol-2-ones **13**. However, when $R^1$ was alkyl or an aromatic moiety that was blocked in the two ortho positions (e.g., from 2,6-dimethylphenyl isocyanate), only the 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13** were obtained. Compounds **7**, **8**, and **9** were not obtained.

A reasonable mechanism for the transformation of **3** into **10** and the unexpected **13** is shown in Scheme II. The

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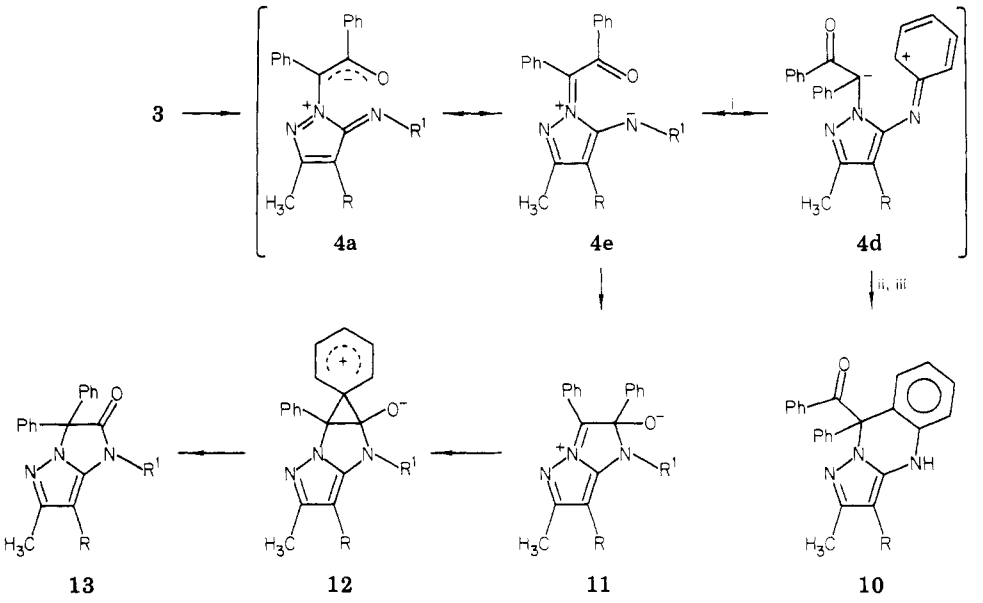
(17) Staudinger, H.; Meyer, J. *Chem. Ber.* **1920**, *53*, 72.

Scheme II[a]




[a] (i) Only if $R^1$ is aromatic; (ii) ring closure, (iii) 1,3-H shift.

intramolecular cycloaddition reaction of the keto azine ketimine **3** would give the resonance-stabilized azomethine imine **4a** ↔ **4e** ↔ **4d**. In **4e**, the exocyclic nitrogen anion would attack the carbonyl group and phenyl migration, via phenonium ion **12**, would give compound **13**; while in **4d**, addition of the enolate anion to the ring carbocation and rearomatization, by 1,3-H shift, to the phenyl ring would yield compound **10**.

In an attempt to change the nucleophilicity of the exocyclic nitrogen, on the assumption that the ratios of **10** to **13** would be altered and that possibly compounds **8** or **9** would be formed, substituents were placed on the para position of phenyl isocyanate. However, neither compound **8** nor **9** were obtained (Scheme I). The slight changes in ratios of compounds **10** to **13** are shown in Table I and are discussed below.

The isolated yields of the corresponding pure compounds and $^1H$ NMR ratio of **10** to **13** are shown in Table I. Examination of Table I shows the following.

1. As the bulk of R increases in the intermediates **3** and **4** ($R^1$ = Ph, see Scheme II), the ratio of **10** to **13** increases (entries a, b, and c).

2. As the bulk of $R^1$ increases in the intermediates **3** and **4** (R = Me or Et), the ratio of **10** to **13** also increases (entries f, g, and h).

These facts suggest that the increasing steric interactions between R and $R^1$ forces the N-aromatic group into a cisoid position relative to the pyrazole-N-substituted benzil moiety, therefore diminishing the contribution of resonance form **4e** and thus allowing resonance form **4d** to be operative (see Scheme II).

3. Entries b and n–r indicate that by changing the para substituents on the phenyl isocyanate in the following order $CH_3O$, $CH_3$, H, Cl, $CF_3$, to $NO_2$ (i.e., in order of increasing $\sigma_p$ value), the ratio of **10** to **13** decreases. Presumably electron-withdrawing substituents (e.g., Cl, $CF_3$, $NO_2$) stabilize the charge on the exocyclic nitrogen anion by field effect, therefore increasing the contribution of resonance form **4e**. On the other hand, electron-donating substituents (e.g., $CH_3O$) stabilized the N-attached ring carbocation in **4d** and destabilized the exocyclic nitrogen anion in **4e**. Therefore, the effect of resonance form **4d** increases and thus **4d** is more operative (see Scheme II).

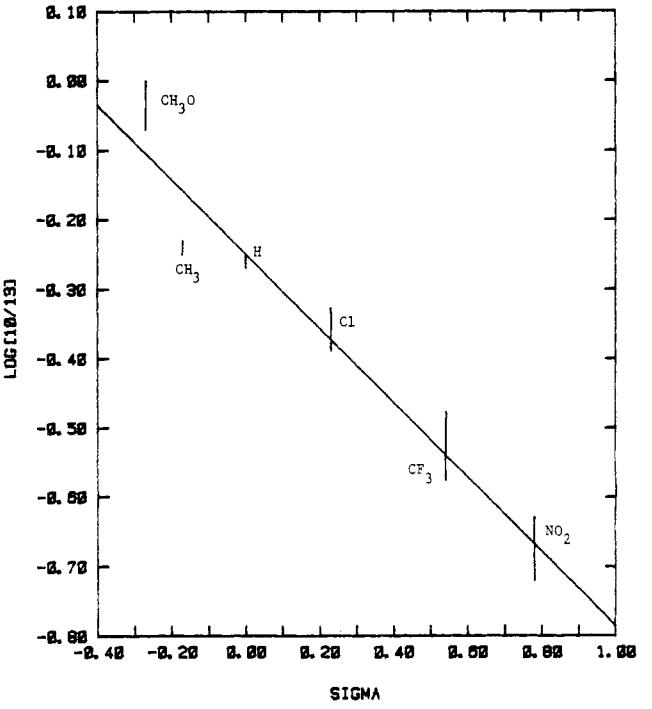


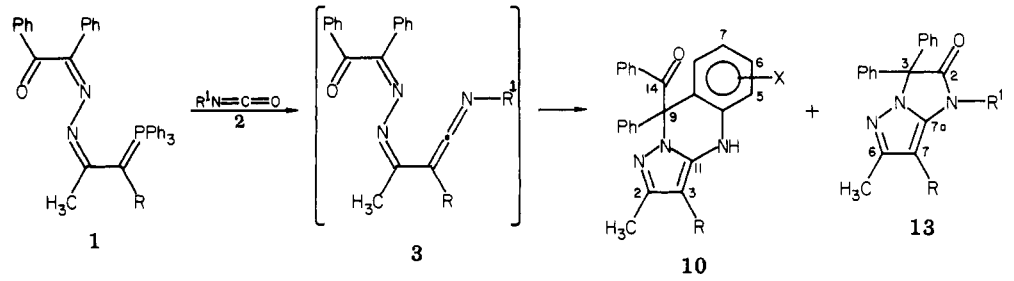

**Figure 1.** Linear relationship between $\sigma$ para value and log [10/13].

Figure 1 shows a linear relationship between the $\sigma_p$ value and the ratio of log [**10**/**13**] ($\rho$ = −0.5).

4. Table I shows different ratios of **10** to **13** between distilled and undistilled isocyanates. Surprisingly, the ratios of **10** to **13** in the reaction of $\alpha$-ethylphosphorane with undistilled isocyanates were almost the same values, 65 ± 2/35 ± 2 (entries, b, n, o, and p). These results were totally reversed compared to the distilled case. There were no trends between substituent groups and products ratio employing undistilled isocyanates. In all cases compounds **10** were the predominant products.

Thus it has been shown again[15a,16] that cumulated azines are good synthons for fused pyrazolo heterocycles, in this instance for 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13** and 4,9-dihydropyrazolo[5,1-*b*]quinazolines **10**.

**Table I. Reactions of Phosphoranes 1 with Isocyanates 2. Isolated Yields and Ratios of 4,9-Dihydropyrazolo[5,1-*b*]quinazolines 10 to 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones 13**



| entry | R | X in 10 | $R^1$ in 13 | reaction time, h | yield, %, of 10 + 13 | ratio[a] of 10/13 | mp,[c] °C |
|---|---|---|---|---|---|---|---|
| a[b] | $CH_3$ | H | $C_6H_5$ | 16 | 82 | 11/89 | 199–200 |
| | | | | | | (14/86) | 193–194 |
| b | $CH_3CH_2$ | H | $C_6H_5$ | 16 | 81 | 35/65 | 190–191 |
| | | | | | | (63/37) | 162–163 |
| c | $CH_3CH_2CH_2$ | H | $C_6H_5$ | 16 | 78 | 66/34 | 161–162 |
| | | | | | | (59/41) | 147–148 |
| d[b] | $CH_2$=$CHCH_2$ | H | $C_6H_5$ | 16 | 80 | 58/42 | 186–187 |
| | | | | | | (50/50) | 149–150 |
| e | $C_6H_5CH_2$ | H | $C_6H_5$ | 16 | 79 | 63/37 | 202–203 |
| | | | | | | (55/45) | 159–160 |
| f | $CH_3$ | 5-$CF_3$ | 2-$CF_3C_6H_4$ | 16 | 73 | 52/48 | 174–176 |
| | | | | | | (57/43) | 188–190 |
| g | $CH_3$ | 5,6-$C_4H_4$ | 1-$C_{10}H_7$ | 16 | 72 | 66/34 | 201–202 |
| | | | | | | (72/28) | 187–188 |
| h | $CH_3CH_2$ | 5-$CF_3$ | 2-$CF_3C_6H_4$ | 16 | 78 | 61/39 | 158–160 |
| | | | | | | (77/23) | 152–153 |
| i | $CH_3$ | | 2,6-$(CH_3)_2C_6H_3$ | 16 | 66 | 0/100 | 219–221 |
| j | $CH_3$ | | $CH_3$ | 48 | 45 | 0/100 | 189–190 |
| k | $CH_3$ | | *t*-Bu | 72 | 38 | 0/100 | 163–164 |
| l | $CH_2$=$CHCH_2$ | | $CH_3$ | 16 | 43 | 0/100 | 123–124 |
| m | $CH_2$=$CHCH_2$ | | *t*-Bu | 78 | 68 | 0/100 | 111–112 |
| n | $CH_3CH_2$ | 7-$CH_3O$ | 4-$CH_3OC_6H_4$ | 16 | 77 | 48/52 | 176–178 |
| | | | | | | (66/34) | 153–154 |
| o | $CH_3CH_2$ | 7-$CH_3$ | 4-$CH_3C_6H_4$ | 16 | 80 | 37/63 | 208–209 |
| | | | | | | (64/36) | 213–214 |
| p | $CH_3CH_2$ | 7-Cl | 4-$ClC_6H_4$ | 16 | 79 | 31/69 | 198–200 |
| | | | | | | (65/35) | 175–176 |
| q | $CH_3CH_2$ | 7-$CF_3$ | 4-$CF_3C_6H_4$ | 16 | 81 | 23/77 | 196–197 |
| | | | | | | | 142–143 |
| r | $CH_3CH_2$ | 7-$NO_2$ | 4-$O_2NC_6H_4$ | 16 | 71 | 18/82 | 237–238 |
| | | | | | | | 177–179 |

[a] Ratios based on 250-MHz $^1H$ NMR of crude reaction mixture. Parentheses values are from reaction with undistilled isocyanate. [b] The structure of compounds **13a** and **10d** were confirmed by X-ray analysis, which will be published elsewhere. [c] The first mp listed is for compound **10**, the second for **13**. If only one mp is listed, then it is for **13**.

**Spectral Characteristics.** Table II (supplementary material) lists the characteristic IR absorption frequencies of the 4,9-dihydropyrazolo[5,1-*b*]quinazolines **10** and the 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13** described above. The compounds **10** exhibit bands at 1675–1710 (C=O), 1620–1630 (pyrazole C=N/C=C), and 3400–3500 $cm^{-1}$ (NH) in their infrared spectra. The compounds **13** show strong bands at 1735–1760 (γ-lactam C=O)[18,19] and 1585–1640 $cm^{-1}$ (pyrazole C=N/C=C).

$^1H$ NMR data for compounds **10** and **13** are collected in Tables III and IV (supplementary material). The two diastereotopic benzylic protons of **10e** were shown as two doublets ($J$ = 16.5), while in **13e** they appear as a singlet. Also, 4,9-dihydropyrazolo[5,1-*b*]quinazolines **10** in $CDCl_3$ solution show the NH peaks hidden under the aromatic region. In $Me_2SO$-$d_6$ solution the NH peaks show a very deshielded absorbption (8.90–10.2 ppm), suggesting a strong hydrogen bonding between NH proton and $Me_2SO$-$d_6$ solvent.[20]

As a general rule it has been found that compounds **13** have larger $R_f$ values than compounds **10**, on the thin-layer chromatography. The only exceptions to this rule are compounds **10f** and **10h** (where $R^1$ = 2-$CF_3C_6H_4$), which have larger $R_f$ values than compounds **13f** and **13h**. The NH proton in compounds **10f** and **10h** show a shielded absorption (8.90 and 8.80 ppm) compared to the $^1H$ NMR of the other **10** species (9.49–10.2 ppm). These facts suggest an intramolecular hydrogen bonding between NH proton and $CF_3$ fluorine atom. (See Figure 2).

Tables V and VI (supplementary material) list selected $^{13}C$ NMR parameters for the compounds **10** and **13**, re-

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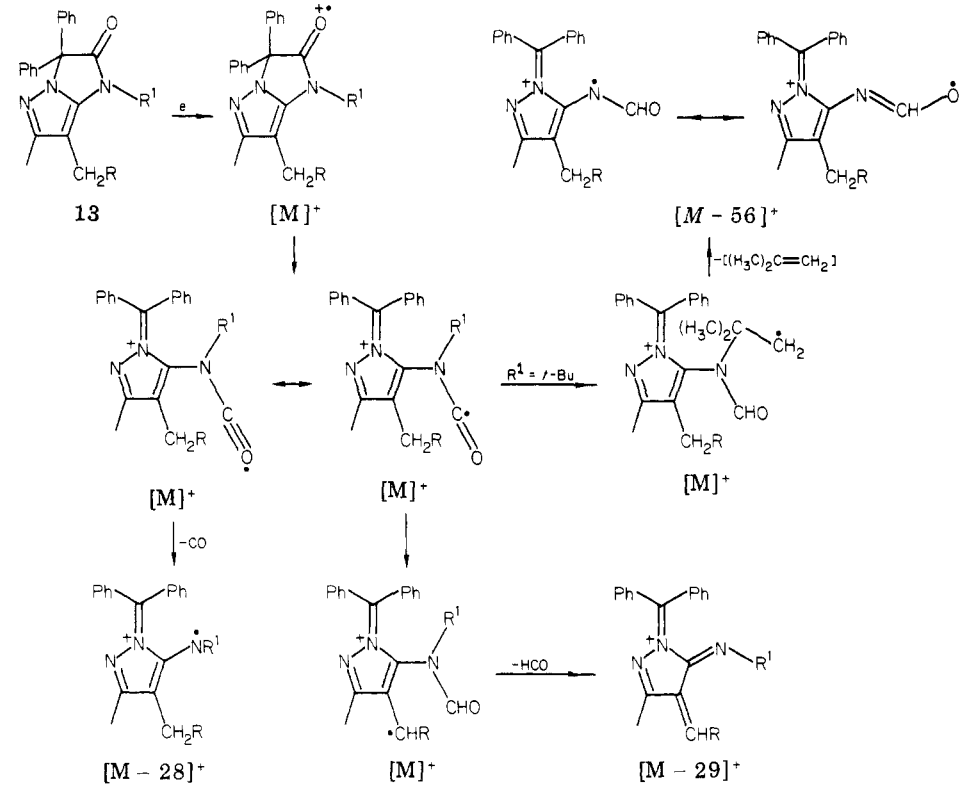
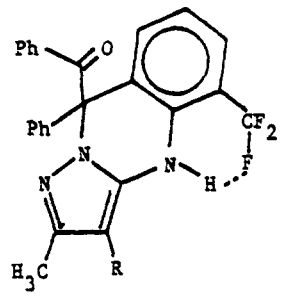
(20) Dyer, J. R. "Application of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1965; p 90.

Scheme III



10f, R=$CH_3$

10h, R=$CH_3CH_2$

**Figure 2.**

spectively. Peaks at 193–195 (PhCO), 140–142 (C2), 92–102 (C3), and 146–149 ppm (C11) characterize the pyrazole backbone[21,22] of the 4,9-dihydropyrazolo[5,1-*b*]-quinazolines **10**. Peaks at 172–174 (NC=O), 139–142 (C6), 93–102 (C7), and 151–153 ppm (C7a) characterize the pyrazole backbone[21,22] of the 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13**.

Table VII (supplementary material) lists the mass spectral data. The 4,9-dihydropyrazolo[5,1-*b*]quinazolines **10** showed the most intense ion $[M - PhCO]^+$ and a small intensity of $[M]^+$ ion in EI mass spectra. On the other hand, in CI mass spectra, compounds **10** showed strong intensity of $[M + 1]^+$. The 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones **13** exhibited strong intensities of $[M]^+$, $[M - 29]^+$, and $[M - 28]^+$ in that order in EI mass spectra. Similar observations have been previously noted and attributed to the loss of carbon monoxide in the hydantoin system.[23] But a significant ion (base peak) corresponding to the expulsion of the isobutylene unit was detected for the *N*-*t*-Bu compounds **13k** and **13m**. A possible overall fragmentation pathway[24] is shown in Scheme III.

Further studies into the preparation of fused nitrogen heterocycles from cumulated azine synthons are underway.

## Experimental Section

Melting points were obtained on a Thomas-Hoover Unimelt capillary apparatus and are uncorrected. IR spectra were recorded on a Unicap SP 1100 infrared spectrophotometer and calibrated by comparison with a standard polystyrene film sample. Precise mass spectra were recorded by using a DuPont 21-492B instrument with a resolution of 3300 or 5000.

The $^1H$ NMR spectra of approximately 10% (w/v) solutions in $CDCl_3$ or $Me_2SO$-$d_6$ were obtained on a Bruker Spectrospin Model WM 250. Chemical shifts are reported in parts per million ($\delta$) vs. tetramethylsilane as an internal standard. In reporting the NMR data, the folllowing abbreviations have been employed: coupling constant in hertz ($J$), singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). The $^{13}C$ NMR data were collected on a Bruker Spectrospin Model WM 250 at 62.9 MHz in $CDCl_3$ or $Me_2SO$-$d_6$ solution [ca. 10% (w/v)].

Dry nitrogen gas was routinely employed as the reaction atmosphere in all reactions. Benzene was dried and distilled from sodium metal. In light of its toxicity, benzene should be replaced by toluene in any attempts to repeat or extend this work. All glassware was baked at 150 °C for a minimum of 4 h before use. Baker silica gel (60–200 mesh) and EM 7747 silica gel for column

(21) Faure, R.; Vincent, E. J.; Claramunt, R. M.; Elguero, J. *Org. Magn. Reson.* **1977**, *9*(9), 508.

(22) The numbering systems used in the $^{13}C$ NMR is as shown in Table I.

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chromatography[25] were used throughout for product separation. Eastman chromagram precoated (silica gel on polyethylene) sheets impregnated with a fluorescent indicator were employed in thin-layer chromatographic operations. Isocyanates were purchased from the Aldrich, Eastman Organic, and Pfalts & Bauer Chemical Companies and distilled prior to use. *p*-Nitrophenyl isocyanate was recrystallized from anhydrous petroleum ether.

**Reactions of Phosphoranes 1 with Aryl Isocyanates 2. Preparations of 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones 13 and 4,9-Dihydropyrazolo[5,1-*b*]quinazolines 10. General Method.** A solution of the phosphorane 1 (2.0 mmol) and isocyanate 2 (2.5 mmol; $R^1$ = *p*-$O_2NC_6H_4$, 4.0 mmol) in 20 mL benzene was stirred under reflux for the amount of time indicated in Table I. After removal of solvent in vacuo, the reaction mixture was chromatographed on a silica gel column, eluting with ethyl acetate/hexane. This yielded the following in order of elution ($R^1$ = 2-$CF_3C_6H_4$, reverse order).

(a) **2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-one (13)** as a colorless solid. Recrystallization from ethanol or ether/petroleum ether afforded an analytical sample. Isolated yields (Table I), melting points (Table I), IR (Table II), $^1$H NMR (Table IV), $^{13}$C NMR (Table VI), and mass spectral data (Table VII) are collected separately.

**(b) 4,9-Dihydropyrazolo[5,1-*b*]quinazoline (10)** as a slightly yellow solid. Recrystallization from ether/petroleum ether afforded an analytical sample. Isolated yields (Table I), melting points (Table I), IR (Table II), $^1$H NMR (Table III), $^{13}$C NMR (Table V), and mass spectral data (Table VII) are collected separately.

**Reactions of Phosphoranes 1 with Alkyl or 2,6-Dimethylphenyl Isocyanates 2. Preparations of 2,3-Dihydro-1*H*-imidazo[1,2-*b*]pyrazol-2-ones 13. General Method.** A solution of the phosphorane 1 (2.0 mmol) and isocyanate 2 (2.5 mmol) in 20 mL of benzene was stirred under reflux for the amount of time indicated in Table I. After removal of solvent in vacuo, the reaction mixture was chromatographed on a silica gel column, eluting with ethyl acetate/hexane, to yield a 2,3-dihydro-*1H*-imidazo[1,2-*b*]pyrazol-2-one (13). Recrystallization from ether/petroleum ether afforded a colorless analytical sample. Isolated yields (Table I), melting points (Table I), IR (Table II), $^1$H NMR (Table IV), $^{13}$C NMR (Table VI), and mass spectral data (Table VII) are collected separately.

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**Registry No.** 1 (R = $CH_3$), 81724-92-7; 1 (R = $CH_3CH_2$), 89726-08-9; 1 (R = $CH_3CH_2CH_2$), 89726-09-0; 1 (R = $CH_2$=$CHCH_2$), 81724-93-8; 1 (R = $C_6H_5CH_2$), 81724-94-9; 2 (R′ = $C_6H_5$), 103-71-9; 2 (R′ = 2-$CF_3C_6H_4$), 2285-12-3; 2 (R′ = 1-$C_{10}H_7$), 86-84-0; 2 (R′ = 2,6-$(CH_3)_2C_6H_3$), 28556-81-2; 2 (R′ = $CH_3$), 624-83-9; 2 (R′ = Bu-*t*), 1609-86-5; 2 (R′ = 4-$CH_3OC_6H_4$), 5416-93-3; 2 (R′ = 4-$CH_3C_6H_4$), 622-58-2; 2 (R′ = 4-$ClC_6H_4$), 104-12-1; 2 (R′ = 4-$CF_3C_6H_4$), 1548-13-6; 2 (R′ = 4-$O_2NC_6H_4$), 100-28-7; **10a**, 89726-10-3; **10b**, 89726-12-5; **10c**, 89726-14-7; **10d**, 89726-16-9; **10e**, 89746-10-1; **10f**, 89726-19-2; **10g**, 89726-21-6; **10h**, 89726-23-8; **10n**, 89726-30-7; **10o**, 89726-32-9; **10p**, 89726-34-1; **10q**, 89746-11-2; **10r**, 89746-12-3; **13a**, 89726-11-4; **13b**, 89726-13-6; **13c**, 89726-15-8; **13d**, 89726-17-0; **13e**, 89726-18-1; **13f**, 89726-20-5; **13g**, 89726-22-7; **13h**, 89726-24-9; **13i**, 89726-25-0; **13j**, 89726-26-1; **13k**, 89726-27-2; **13l**, 89726-28-3; **13m**, 89726-29-4; **13n**, 89726-31-8; **13o**, 89726-33-0; **13p**, 89726-35-2; **13q**, 89726-36-3; **13r**, 89726-37-4.

**Supplementary Material Available:** Spectroscopic data in Tables II–VII (8 pages). Ordering information is given on any current masthead page.

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# Oxidative Cleavage of Substituted Naphthalenes Induced by Irradiated Semiconductor Powders

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Electron-rich members of a series of substituted naphthalenes react with oxygen to give ring-cleaved products upon long wavelength ultraviolet irradiation of $TiO_2$ powders suspended in oxygen-saturated acetonitrile solutions of the arene. Reactivity within the series parallels trends in the oxidation potential, i.e., the species with the less positive oxidation potential appears to react more efficiently. A mechanism involving sensitized formation of the substituted naphthalene cation radical is suggested for the semiconductor-mediated photocatalysis.

Recent interest in photoreactions occurring at surfaces and in new methods for the activation of oxygen to effect the functionalization of hydrocarbons has stimulated the investigation of irradiated semiconductor powders as redox photocatalysts. The photoelectrochemical properties of excited metal oxides render them effective photooxidation catalysts,[1] but so far only limited use of these sensitizers for synthetically useful conversions has been described.

In particular, the photoinduced oxidation of aryl systems has been peripherally studied. The $TiO_2$-photocatalyzed oxidative cleavage of aryl olefins gives rise, in excellent chemical yields, to carbonyl compounds by initial oxygenation of the double bond,[2,3] but no oxygenation of the aryl rings could be detected. Similarly, the semiconductor-sensitized photooxidation of aryl amines, e.g., aniline or toluidine[4] and of alkylbenzenes, e.g., toluene,[5] leads to products involving side chain oxidation. In contrast, the photooxygenation of benzene,[6] benzoic acid,[7] or toluene[8]

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