J. Org. Chem. 1983, 48, 2287–2289

Since the pressure dependence of the kinetics of ketene imine 1 is very similar to that of 3, we conclude that it, like 3, decomposes by a radical pathway with return ($k_{-1}$, Scheme I). The absence of the additional coupling products from 1 is unusual and should be probed in more detail.

## Experimental Section

**Diphenyl-*N*-benzylketene Imine.** This compound (1; R = H: Ar = phenyl) was prepared by following the procedures outlined by Singer et al.[2] Benzylamine was reacted with a mixture of dibromine and triphenylphosphine to yield (benzylamino)triphenylphosphonium bromide. Subsequent neutralization of this reagent gave (triphenylphosphoranediyl)benzylamine, which, on reaction with diphenylketene, gave diphenyl-*N*-benzylketene imine. Chromatography of this crude compound on basic alumina gave pure ketene imine as a yellow oil; $^1$H NMR ($CCl_4$) $\delta$ 7.1–7.3 (15, m), 4.7 (2, s) (lit.[2] yellow oil, $^1$H NMR ($CCl_4$) 7.2–7.4 (15, m), 4.7 (2 s)). On thermal decomposition in chlorobenzene the characteristic $CH_2$ NMR singlet in the ketene imine disappeared and a new $CH_2$ NMR singlet appeared at 1.1 ppm higher field. Singer[2] reports that the $CH_2$ NMR singlet of the product nitrile is found at 1.0 ppm higher field than that for the ketene imine in $CCl_4$.

**Kinetic Studies.** A 0.356 M solution of 1 in purified chlorobenzene was prepared under an atmosphere of nitrogen and vacuum degassed. After being flushed with argon the flask was sealed and stored at −12 °C until used in the kinetic experiments. In a glovebag under a nitrogen atmosphere, samples were withdrawn and placed in Teflon reaction vessels. The Teflon cells were sealed and heated under pressure at 60.12 °C as previously described.[9]

After decomposition and quenching, the samples were transferred, in a glovebag under an $N_2$ atmosphere, into NMR tubes that were tightly capped. Within 15 min each sample was repetitively scanned (ten times) over the chemical shift range 3.0–5.5 by using a carefully tuned Varian EM-390 90-MHz NMR spectrometer. Low sample concentrations made electronic integration imprecise. Since the resonance signals were very sharp, the relative proton counts for the ketene imine at $\delta$ 4.7 and for the nitrile at $\delta$ 3.6 were estimated from peak heights ($R$ and $P$, respectively). The rate of disappearance of ketenimine was monitored by following the decrease in the ratio $R/(R + P)$ as a function of time. Reasonable first-order plots were obtained through 2 half-lives. No other extraneous signals were observed in the proton NMR spectra.

**Acknowledgment.** Support by the National Science Foundation and the award of University of California, Riverside Minigrants to A.P.S. are gratefully acknowledged. We also thank Professor Singer for helpful discussions.

**Registry No.** Diphenyl-*N*-benzylketene imine, 52826-48-9.

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[9] Neuman, R. C., Jr.; Behar, J. V. *J. Am. Chem. Soc.* **1969**, *91*, 6024.

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## Reactions of Dibenzoyldiimide with Alkoxide

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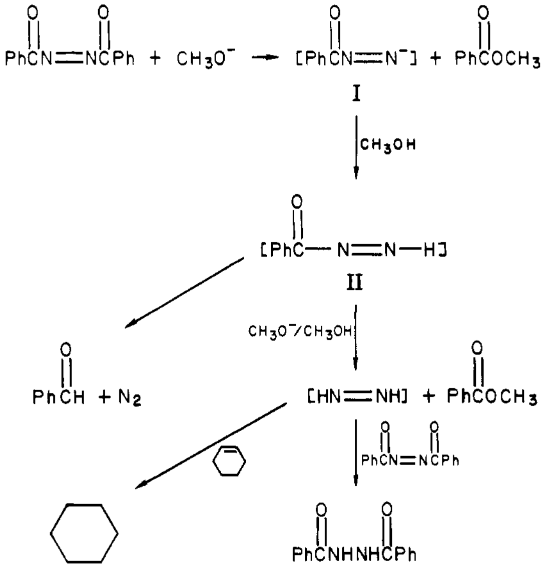
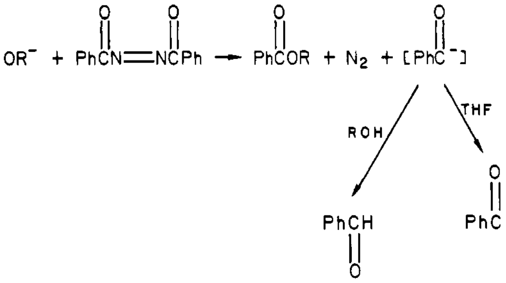
Many attempts to form acyl anions have been unsuccessful.[1] Even the intermediacy of these species in various reactions has been questioned.[2] Since Battaro[3] was able to produce a phenyl anion through the decomposition of an azo compound, we decided to investigate the action of alkoxide ion on dibenzoyldiimide in an attempt to produce a benzoyl anion. If this intermediate were produced in protic media, benzaldehyde would be an expected product; however, in aprotic media benzil would be anticipated.

Scheme I





A summary of the products obtained from the reaction of dibenzoyldiimide with various bases is found in Table I. In protic solvents, the appearance of substantial amounts of dibenzoylhydrazine (entries 1, 2, and 6 of Table I), clearly calls for an intermediate other than the benzoyl anion. As postulated in Scheme I, the alkoxide forms the ester and a benzoyldiimide anion, I, that is protonated by the solvent to form benzoyldiimide, II. Bimolecular decomposition of II to benzaldehyde and nitrogen, as described by Kosower and Huang for phenyldiimide,[4] competes with diimide formation. The diimide then reduces the starting dibenzoyldiimide to form dibenzoylhydrazine. This pathway is supported by the fact that in the presence of cyclohexene, the yield of dibenzoylhydrazine is substantially decreased and cyclohexane is formed. Reaction of diethyl azodicarboxylate with sodium ethoxide also gives rise to hydrazine.[5]

The reaction of dibenzoyldiimide with methoxide ion was carried out in an aprotic solvent to see if the benzoyldiimide anion, I, might lose nitrogen and form the sought after benzoyl anion. The products obtained were different but surprisingly included tribenzoylhydrazine, compound III, benzoic acid, benzaldehyde, methyl benzoate, and a trace of benzil. From the structure of hy-

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[1] (a) Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943. (b) Govidan, M.; Pinnick, H. W. *J. Org. Chem.* **1981**, *46*, 5011.

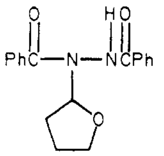
[2] Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118.

[3] Battaro, J. C. *J. Chem. Soc., Chem. Commun.* **1978**, 990.

[4] Huang, P. C.; Kosower, E. M. *J. Am. Chem. Soc.* **1968**, *90*, 2367.

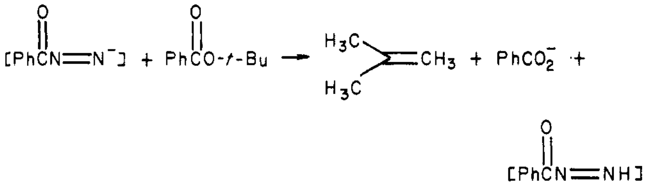
[5] White, R. E.; Kovacic, P. *J. Am. Chem. Soc.* **1974**, *96*, 7284.

0022-3263/83/1948-2287$01.50/0



drazine III, it is obvious that the solvent is involved in the reaction. Abstraction of the α hydrogen in THF is known to be important in certain other radical reactions;[6] hence the radical pathway as shown in Scheme II is proposed. Interestingly, increasing the methoxide concentration enhances the decomposition rate. An equimolar mixture of dibenzoyldiimide and methoxide required 4 to 7 days for the red color of the azo compound to dissipate; however, when only half as much base was used, 6 to 10 days were required for complete reaction. In both cases the same products were obtained. The electron-transfer reaction proposed in Scheme III may account for the rate enhancement. The trace of ester observed is also consistent with this pathway. Similarly, the complete absence of dibenzoylhydrazine is a further indication that benzoyldiimide is not formed.

The radical processes postulated in Schemes II and III were not involved in the reaction of dibenzoyldiimide with *tert*-butoxide ion in either *tert*-butyl alcohol or THF for no tribenzoylhydrazine or III were formed. As shown in Table I only trace amounts of ester were observed. The small amount of ester and the presence of dibenzoylhydrazine are attributable to the fact that *tert*-butyl esters decompose by β-elimination in the presence of strong base.[7]



$$[\mathrm{PhC(=O)N{=}N^-}] + \mathrm{PhC(=O)O}\text{-}t\text{-}\mathrm{Bu} \rightarrow (\mathrm{H_3C})_2\mathrm{C{=}CH_3} + \mathrm{PhCO_2^-} + [\mathrm{PhC(=O)N{=}NH}]$$

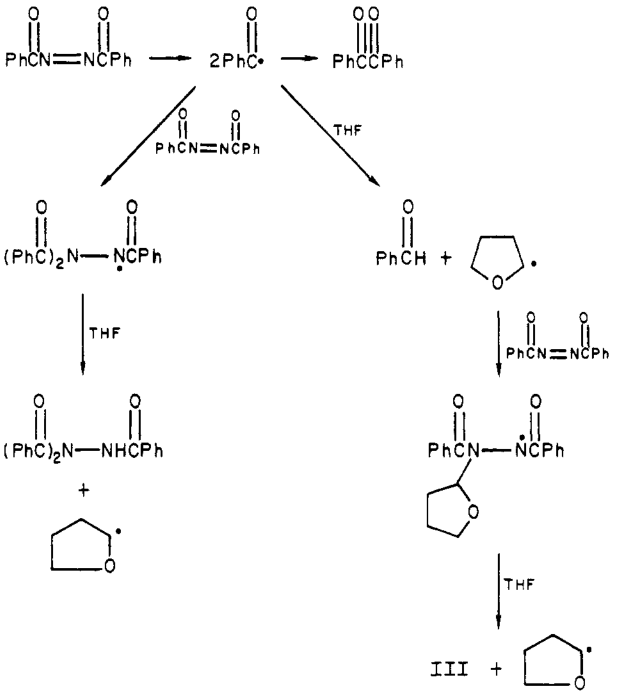
Since *tert*-butyl benzoate is not affected by treatment with potassium *tert*-butoxide under nitrogen for 1 day, the benzoyldiimide anion is likely the proton-abstracting species that generates benzoyldiimide, the precurser to dibenzoylhydrazine as shown in Scheme I. The presence of large amounts of benzoic acid is also consistent with this hypothesis. In entry 6 both the alcohol and the ester are sources of protons, so the amount of dibenzoylhydrazine would be expected to be larger than in 7 where only the ester can provide protons.

Thus, in neither protic nor aprotic solvents is there evidence for a benzoyl anion intermediate.

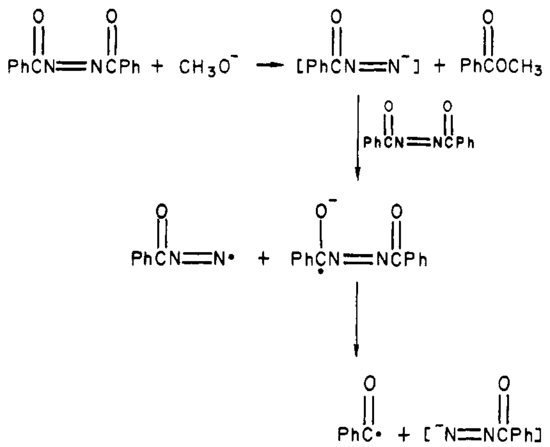
## Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 33 or a Beckman Acculab 1 spectrophotometer. The mass spectrum was obtained with an Associated Electrical Industries MS 12 recording mass spectrometer at 70 eV using an injection probe. The $^1$H NMR spectra were taken with a Varian HA-100 or EM-390 NMR spectrometer. The $^{13}$C NMR spectrum was taken with a JEOL FX 60 spectrometer. The microanalysis was performed by Atlantic Microlab Inc., Atlanta, GA. Gas chromatography was performed on a HP 5880A gas chromatograph with a 12-m SP 2100 fused quartz, 0.2-mm inner diameter column packed with methyl silicone using helium as the carrier gas.

Scheme II



Scheme III



Methanol and *tert*-butyl alcohol were distilled and dried over 3-Å molecular sieves. Tetrahydrofuran (THF) was first dried with calcium chloride and then refluxed and distilled from sodium and benzophenone before use.[8] Sodium methoxide was kept under reduced pressure in a desiccator. Potassium *tert*-butoxide was purified by sublimation.[9]

Dibenzoyldiimide (mp 118–119 °C) was prepared from dibenzoylhydrazine by literature procedures.[10]

**Reaction of Dibenzoyldiimide with Sodium Methoxide in Methanol.** To 2.38 g (10.0 mmol) of dibenzoyldiimide in 50 mL of methanol was added 0.54 g (10.0 mmol) of sodium methoxide under $N_2$. The red color immediately dissipated as heat evolved and gas formed. The next day the solvent volume was reduced, pentane was added, and the salt was separated and dried. The salt was treated with dilute acid, washed with water, and dried, giving dibenzoylhydrazine, 0.98 g (4.08 mmol), mp 239–241 °C (lit.[11] mp 241–243 °C). The IR and NMR spectra were identical with those of an authentic sample. A portion of the benzoic acid was obtained by ether extraction of the aqueous solution, and the

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[6] (a) Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1515. (b) Grootvald, H. H.; Blomberg, C.; Bickelhaupt, F. *Tetrahedron Lett.* **1971**, 1999.

[7] *tert*-Butyl carbamoates are known to undergo decarbamoylation with the liberation of isobutene in the presence of phenyllithium: Buckly, T. F., III; Rapoport, H. *J. Am. Chem. Soc.* **1981**, *103*, 6157.

[8] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergammon Press: New York, 1981.

[9] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. I, p 911.

[10] Shabarov, Yu S.; Vasil'ev, N. I.; Levina, R. Ya *Dokl. Akad. Nauk. SSSR* **1959**, *129*, 600.

[11] Landis, M. E.; Mitchell, J. C. *J. Org. Chem.* **1974**, *44*, 2288.

*J. Org. Chem.* **1983**, *48*, 2289–2291

Table I. Reaction of Dibenzoyldiimide with Alkoxides

| | | products (mmol/mmol of dibenzoyldiimide) | | | | | |
|---|---|---|---|---|---|---|---|
| entry | $OR^-$/solvent | PhCONHNHCOPh | PhCHO | PhCOOH | $PhCOOCH_3$ | other | reaction time |
| 1 | $OMe^-$/MeOH | 0.408 | 0.036 | 0.251[d] | 0.571 | | immediate |
| 2 | $OMe^-$/MeOH[a] | 0.356 | 0.024 | 0.061[d] | 0.851 | 0.138 cyclohexane | immediate |
| 3 | $OMe^-$/THF | 0 | 0.137 | 0.219[d] | 0.124 | see text | 4–7 days |
| 4 | $OMe^-$/THF[b] | 0 | 0.131 | 0.315[d] | 0.077 | see text | 6–10 days |
| 5 | $OMe^-$/THF[c] | 0 | 0.043 | 0.253[d] | 0.163 | *c* | |
| 6 | O-*t*-$Bu^-$/*t*-BuOH | 0.134 | 0.320 | 1.13 | 0 | *e* | immediate |
| 7 | O-*t*-$Bu^-$/THF | 0.038 | 0.152 | 1.09 | 0 | *e* | immediate |

[a] Cyclohexene added. [b] 0.5 equiv of $OMe^-$. [c] Three equivalents of *tert*-butyl benzoate included; 98% recovered. [d] Benzoic acid is formed from methyl benzoate and methoxide: Bunnett, J. F.; Robison, M. M.; Pennington, F. C. *J. Am. Chem. Soc.* **1950**, *72*, 2378. [e] Trace *tert*-butyl benzoate observed; isobutene also formed.

remaining benzoic acid, methyl benzoate, benzaldehyde, and other minor products were determined by NMR and GC analysis (see Table I).

**Reaction of Dibenzoyldiimide with Sodium Methoxide in the Presence of Cyclohexene.** To 2.38 g (10.0 mmol) of dibenzoyldiimide and 8.0 g (97.6 mmol) of cyclohexene in 50 mL of dried methanol under $N_2$ was added 0.54 g (10.0 mmol) of sodium methoxide. The color immediately changed to light yellow as heat and gas were evolved. After 2 h, hexane was used to precipitate dibenzoylhydrazine (0.86 g, 3.56 mmol). The solution was analyzed by GC (see Table I).

**Reaction of Dibenzoyldiimide with Sodium Methoxide in THF.** To 2.20 g (9.24 mmol) of dibenzoyldiimide in 50 mL of THF, was added 0.50 g (9.26 mmol) of sodium methoxide under $N_2$. The reaction mixture was allowed to stir 4–7 days until the red color disappeared. The mixture was filtered and the solid washed with hexane and with dilute acid, resulting in isolation of 0.07 g of benzoic acid. On cooling of the hexane filtrate, 1.36 g of solid settled from the solution. Recrystallization and TLC were used to separate tribenzoylhydrazine (1.58 mmol) and compound III (2.63 mmol); the amount of each was determined by NMR. The isolated tribenzoylhydrazine had mp 200–203 °C (lit.[12] mg 206 °C). Compound III: $^1H$ NMR ($CDCl_3$) $\delta$ 1.94 (m, 2 H), 2.18 (m, 2 H), 3.76 (m, 1 H), 4.04 (m, 1 H), 6.00 (t, 1 H), 7.38 (m, 6 H), 7.66 (m, 4 H), 8.50 (s, 1 H); IR (nujol) 3277, 1695, 1680 $cm^{-1}$; $^{13}C$($CDCl_3$) 171.98, 167.37, 134.428, 132.219, 130.660, 128.648, 128.190 127.671, 127.281, 89.001, 69.001, 28.783, 25.404; mass spectrum $(m/e)^+$ 310, 251, 240, 188, 147, 121; mp 185–187 °C. Anal. Calcd for $C_{18}H_{18}N_2O_3$; C, 69.66; H, 5.84; N, 9.03. Found: C 69.65; H, 5.85; N, 9.00. The solvent volume was reduced, and the remaining residue was analyzed by GC. Benzoic acid, benzaldehyde, methyl benzoate, and benzil (0.17 mmol) were detected (see Table I).

In a separate experiment, 2.20 g (9.24 mmol) of dibenzoyldiimide and 0.25 g (4.63 mmol) of sodium methoxide in 50 mL of THF required 6–10 days for the color to dissipate. The rate of the decomposition also appears to be dependent on stirring. From the reaction mixture tribenzoylhydrazine (0.334 mmol), compound III (4.435 mmol), and benzil (0.157 mmol) were obtained in addition to the compounds listed in Table I. Dibenzoyldiimide (0.9 g) in THF (30 mL) in the absence of base decomposes after 13 days, as noted by the disappearance of red color.

**Reaction of Dibenzoyldiimide with Sodium Methoxide in THF with Added *tert*-Butyl Benzoate.** To 2.30 g (9.66 mmol) of dibenzoyldiimide in 50 mL of THF under $N_2$ were added 0.52 g (9.63 mmol) of sodium methoxide and 5.30 g (29.8 mmol) of *tert*-butyl benzoate. After 6 days the solution was decolorized and the hydrazines were precipitated by addition of hexane, giving tribenzoylhydrazine (0.94 mmol) and compound III (2.93 mmol). GC analysis revealed the presence of benzil, methyl benzoate, benzoic acid, benzaldehyde, and recovered *tert*-butyl benzoate as recorded in Table I.

**Reaction of Dibenzoyldiimide with Potassium *tert*-Butoxide in THF.** To 2.38 g (10.0 mmol) of dibenzoyldiimide in 50 mL THF under $N_2$ was added 1.12 g (10.0 mmol) of potassium *tert*-butoxide. The solution turned light yellow as heat and gas were evolved. After 1.5 h the light yellow salt was removed by filtration, washed with hexane, and treated with dilute acid. Ether was used to separate the dibenzoylhydrazine, 0.09 g (0.37 mmol), and benzoic acid, 0.31 g.

GC analysis of the remaining solution indicated the presence of benzaldehyde, more benzoic acid, some unidentified compounds, and a trace amount of *tert*-butyl benzoate as shown in Table I.

During the reaction the gases produced were bubbled through a 5% $Br_2$ in $CCl_4$ solution which was decolorized.

**Reaction of Dibenzoyldiimide with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol.** To 1.19 g (5.00 mmol) of dibenzoyldiimide in 50 mL of dried *tert*-butyl alcohol was added 0.56 g (5.00 mmol) of potassium *tert*-butoxide. The solution became light yellow as heat evolved and gas formed. After 2 h, the salt was separated, dried, and treated with dilute acid. Ether was used to separate dibenzoylhydrazine (0.67 mmol) and benzoic acid (0.67 g). The solution volume was decreased before GC analysis, which indicated the presence of benzaldehyde, benzoic acid, and only a trace of *tert*-butyl benzoate, as shown in Table I.

**Registry No.** III, 85849-97-4; THF, 109-99-9; dibenzoyldiimide, 959-31-9; dibenzoylhydrazine, 787-84-8; sodium methoxide, 124-41-4; potassium *tert*-butoxide, 865-47-7; benzoyl anion, 78944-74-8.

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[12] Horner, L.; Naumann, W. *Liebigs Ann. Chem.* **1954**, *587*, 93.

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# Unusual Consecutive Rearrangements in the Demjanow Ring-Expansion Reaction of 2-(Aminomethyl)-$D_{2d}$-dinoradamantane and 9-(Aminomethyl)noradamantane

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Introduction of carbonyl group into $D_{2d}$-dinoradamantane (1) degenerates its $D_{2d}$ symmetry to give rise to $D_{2d}$-dinoradamantan-2-one (2) ($C_8H_{10}O$) of chiral $C_2$ symmetry, which is conspicuous in having four asymmetric carbon atoms interwoven in the molecular framework of eight carbon atoms (Scheme I).

Our continuing interests in high-symmetry chiral cage-shaped molecules prompted us to prepare the (−) enantiomer (2)[1] of this interesting compound, and we have suggested the 1*R*, 3*R*, 5*R*, 7*R* configuration to it by comparing its (−)-Cotton effect around 290 nm with that of (+)-4-isopropyltricyclo[3.3.0.0$^{3,7}$]octan-2-one (3) prepared from (−)-*endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid of known absolute configuration.[2]

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[1] Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Chem. Soc., Chem. Commun.* **1976**, 678. Nakazaki, M.; Naemura, K.; Arashiba, N. *J. Org. Chem.* **1978**, *43*, 888.

0022-3263/83/1948-2289$01.50/0