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KETENIMINES VIA THE PHOTOLYSIS OF DIPHENYLDIAZOMETHANE IN THE PRESENCE OF ISONITRILES.

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The terminal carbon of isonitriles displays divalent character in a number of reactions and should undergo α-addition to divalent carbon and univalent nitrogen species. Several workers (1) have reported results consistent with such α-additions but their reaction conditions precluded isolation of the initially formed products, ketenimines or carbodiimides. We now wish to report our results on the synthesis and isolation of ketenimines by this route.

Photolysis of diphenyldiazomethane (2) in the presence of cyclohexyl- or *t*-butylisocyanide leads to the formation of diphenyl-N-(cyclohexyl)- and diphenyl-N-(*t*-butyl) ketenimine (1 and 2, respectively) in isolated yields of 1, 25-35% and 2, 40-50%.

$$(C_6H_5)_2C{=}N_2 \xrightarrow[\text{RNC}]{h\nu} (C_6H_5)_2C{=}C{=}N{-}R$$

1, R = C_6H_{11}

2, R = $(CH_3)_3C$

The efficiency of the reaction is higher than that indicated by the isolated ketenimine yields. The amide corresponding to 2 was recovered in 20% yield during alumina chromatography of the reaction mixture (and presumably arises from hydration of 2 on the column). The yield of 1 also is a low estimate since it was recovered by rather inefficient direct crystallization of the reaction mixture. Ketenimine 1 could not be chromatographed on alumina or Florisil as it rapidly decomposes on both these adsorbents.

The spectroscopic data used for the structure elucidation of 1 and 2 appear in Table 1. Satisfactory combustion data were obtained on both ketenimines. 1, calcd. for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.01; H, 7.94; N, 5.17.

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2, calcd. for $C_{18}H_{19}N$: C, 86.67; H, 7.68; N, 5.62. Found: C, 87.13; H, 7.70; N, 5.54.

Table 1. Spectroscopic Data for the Ketenimines.

Ketenimine	IR[a]	UV[b]	NMR[c]		
			Aromatic	δ	Aliphatic
1	2020 cm^{-1}	2770 A (log ε 4.280)	7.1-7.4 m		1.1-1.2 m
2	2020 cm^{-1}	2760 A (log ε 4.250)	7.1-7.3 m		1.3 s

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[a] Characteristic band in carbon tetrachloride. [b] In cyclohexane. [c] In carbon tetrachloride, m=multiplet, s =singlet.

The major side product is tetraphenylethane (3) which is formed in 6-10% yield under our conditions. Typically, diphenyldiazomethane (0.018 moles) in 250 ml of petroleum ether (30-60°) was added dropwise over three hours to a nitrogen flushed, vigorously stirred solution of the isonitrile (0.10 moles) in 700 ml of petroleum ether. During the addition, the reaction mixture was irradiated by the light from a 450-w Hanovia mercury arc filtered through Pyrex (5). After the addition was complete, the reaction mixture was irradiated for an additional hour, the light yellow solution was concentrated *in vacuo*, and the ketenimines were isolated as described above. Nitrogen yields of 90-100% were observed in all runs.

No reaction results from mixing diphenyldiazomethane and an isonitrile together in the dark at room temperature. Even in refluxing benzene after three days, the dark reaction results only in the slow formation of a complex mixture containing ketenimine, tetraphenylethane, and benzophenone azine among others. The photoreaction definitely is not initiated by excitation of the isonitrile, since isonitriles do not absorb> 3000 A (6).

We believe the reaction proceeds by photolysis of the diphenyldiazomethane to form diphenylcarbene and α-addition of the isonitrile to the latter. However, at this time we cannot exclude a reaction between the isonitrile and an electronically excited diazo species followed by loss of nitrogen.

Further work is in progress to test the generality and elucidate the mechanism of this reaction.

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