

THE REACTION OF TETRAPIPERIDINOETHYLENE WITH CH-ACIDIC COMPOUNDS¹

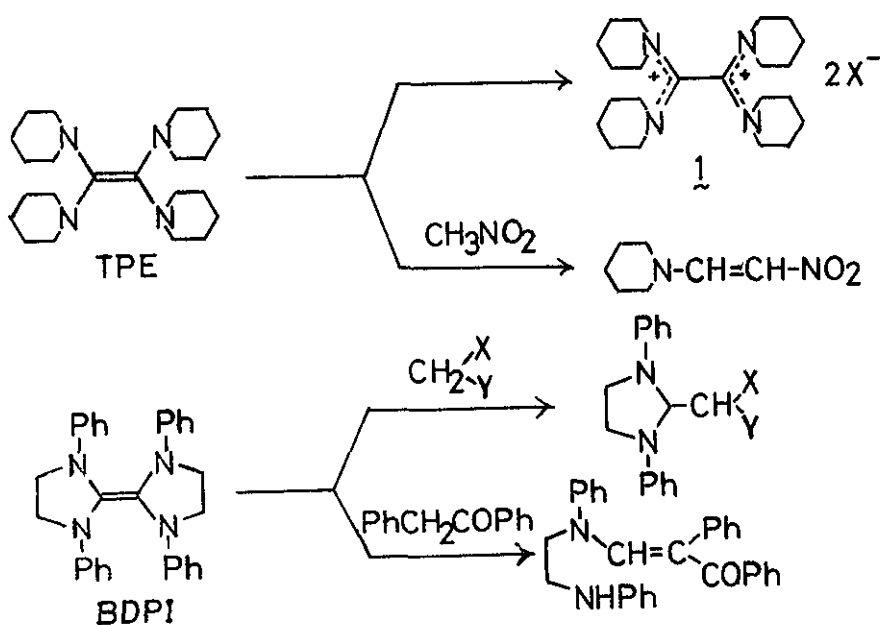
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Tetrapiperidinoethylene (TPE) reacts with CH-acidic compounds such as acetophenones, 2-acetylthiophene, 3-acetylpyridine, phenylacetonitrile, phenyl ethyl ketone and α -tetralone to afford the corresponding enamines. On the other hand, in the reaction with malononitrile TPE gives the oxamidine salt.

Tetraaminoethylenes such as tetrakis(dimethylamino)ethylene and bi(1,3-diphenylimidazolidin-2-ylidene) (BDPI) are exceptionally strong π -bases and characterized by the versatility of their chemical reactivity.² Previously, we have reported some unusual reactions of a new tetraaminoethylene, tetrapiperidinoethylene (TPE).¹ Thus, TPE is easily oxidized with halogens, and halogen-compounds such as haloforms, carbon tetrachloride as well as benzyl and benzoyl chloride, producing the corresponding oxamidine dihalides I ($X=\text{Cl}$, Br , or I). It was also reported that TPE reacted with phenylnitromethane to give the oxamidine dinitrite I ($X=\text{NO}_2$), while 1-nitro-2-piperidinoethylene was formed in the reaction with nitromethane. Wanzlick and his coworkers have reported

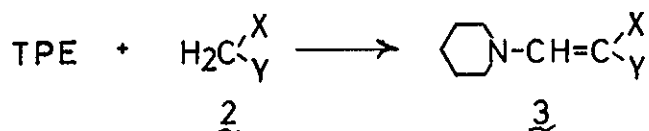


Scheme 1

that BDPI reacted with CH-acidic compounds such as nitromethane,³ ethyl acetate,⁴ acetonitrile⁴ and methyl alkyl(or aryl) sulfones⁵ to yield the corresponding 2-substituted 1,3-diphenylimidazolidines, while in the reaction with deoxybenzoin N,N'-diphenyl-N-(β -benzoylstyryl)ethylenediamine was produced as illustrated in Scheme 1. Consequently, it seemed of interest to investigate the reaction of TPE with other CH-acidic compounds than nitromethane.

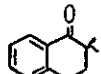
When TPE was heated with excess acetophenone (2a) under an atmosphere of nitrogen at 140-145° for 5 hr, trans-1-benzoyl-2-piperidinoethylene (3a) was obtained in a good yield. Similarly, p-methylacetophenone (2b), 2-acetylthiophene (2c), 3-acetylpyridine (2d), phenylacetonitrile (2e), phenyl ethyl ketone (2f), and α -tetralone (2g) reacted with TPE to afford the corresponding enamines, 3b-3g. The yields and physical properties of 3 are given in Table I. However, the reaction of TPE with deoxybenzoin, dibenzyl ketone, dimethyl

sulfoxide, methyl phenyl sulfone and nitroethane did not take place. The structures of all **3** were confirmed by their spectral data (Table I) as well as by their microanalyses. Also, **3a** was identical with an authentic sample, mp 92-93° (lit.⁶ mp 80-81°), prepared by Benary's method.⁶



a: X=H, Y=PhCO; b: X=H, Y=p-MeC₆H₄CO; c: X=H, Y=-CO;
d: X=H, Y=-CO; e: X=CN, Y=Ph; f: X=Me, Y=PhCO; g: XY=

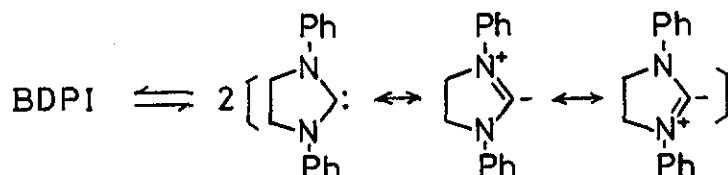
Table 1. Enamines $\mathbf{3}$ 

X	Y	Yield %	Mp. °C	ir, cm ⁻¹		nmr, δ ppm ^a	
				νC=O	νC=C	H _a	H _b
<u>3a</u>	H _b PhCO	83	92-93	1635	1540	7.67(d, 12Hz)	5.83(d, 12Hz)
<u>3b</u>	H _b p-MeC ₆ H ₄ CO	70	89-90	1630	1540	7.72(d, 12Hz)	5.88(d, 12Hz)
<u>3c</u>	H _b  CO	58	134.5-135	1625	1540	7.80(d, 13Hz)	5.77(d, 13Hz)
<u>3d</u>	H _b  CO	10	oil ^b	1640	1540	8.03(d, 13Hz)	6.10(d, 13Hz) ^c
<u>3e</u>	CN Ph	83	102-104	1620		6.70(s)	
<u>3f</u>	Me PhCO	84	91-92	1620	1540	6.92(s)	
<u>3g</u>		77	83-84	1630	1540	7.65(s) ^d	

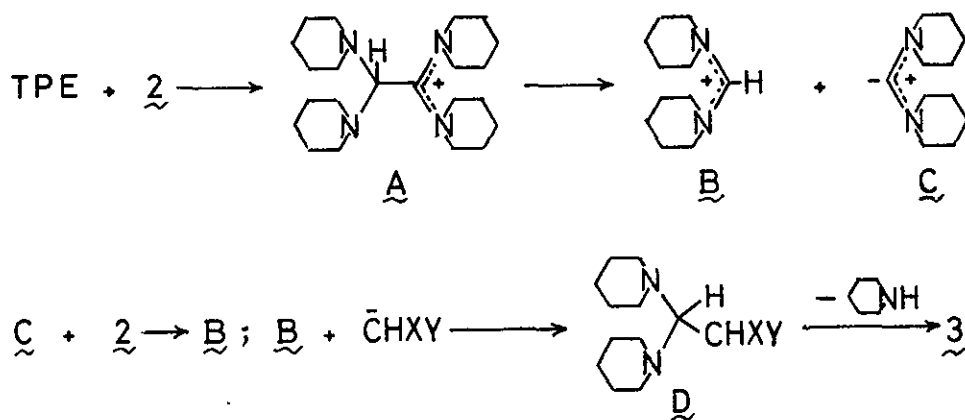
^aInternal standard: TMS. Unless otherwise provided, the nmr spectra were measured in CDCl₃. ^bPicrate: mp 193° dec. ^cMeasured in pyridine-d₅.

^a Measured in CCl₄.

Wanzlick and Ahrens⁴ have suggested that BDPI dissociates readily and reversibly into bivalent carbon intermediates. However, Lema1 et al.⁷ and Winberg and his coworkers⁸ have presented evidence that the proposed equilibrium

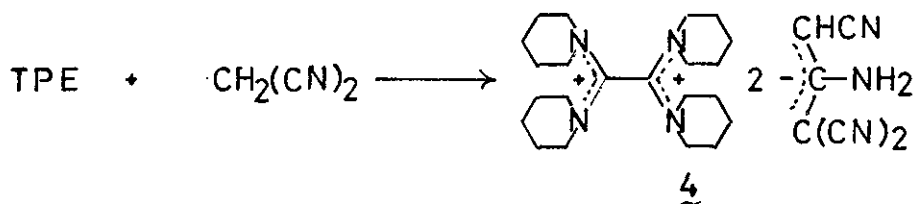


does not occur with BDPI and its derivatives. Accordingly, TPE does not appear to be in equilibrium with the corresponding bivalent carbon intermediates. Although further study is under progress, we tentatively propose a potential pathway for the formation of 3 in the reaction of TPE with 2 as depicted in Scheme 2. Every known reactions of the powerful π -bases can be interpreted in terms of electrophilic attack upon the π -electron system. Therefore, 2 would attack on the π -system of TPE to form A, followed by conversion into reactive species B and C. The species B would react with carbanion intermediate generated from 2 to yield D, and then concurrent elimination of pyrrolidine from D would give the final product 3.



Scheme 2

The reaction of TPE with excess malononitrile (5mol to TPE) in THF under reflux for 1 hr afforded the oxamidinium salt 4, mp 149° dec., as reddish brown prisms in 64% yield. The structure of 4 was confirmed by the following evidence. The ir spectrum of 4 exhibited remarkably strong absorption bands which can be ascribed to the $[>N=C=N<]^+$ at 1620 and 1640 cm^{-1} . The ion peak which



corresponded to the molecular ion of TPE (m/e 360) appeared as the ion peak of the highest mass number in the mass spectrum of 4. When 4 was treated with benzoyl chloride in refluxing acetonitrile for 1 hr, oxamidinium dichloride 5 ($X=\text{Cl}$),¹ mp 240-241° dec., and malononitrile dimer, mp 170-171° (lit.⁹ mp 172-173°), were obtained in almost quantitative yields respectively. In the treatment with silver nitrate in acetonitrile at room temperature for 20 hr, 4 was transformed into oxamidinium dinitrate 6 ($X=\text{NO}_3$),¹ mp 222-223° dec., in 95% yield. In addition, TPE reacted with malononitrile dimer in refluxing THF for 1 hr to give 4 in 81% yield.

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