*2,2'-Dimethoxybenzene.* The 2,2'-dimethoxyazobenzene[18] (2.6 g.) in ether (50 ml.) and benzene (20 ml.) was treated at 0° with lithium aluminum hydride (0.6 g.) in ether (20 ml.). The color of the solution changed from red through yellow to apple green. After stirring at room temperature for 30 min., aqueous ammonium chloride was added at 0°. The organic layer was separated, washed with water, dried and the solvent removed. The residue was chromatographed on alumina from benzene giving a yellow fore-band, which afforded yellow crystals (0.32 g.) of the azo compound, m.p. 152–153°,[20] and a main band of unchanged azoxy compound.

*2,2'-Diiodoazobenzene.* The 2,2'-diiodoazoxybenzene[15b] was similarly reduced to the azo derivative, orange needles, m.p. 194°[21]

*2,4,6,2',4',6'-Hexabromoazobenzene.* This was obtained by a Wallach rearrangement of hexabromoazoybenzene[21] as dark purple crystals, m.p. 213°.[22]

*Absorption spectra.* The spectra were determined in absolute ethanol as solvent with an Unicam S.P. 5000 spectrophotometer, using 1-cm. quartz cells with the concentration of compound chosen to give optical densities between 0.4 and 0.8.

*Acknowledgment.* The authors are grateful to Professor J. Lichtenberg (Mulhouse) for samples of 4-fluoro- and 4,4'-difluoroazobenzenes, to Dr. R. W. Kiersted (New York) for a sample of 4-methylazobenzene and to Mrs. I. Boston, Spectroscopic Laboratory, Department of Chemistry, Imperial College of Science and Technology, London, for determining many of the spectra.

LONDON, W3, ENGLAND
MAYAGUEZ, P. R.

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[20] K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.*, 4003 (1954), give m.p. 153°.

[21] P. H. Gore and G. K. Hughes, unpublished results.

[22] J. T. Edwards, *J. Chem. Soc.*, 222 (1956), gives m.p. 212–3°.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF PUERTO RICO AT MAYAGUEZ AND BRUNEL COLLEGE OF TECHNOLOGY]

# Absorption Spectra of Aromatic Azo and Related Compounds. IV. Benzanils[1]

OWEN H. WHEELER[2a] AND PETER H. GORE[2b]

*Received December 14, 1960*

The ultraviolet absorption of a number of substituted benzanils has been measured in anhydrous methanol. Some previous measurements are incorrect, because of the ready hydrolysis of the compounds in aqueous solvents. The electronic and steric effects of various substituents are discussed and compared with previous data on substituted azobenzenes.

Although the ultraviolet spectrum of benzanil itself has been reported a number of times[3] the only detailed study of substituted benzanils is that of Smets and Delvaux[4] who measured the spectra of some twenty benzanils in neutral, acid, and alkaline solution. However, their data showed no systematic relationships of wavelength and intensity. Thus, *N*-4-methoxy- and $\alpha$-4-methoxybenzanil[5] were reported to have $\lambda_{max}$ 276 ($\epsilon$ 19,500) and 230 m$\mu$ ($\epsilon$ 26,000), respectively, and *N*-3-nitro- and $\alpha$-3-nitrobenzanil to have $\lambda_{max}$ 264 ($\epsilon$ 39,200) and 277 m$\mu$ ($\epsilon$ 17,000), respectively (all in neutral solution). In previous studies of the structurally related azobenzenes,[1] phenylnitrones,[6a] and azoxybenzenes[6b] differences in the spectra were observed to be systematic. Because of the apparent anomaly of the benzanils it was decided to prepare a new series of these compounds and to investigate their spectra.

Preliminary measurements gave variable values of both wavelength intensities with different samples of 95% ethanol, and the spectra changed further on standing. In 100% methanol, however, the spectra were completely reproducible and did not vary with time (Table I).[7] The reason for the variable results previously found using 95% ethanol can not be due to a photochemical reaction,[8a] as irradiation had little effect on the spectra of benzanil in methanol (Table I). However, in the presence of water (95% methanol) a slow, presumably hydrolytic change took place, and this was very greatly accelerated by traces of mineral acid (Table I).[8b] The final spectrum was that expected for a mixture of the hydrolysis products of benzanil; benzaldehyde $\lambda_{max}$ 242 ($\epsilon$ 14,000), 248 m$\mu$ ($\epsilon$ 12,500)[9] and aniline $\lambda_{max}$ 230 m$\mu$ ($\epsilon$ 8,000).[10] The data of Smets

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[1] Part III, *J. Org. Chem.*, **26**, 3295 (1961).

[2] (a) University of Puerto at Mayaguez, P. R. (b) Brunel College of Technology, London, W.3, England.

[3] (a) P. Ramant-Lucas and J. Hoch, *Bull. soc., chim. France*, **3**, 918 (1936); (b) L. N. Ferguson and G. E. K. Branch, *J. Am. Chem. Soc.*, **66**, 1467 (1944); (c) P. Grammaticakis, *Bull. soc. chim. France*, 965 (1951); (d) F. Bohlmann, *Ber.*, **84**, 860 (1951); and earlier references cited therein.

[4] G. Smets and A. Delvaux, *Bull. soc. chim. Belges*, **56**, 106 (1947).

[5] *N*-denoted substitution in the ring attached to the nitrogen atom and $\alpha$- in the other ring.

[6] (a) O. H. Wheeler and P. H. Gore, *J. Am. Chem. Soc.*, **78**, 3363 (1956); (b) P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956).

[7] Our own values agree best with the determination of Bohlmann, ref. 3d.

[8] (a) *Cf.* M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957); (b) M. J. Kamlet, personal communication.

[9] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

[10] E. A. Braude, *Ann. Rep. Chem. Soc. (London)*, **42**, 105 (1945).

TABLE I

SPECTRA OF BENZANIL IN VARIOUS SOLVENTS[a]

| | 100% Methanol |
|---|---|
| Initially | 260 (16,000), 305 (8,600)[b] |
| After 20 hr. | 260 (16,000), 305 (8,550)[b] |
| After 48 hr. | 260 (16,000), 305 (8,550)[b] |
| After 9 days | 260 (15,500), 305 (8,000)[b] |
| Sunlight 1 hr.[c] | 260 (15,500), 305 (8,800)[b] |
| U.V. lamp 10 min.[d] | 260 (15,450), 305 (8,800)[b] |
| | 95% Methanol |
| Initially | 260 (15,500), at 300 (9,050) |
| After 2 hr. | 260 (15,500), at 300 (9,000) |
| After 24 hr. | At 260 (12,100), at 300 (6,550)<br>max. 252 (13,600) |
| After 8 days | At 260 (5,300), at 300 (1,400)<br>max. 242 (17,700) |
| | $1.5 \times 10^{-3}$M HCl 95% Methanol |
| After 5 min. | At 260 (3,100), max. 247 (9,200) |
| After 10 min. | At 260 (2,700), max. 245 (10,400) |
| After 30 min. | At 260 (2,600), max. 245 (14,000) |
| After 1 hr. | At 260 (2,600), max. 245 (14,000) |

[a] Wave lengths ($\lambda$) in m$\mu$; molar extinction coefficients ($\epsilon$) in parenthesis. [b] Inflection. [c] Irradiation in Pyrex vessel with direct sunlight. [d] Irradiation in Pyrex vessel with a long wave-length ultraviolet lamp.

TABLE II

| Substituent | Bands[a] | | |
|---|---|---|---|
| | $E_1$ | $E_2$ | K |
| | E.a.[b] | 260 (16,000) | 305 (8,600)[c] |
| α-*p*-Nitro | E.a. | 290 (13,500) | 335 (10,400)[c] |
| α-*p*-Hydroxy | 226 (16,800) | 295 (17,500) | 314 (18,800) |
| α-*p*-Methoxy | 223 (17,400) | 286 (18,000) | 312 (17,500) |
| *N*-*p*-Nitro | E.a. | 264 (17,500) | 335 (16,400) |
| *N*-*p*-Hydroxy | E.a. | 263 (18,600) | 332 (18,900) |
| *N*-*p*-Chloro | 222 (13,400)[c] | 262 (16,100) | 312 (9,400) |
| *N*-*p*-Bromo | E.a. | 263 (17,450) | 312 (10,700) |
| *N*-*p*-Iodo | 227 (14,500)[c] | 262 (20,200) | 316 (11,600) |
| *N*-*m*-Nitro | E.a. | 262 (15,900) | 315 (6,900)[c] |
| *N*-*m*-Chloro | E.a. | 260 (17,200) | 312 (7,400) |
| *N*-*o*-Nitro | E.a. | 264 (15,700) | 323 (8,900) |
| *N*-*o*-Hydroxy | E.a. | 263 (14,500) | 345 (8,300) |
| *N*-*o*-Chloro | E.a. | 260 (18,200) | 312 (6,600)[c] |
| *N*-*o*-Bromo | E.a. | 260 (17,100) | 315 (5,050)[c] |
| *N*-*o*-Iodo | E.a. | 253 (18,100) | 315 (4,300)[c] |
| *p,p'*-Dinitro | 227 (18,100) | 279 (15,100) | 340 (10,200) |
| *p,p'*-Dihydroxy | 221 (15,800) | 282 (15,300) | 330 (17,500) |
| *p,p'*-Dichloro | E.a. | 268 (18,600) | 316 (12,100) |
| *p,p'*-Dibromo | E.a. | 272 (22,800) | 320 (14,200) |
| *p,p'*-Diiodo | 228 (16,000) | 283 (19,900) | 322 (16,100) |

[a] Spectra determined in anhydrous methanol. Wavelengths ($\lambda$) in m$\mu$; molar absorption intensities ($\epsilon$) in parenthesis. [b] E.a. denotes end absorption below 220 m$\mu$. [c] Inflection or shoulder.

and Delvaux, determined in aqueous media and in the presence of acid, must therefore be considered unreliable.

The spectra of the substituted benzanils were accordingly determined in anhydrous methanol (Table II). The compounds showed two distinct regions of absorption [designated $E_2$-(electronic) and K-(conjugation) bands; see below] as well as high end-absorption below 220 m$\mu$, which could be resolved as a maximum at 220–230 m$\mu$ ($E_1$-band) in a few cases. The band at *ca.* 260–290 m$\mu$ was generally more intense than that at *ca.* 310 m$\mu$ and this later band was encountered as a shoulder or inflection in many cases. Both these bands vary in wave length and intensity on substitution. The absorption in the region of 220 m$\mu$ is considered by analogy[6,8] to arise from electronic transitions in the benzene ring, and is related to the E-band of benzene (*ca.* 205 m$\mu$, $\epsilon$ 6,300[11]) displaced by substitution to higher wavelengths.

The higher intensity ($\epsilon$ 16,000–20,000) band in the region 260–290 m$\mu$ can be attributed to an $E_2$-band, arising from electronic transitions in part of the molecule, involving one benzene ring and the central (—CH=N—) linkage.[12] *N*-Methylbenzalimine ($C_6H_5\ CH = N\ CH_3$, $\lambda_{max}$ 247 m$\mu$, $\epsilon$ 17,200[3b]) and *N*-ethylbenzalimine ($C_6H_5CH = N\ C_2H_5$; $\lambda_{max}$ 245 m$\mu$, $\epsilon$ 15,900[3b]), lacking the substituent effect of one phenyl ring have maxima at slightly shorter wave lengths, but of the same intensity as the $E_2$-band in benzanil, and do not exhibit maxima at higher wave lengths. Similarly *N*-phenyldiethylketimine ($C_6H_5\ N{=}C\ (C_6H_5)_2$; $\lambda_{max}$ 250, $\epsilon$ 12,000; 300 m$\mu$ $\epsilon$ 2,000[13]) has a high intensity maximum very similar to that in benzanil. An $E_2$-band was not found, however, in the spectra of azobenzenes. The second high intensity band at longer wave length (*ca.* 310 m$\mu$) is considered to be due to an electronic transition throughout the whole molecule involving both aromatic rings and the central —CH=N— linkage, and is accordingly a conjugation (K-band). A band of very similar wave length and intensity was also found in azobenzenes,[1] azoxybenzenes[6b] and phenylnitrones.[6a]

The effect of substituents on the position and intensity of the $E_2$- and K-bands will be considered in turn. Substituents in a *para* position in the *N*-ring produced only small wavelength shifts of the $E_2$-band ($NO_2$ + 4, HO + 3, Cl + 2, Br + 3, and I + 2 m$\mu$). However, *para*-substituents in the α-ring produced much larger displacement of this band ($NO_2$ + 30, HO + 35, MeO + 26 m$\mu$). This would be expected on the basis of the assignment, as the formation of electronically excited polar forms involving half the molecule will be aided by the unshared pair of electrons on the nitrogen atom, which, in the case of the α-substituted compounds, will be at the end of the conjugate system. The sequence $CH_3O < NO_2 < HO$ of displacements for the *p*-α-derivatives is the one expected from the relative magnitudes of their mesomeric effects.[14] The bathochromic spectral shifts for *N*-*m*- and *N*-*o*-compounds

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[11] K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

[12] A similar $E_2$-band is found in some azoxybenzenes, ref. 6b.

[13] V. de Gaouck and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1457 (1939).

[14] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., Chapt. II.

like those for the *N*-*p*-compounds were too small to demonstrate the influence of substituents. An exception occurred with *N*-*o*-iodobenzanil, which showed a negative displacement (hypsochromic shift) of −7 mμ with respect to benzanil itself, or −9 mμ with respect to the corresponding *para* isomer. This displacement is most probably due to the large steric size of the iodine atom which results in a distortion of the molecule from the planar configuration necessary for full resonance interaction with the central grouping. The effect of two *para* substituents ($NO_2$ 19, HO 22, Cl 8, Br 12, I 23 mμ) was greater than that of a single substituent in the *N*-*p*-position but the shifts for the *p,p'*-dinitro and *p,p'*-dihydroxy compounds were still less than those for the α-mono substituted derivatives (+30 and +35 mμ, respectively). The order of the displacements of the dihalogen compounds of $Cl < Br < I$ is the order commonly encountered in the spectra of aromatic compounds,[15] and has been noted in azobenzenes[1] and azoxybenzenes,[6b] being probably due to the order of mesomeric release of electronic charge.[15]

The K-band of the benzanils showed very considerable differences in both wave length and intensity on substitution. In the case of the α-*p*-compounds the shifts in wave length were small for a hydroxy (+9 mμ) or methoxy (+7 mμ) substituent, but were quite large for a nitro group (+30 mμ), reflecting the increased conjugation possible with this group. The *N*-*p*-hydroxy and *N*-*p*-nitrobenzanils also showed large displacements (of +27 and +30 mμ, respectively) and the halogen atoms exhibited increases in both wavelength (Cl, Br + 7, I + 11 mμ) and intensity with the same general order ($Cl \sim Br < I$) as observed in the $E_2$-band. The differences in the *N*-*ortho* compounds, however, were less regular. The *N*-*o*-nitro derivative has a displacement (of +18 mμ) which is consistent with the smaller mesomeric effect of the nitro groups in an *ortho* position. However the large displacement (+40 mμ) of the *o*-hydroxy compound is most probably due to hydrogen-bonding of the hydrogen atom of the hydroxyl group with the unshared electron-pair of the nitrogen atom, and hydrogen-bonding has also been detected in the near infrared spectra of the α-*o*-hydroxy derivative.[16] The *N*-*o*-halogen compounds showed displacements in wavelength from chloro to bromo (Cl + 7, Br + 10 mμ), but no further displacement for the iodo analogue and the intensity of absorption decreases in the order $Cl > Br > I$, the reverse of the behavior of the *para* isomers. These differences are consistent with the increasing steric effect of these halogen atoms (*cf.* the $E_2$-band of *N*-*o*-iodobenzanil, and quantitative discussion below). The wave-length displacements of the *p,p'*-disubstituted benzanils followed the same order as that of the corresponding *N*-*p*-mono substituted compounds ($NO_2$ + 35, HO + 25, Cl + 11, Br + 15, I + 17 mμ) and their values were only slightly greater showing that a second substituent does not lead to any further large increase in conjugation in the molecule. A similar effect was noted in azobenzenes and azoxybenzenes,[6b] although in these cases a second substituent has a proportionally larger effect.

The angle of deformation (θ) from coplanarity produced by an ortho-substituent can be calculated from the relation $\cos^2\theta = \epsilon o/\epsilon p$,[9] where $\epsilon o$ and $\epsilon p$ are the intensities of absorption of the *ortho* and *para* isomers, respectively; the assumption being made that the intensity of the *ortho* isomer in the absence of steric effects could be the same as that of the para isomer. The angles so calculated for the *N*-*o*-halogenobenzanils were 33° for chloro, 46° for bromo, and 53° for iodo. The sterically analogous *o*-dichloroazobenzene[6b] gave 35° while the bulkier azoxybenzenes[1] had higher values (Cl 51°, Br 59°, and I 59°).

It is interesting to compare the spectra of the benzanils with the spectra of the closely related azobenzenes, the structural difference being in the central linkage (—CH=N— versa —N=N—). The benzanils showed no absorption maximum above 350 mμ, whereas azobenzenes[1] have a weak intensity maximum (the R-band) near 440 mμ. In addition the $E_2$-band shown by all benzanils was not found in the spectra of azobenzenes. The

TABLE III

| Substituent | M.P. | Lit. M.P. |
|---|---|---|
| — | 50–51° | 52° |
| α-*p*-Nitro | 92° | 93°[b] |
| α-*p*-Hydroxy | 200° | 195°[a] |
| α-*p*-Methoxy | 64° | 64°[c] |
| *N*-*p*-Nitro | 118° | 117–119°[c] |
| *N*-*p*-Hydroxy | 190° | 190–191°[a] |
| *N*-*p*-Chloro | 64° | 62–63°[b] |
| *N*-*p*-Bromo | 68° | 66°[c] |
| *N*-*p*-Iodo | 86° | 82–84°[c] |
| *N*-*m*-Nitro | 73° | 74°[a] |
| *N*-*m*-Chloro | 35° | Oil[c] |
| *N*-*o*-Nitro | 72°[d] | — |
| *N*-*o*-Hydroxy | 84° | 89°[e] |
| *N*-*o*-Chloro | 56–57° | Oil[c] |
| *N*-*o*-Bromo | 45° | Oil[c] |
| *N*-*o*-Iodo | 56–57°[f] | — |
| *p,p'*-Dinitro | 205° | 202–203°[g] |
| *p,p'*-Dihydroxy | 215° | 202°[a] |
| *p,p'*-Dichloro | 115° | 110–111°[c] |
| *p,p''*-Dibromo | 145°[h] | — |
| *p,p'*-Diiodo | 185°[i] | — |

[a] Reference 4. [b] O. Fisher, *Ber.*, **14**, 2525 (1881). [c] A. Roe and J. A. Montgomery, *J. Am. Chem. Soc.*, **75**, 910 (1953). [d] *Anal.* Calcd. for $C_{13}H_{10}N_2O_2$: C, 69.0; H, 4.45. Found: C, 68.6; H, 4.5. [e] Z. Holzbecker, *Chem. Listy*, **47**, 1023 (1953). [f] *Anal.* Calcd. for $C_{13}H_{10}NI$: C, 50.8; H, 3.3. Found: C, 50.6; H, 3.4. [g] K. A. Jensen and N. H. Bang, *Ann.*, **548**, 106 (1941). [h] *Anal.* Calcd. for $C_{13}H_9NBr_2$: C, 46.0; H, 2.7. Found: C, 46.8; H, 2.9. [i] *Anal.* Calcd. for $C_{13}H_9NI_2$: C, 36.0; H, 2.1. Found: C, 36.3, H, 2.0.

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(15) W. H. Schubert, J. M. Craven, and H. Steadly, *J. Am. Chem. Soc.*, **81**, 2695 (1959).

(16) H. Hayer, *Z. Electrochemie*, **47**, 451 (1941).

K-band of the benzanils was generally at a shorter wavelength and of lower intensity than that of the azobenzenes. The reason no doubt lies in the smaller resonance energy of the —C=N— group and the heats of combustion of benzanil and azobenzene[17] show that the former has a considerably lower resonance energy.

A further difference between benzanils and azobenzenes is the formation of stable *cis*-isomers of the latter. Attempts to isolate *cis*-benzanils have not been successful.[18] Irradiation of solutions of benzanil produced no change in magnetic susceptibility[19] and as found in the present work (Table I) no appreciable change in the absorption spectra.

## EXPERIMENTAL

*Compounds.* The benzanils were prepared by condensing centimolar quantities of the appropriate benzaldehyde and aniline, by dissolving them in the minimum volume of absolute ethanol, warming slightly on a steam bath and allowing to stand at room-temperature overnight. They were recrystallized from ethanol, or from benzene-hexane, in the case of the more soluble compounds. Their melting points, together with literature values, are given in Table III. The anilines used were Eastman-Kodak white label samples. Many of the substituted benzaldehydes were freshly prepared by the Étard oxidation of substituted toluenes.[20] The solid benzanils are stable and samples have been stored in tightly stoppered tubes for over 2 years without any change in melting point or spectrum.

*Absorption spectra.* The absorption spectra were determined in Merck reagent grade methanol, dried with magnesium methoxide, employing a Beckman D. U. spectrometer mounted in an air-conditioned room with relative humidity of 40–45% and temperature 22 ± 1°. The cells used were conventional silica cells with loose-fitting caps and no special precautions were taken to exclude atmospheric moisture. The spectra were determined immediately on making up the solution and again after 1 hr., when in no case were any differences noted.

*Acknowledgment.* The authors are greatful to Dr. M. J. Kamlet of the U. S. Naval Ordnance Laboratory, Silver Spring, Md., for communicating his own findings on the hydrolysis of benzanils in aqueous solution.

MAYAGUEZ, PUERTO RICO
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[17] G. E. Coats and L. E. Sutton, *J. Chem. Soc.*, 1187 (1948).

[18] F. Kröhnke, *Ber.*, **71**, 2593 (1938); J. Van Alpen, *Rec. trav. chim.*, **61**, 875 (1942). The two crystalline forms of α-*o*-hydroxybenzanil have been shown to be allotropes. V. de Gaouch and R. J. W. Le Fèvre, *J. Chem. Soc.*, 741 (1938).

[19] S. S. Bhatnajer, P. L. Kapur and M. S. Hashmi, *J. Ind. Chem. Soc.*, **15**, 573 (1938).

[20] O. H. Wheeler, *Can. J. Chem.*, **36**, 667 (1958).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRANDEIS UNIVERSITY]

# Some Reactions of Tetraarylethylenimines[1]

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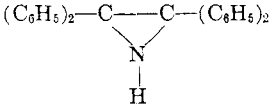
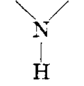
*Received December 30, 1960*

Reactions of 2,2,3,3-tetraphenylethylenimine I and 2,2-diphenyl-3,3-di-*p*-tolylethylenimine II have been studied. Compound I was converted (a) to tetraphenylethane by catalytic hydrogenation, (b) to benzophenone by periodic acid, and (c) to tetraphenylethylene, tetraphenylethylene oxide, and benzophenone by treatment with hydrochloric acid. Compound II was converted to *p,p′*-dimethylbenzophene and to a hydrocarbon by treatment with hydrochloric acid. The course of the reactions is discussed.

Study of the decomposition of azobisdiphenylmethane in the presence of thiophenol,[2] and then in the presence of benzophenone azine led to the conclusion that diphenylmethyl radical adds rapidly to benzophenone azine, leading to 2,2,3,3-tetraphenylethyleneimine

(I) 

Subsequent experiments[3] indicated that I was also formed in decomposition of the azo compound in the presence of benzophenone hydrazone, ammonia being formed in this reaction. Also, diphenylmethyl radical from decomposition of the azo compound reacted rapidly with the azine from *p,p*-dimethylbenzophenone, leading to 2,2-diphenyl-3,3-di-*p*-tolylethylenimine[3]

(II) 

Although the oxide[4] and sulfide[5] of tetraphenylethylene have been known for some time, the

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[1] We are pleased to acknowledge generous support of this work by the National Science Foundation, Grant G.4244, and Fulbright and Guggenheim Fellowships to S.G.C.

[2] C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957).

[3] C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **82**, 4688 (1960).

[4] A. Behr, *Ber.*, **5**, 277 (1872).