or C=O; nmr ($CCl_4$) δ 6.7-7.6 (m, 19, aromatic H) and 5.87 ppm (s, 1, aliphatic H).

*Anal.* Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53; mol wt, 364. Found: C, 85.85; H, 5.51; mol wt (benzene), 377.

**Registry No.**—**1a**, 30316-41-7; **1b**, 30316-42-8; **7**, 4970-23-4; **9**, 30309-97-8; **10**, 30309-98-9; **16**, 30309-99-0; **18**, 30310-00-0.

**Acknowledgment.**—The author is indebted to Mr. H. J. Tarski for excellent general technical assistance, to Mr. T. Hines for meticulous performance of nmr experiments, and to Dr. R. Pettit for comments on the manuscript. Analytical assistance was generously provided by several other colleagues in the analytical section of this laboratory.

---

# Chemical Syntheses with Bergmann–Schlenk Adducts. VII.[1] Benzil Dianil

E. J. MacPherson and James G. Smith*

*Department of Chemistry, University of Waterloo, Waterloo, Ontario*

*Received December 23, 1970*

The reduction of benzil dianil (1) with sodium in tetrahydrofuran produced the *N,N'*-disodio-*N,N'*-diphenyl-α,α'-stilbenediamine (2). Chemical reactions of this compound with ethyl chloroformate, diethyl oxalate, methyl iodide, allyl bromide, 1,3-dihalopropanes, and water were examined. A cis configuration is suggested for 2.

In continuing our study[1] of the synthetic utility of Bergmann–Schlenk adducts of conjugated bisimines, a compound in which the azomethine groups were united through the carbon atoms rather than the nitrogens was selected. The natural choice was benzil dianil (1) but the preparation of this venerable compound offered some difficulties. Julian's procedure,[2] utilizing benzil as starting material, proved adequate but required careful control of the reaction conditions. The seemingly more convenient procedure[3] for the preparation of 1 using *N*-benzylideneaniline as starting material was, in our hands, only sporadically successful. However, as Becker has recently shown,[4] this reaction depends on the initial formation of α,α'-dianilinostilbene and its subsequent oxidation to benzil dianil (1). By slightly modifying Becker's procedure, a convenient synthesis of 1 was obtained.

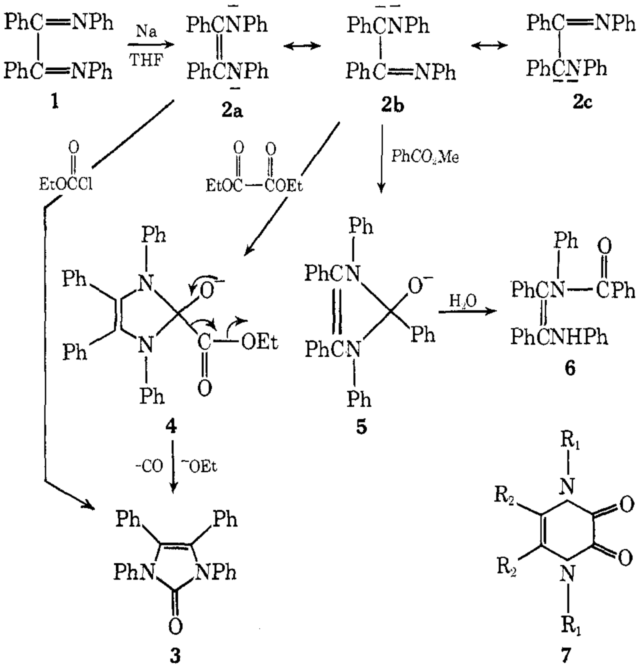
With tetrahydrofuran as solvent and sodium metal as reducing agent, benzil dianil (1) was rapidly converted to an adduct 2, containing 2 g-atoms of sodium per mole of dianil. The initially formed radical anion provided an opaque red-brown solution which changed to a transparent red as the formation of the dianion 2 neared completion.

As observed earlier,[1] the reaction of only one of the two azomethine groups would appear to reflect stabilization of the dianion by the remaining azomethine group participating in the delocalization of the added electrons. Resonance structures involving an azaallylic[5] anion (2a–c) can be formulated.

**Acylation.**—Several reactions were used to characterize the dianion 2 and those employing esters are summarized in Scheme I. With either 1 or 2 mol of ethyl chloroformate, an excellent yield of the known compound 1,3,4,5-tetraphenyl-1,3-imidazolin-2-one (3) was isolated. Surprisingly, this same product was isolated when diethyl oxalate was used. Since the expected amount of carbon monoxide was evolved, the initially formed product 4 readily decarbonylates to provide 3. The unstable intermediate has been formulated as 4 rather than the alternative 7 ($R_1 = R_2 = Ph$, which might conceivably be formed and suffer a base-catalyzed benzil–benzilic acid rearrangement to 4) since the known compounds[6,7] 7 ($R_1 = Ph$, $R_2 = H$ and $R_1 = Me$, $R_2 = H$) appear quite stable.

Scheme I

Acylation of the Benzil Dianil Disodium Adduct



Diethyl dimethylmalonate failed to react with the dianion 2.

With methyl benzoate the dianion 2 provided *N*-benzoyl-α,α'-dianilinostilbene (6) identical with an authentic sample.[8,9] Formation of only a monobenzoyl derivative is reminiscent of the behavior of the diastereomeric *N,N'*-disodio-*N,N'*-1,2-tetraphenylethylenediamines.[9] The explanation offered there applies equally

---

(1) E. J. MacPherson and J. G. Smith, *Can. J. Chem.*, **48**, 1904, 1915 (1970), papers V and VI of this series.

(2) P. L. Julian, E. W. Meyer, A. Magnani, and W. Cole, *J. Amer. Chem. Soc.*, **67**, 1203 (1945).

(3) J. S. Walia, J. Singh, M. S. Chattha, and M. Satyanarayana, *Tetrahedron Lett.*, 195 (1969).

(4) H.-D. Becker, *J. Org. Chem.*, **35**, 2099 (1970).

(5) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 187.

(6) J. Honzl, *Collect. Czech. Chem. Commun.*, **25**, 2651 (1960).

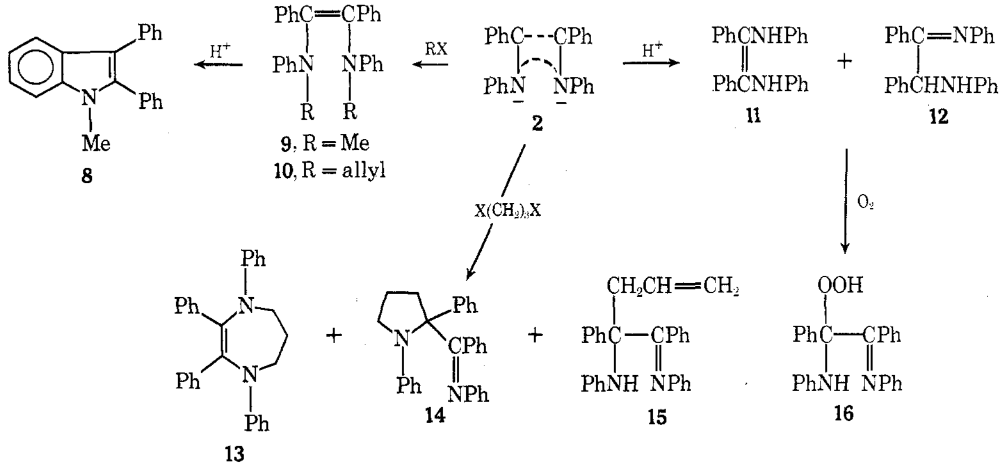
(7) G. W. H. Cheeseman and E. S. G. Torzs, *J. Chem. Soc.*, 6681 (1965).

(8) A. E. Everest and H. McCombie, *ibid.*, **99**, 1752 (1911).

(9) J. G. Smith, *Can. J. Chem.*, **44**, 59 (1966).

Scheme II

Alkylation and Protonation of the Benzil Dianil–Disodium Adduct



well here; after the introduction of one benzoyl group, the remaining anion "protects" itself by reacting with the carbonyl group forming **5**.

**Alkylation.**—In the acylation reactions, only substitution on the nitrogens was observed. Such a behavior is not unexpected for esters, a similar pattern having been noted for the dianion generated from benzophenone anil.[10] In an attempt to encourage substitution at the potential carbanionic center of **2**, several alkylation reactions were studied.

Both methyl iodide and allyl bromide effected alkylation on the nitrogen forming *N*,*N*′-dimethyl-$\alpha,\alpha'$-dianilinostilbene (**9**) and the analogous *N*,*N*′-diallyl compound **10**. Both **9** and **10** possessed uv spectra reflecting their similar conjugated systems and neither showed absorption in the ir spectrum due to a C═N group. Equivalent allyl and methyl groups were indicated by the nmr spectrum although in the case of **9** the methyls became nonequivalent in $CDCl_3$. The inability to form a dinitrophenylhydrazone from **9** also supported the absence of a C═N group. A final structure proof for **9** was obtained by converting it in refluxing[11] methanolic HCl to 1-methyl-2,3-diphenylindole (**8**) and *N*-methylaniline.

Both methylene iodide and 1,2-dibromoethane were examined in an attempt to prepare imidazoline and tetrahydropyrazine derivatives. No definite products could be isolated from the reaction mixtures (Scheme II).

A more successful reaction occurred with 1,3-diiodo- and 1,3-dibromopropane. Although the reaction mixtures were complex, 4,5,6,7-tetrahydro-1,2,3,4-tetraphenyl-1*H*-1,4-diazepine (**13**) and 1,2-diphenyl-2-(*N*-phenylbenzimidoyl)pyrrolidine (**14**) were isolated. The former compound showed no NH or C═N absorption in the ir spectrum; the uv spectrum resembled that of **9** and **10** and, similar to these last two, **13** fluoresced under ultraviolet radiation. The nmr spectrum showed a triplet for the two $NCH_2$ groups and a quintet for the remaining $CH_2$, and the mass spectrum gave a strong parent ion. The pyrrolidine derivative **14** showed absorption in the ir due to C═N; the uv spectrum resembled that of *N*-benzylideneaniline and it did not fluoresce in ultraviolet radiation. Its mass spectrum showed a weak parent ion, the chief fragmentation being cleavage of the bond joining the benzylic carbons forming ions of *m/e* 222 and 180.

Accompanying **13** and **14** were a number of other products from which the *N*,*N*′-diallyl derivative **10** and a monoallyl compound believed to be **15** were obtained. Isolation of these compounds was complicated by the instability of their solutions to light and oxygen. At least one of the unidentified compounds decomposed during short periods of storage to form isolable quantities of benzanilide and benzil monoanil.

Obviously this last alkylation is accompanied by appreciable amounts of dehydrohalogenation. Further complicating the reaction is the competitive alkylation on the carbanionic center and on the amino anionic center of the azaallylic anion, the former producing **14** while the latter, **13**. The more reactive 1,3-diiodopropane is the less discriminating and produces more of the carbon–nitrogen dialkylation product **14**.

**Protonation.**—Treatment of the dianion **2** with water, methanol, or acetic acid generated a reaction mixture which by tlc consisted of two components. The minor component, which fluoresced yellow-green under uv light, was isolated by crystallization and proved to be identical with the $\alpha,\alpha'$-dianilinostilbene **11** described by Becker.[4] Attempts to isolate the major (nonfluorescent) component by recrystallization or chromatography led either to the regeneration of benzil dianil or to the formation of a hydroperoxide.

This hydroperoxide was more conveniently generated by oxygenating the protonated mixture. Its ir spectrum showed absorption for amino, hydroxyl, and azomethine groups and satisfactory analyses, peroxide titrations, and mass spectra for the structure **16** were obtained. On thermal decomposition, **16** formed benzil dianil.

The sensitivity of enamines (*cf.* **11**) to oxidation is well known[4,12] and imines (*cf.* **12**) have frequently been reported to form hydroperoxides.[13,14] However, **16** cannot be considered as evidence for the existence of

---

[10] J. G. Smith and C. D. Veach, *Can J. Chem.*, **45**, 1785 (1967).

[11] The ease of this reaction lends credence to Julian's suggestion[2] that compounds such as **9** are intermediates in the Bischler synthesis of indoles from benzoins and arylamines.

[12] A. G. Cook, Ed., "Enamines," Marcel Dekker, New York, N. Y., 1969, p 285.

[13] C. L. Stevens and R. J. Gasser, *J. Amer. Chem. Soc.*, **79**, 6057 (1957).

[14] L. A. Cohen and B. Witkop, *ibid.*, **77**, 6595 (1955).

**12** in the protonation mixture since the hydroperoxide **16** can be formed from **11** itself.

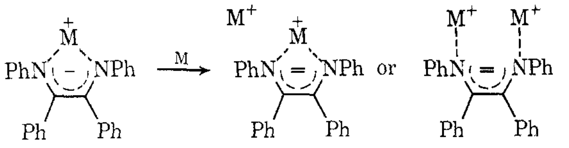
The major product formed on protonation must be either the imine **12** or the geometric isomer of **11**. We favor the former possibility for two reasons. First, the major product can be partially isomerized to **11** by sodium cyanide in dimethylformamide. Such an isomerization has been observed for a related pair of compounds[4] whose oxidative stabilities were sufficiently great that their structural relationship could be established. Secondly, the major product showed no fluorescence on irradiation with uv light. Fluorescence would be expected for compounds such as **11** which are related to stilbene and indeed is observed for **9**, **10**, and **13**. However, for compounds **14** and **16** which are related to *N*-benzylideneaniline, no fluorescence is observed.

## Discussion

As might be expected, the charge density of the dianion **2** is concentrated on the more electronegative nitrogen atoms. Thus acylation, and to a large extent alkylation, occurs at these centers producing derivatives of α,α′-dianilinostilbene. Only in the case of the 1,3-dihalopropanes is carbon alkylation observed as well. Here, dialkylation at the nitrogens is sterically unfavorable due to formation of the seven-membered ring and formation of the more favorable five-membered ring occurs in detectable amounts. However, the reactivity of the dihalide is an important factor. In the case of 1,3-dibromopropane, the slower alkylation reaction allows side reactions, presumably dehydrohalogenation, to dominate with a consequent formation of unstable by-products.

We favor the view that the dianion **2** is predominantly in a cis configuration. Such a formulation explains most simply the easy formation of the imidazolinone ring from both ethyl chloroformate and diethyl oxalate, the formation of only a monobenzamide with methyl benzoate, and the remarkably facile cyclodehydrogenation of the analogous dilithio dianion to a phenanthrene ring.[15] The possibility of a rapid isomerization of a trans dianion to a cis, followed by a subsequent slow reaction with the added reagent cannot be excluded. However, it would be surprising if such a sequence did not produce mixtures of trans and cis products and this has not been observed.

Indeed, the existence of a cis 1,4 dianion is not without precedence. Bauld[16] has demonstrated that the radical anion and the dianion of benzil both favor a cis configuration, especially in nonpolar solvents. His explanation is applicable here. The radical anion first formed adopts the cis configuration in order that the two nitrogen atoms which bear most of the negative charge density may coordinate efficiently with the counterion. Isomerization of the radical ion to a trans configuration is slower than the rate of electron transfer from metals. Consequently, the dianion which arises then has the cis configuration as represented in **17a** or **17b**.



**17a** **17b**

## Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Ir spectra were recorded on a Beckman IR-10 and uv spectra on a Cary spectrometer. Nmr spectra were determined with a Varian T60 or 100-Mc spectrometer with tetramethylsilane as internal standard. Tlc was performed with Eastman chromagram precoated silica gel sheets with fluorescent indicator and visualized with uv light. Mass spectra were determined on a Perkin-Elmer RMU6 spectrometer. For several of the compounds it was found necessary to use degassed solvents and to operate as much as possible under nitrogen.

**Benzil Dianil (1).** The procedure of Julian[2] provided benzil dianil (**1**) in 50% yield, mp 140–145°.

In a more convenient procedure, α,α′-dianilinostilbene[4] (**11**) (36.2 g, 0.1 mol) suspended in 250 ml of chloroform and 50 ml of anhydrous methanol was treated with a stream of dry oxygen until all the solid had dissolved. The solvent was evaporated, the residue washed with a small amount of ethanol, and the residue recrystallized from ethanol to give 33 g (90%) of **1**, mp 143–145°.

**Preparation of Benzil Dianil Disodium Adduct 2.**—The sodium adduct was prepared by shaking a solution of 1.8 g (0.005 mol) of benzil dianil in 100 ± 10 ml of anhydrous tetrahydrofuran with an excess of sodium in a modified Schlenk tube for 8 hr. Details of similar reactions and the measurement of sodium uptake have been described elsewhere.[1,9,10]

Initiation of reaction occurred almost immediately as indicated by an opaque brown-red color developing in the solution. After 2 hr the solution became red and transparent and titration indicated 2 g-atoms of sodium per mole of initial dianil. No further change was detected in the next 24 hr.

For subsequent reactions, the solution was drained from the excess metal into a nitrogen-filled flask to which the second reagent was injected through a septum.

**Preparation of 1,3,4,5-Tetraphenyl-4-imidazolin-2-one (3).**—The adduct **2**, cooled to −60°, was treated with 0.54 g (0.005 mol) of ethyl chloroformate. After warming to room temperature and stirring for 24 hr, the reaction was quenched with water and the product isolated by ether extraction. Evaporation of the solvent gave 1.92 g of crude product, mp 195–203°. Recrystallization from cyclohexane gave 1.54 g (80%) of **3**, mp 206–207°, undepressed on admixture with an authentic sample:[4] ir (KBr) 1705 cm$^{-1}$ (C=O); uv max (95% EtOH) 295 mμ (ε 10,600); mass spectrum (70 eV) *m/e* (rel intensity) 389 (30), 388 (100, M$^+$), 387 (15), 180 (31), 77 (26).

Repetition of this experiment with 1.08 g (0.01 mol) of ethyl chloroformate gave 1.95 g (100%) of **3**, mp 203–206°.

The adduct **2** was treated with 0.73 g (0.005 mol) of diethyl oxalate in a closed system so that any evolved gases could be collected. Over the next 12 hr, 104 ml (corrected to STP, 93%) of carbon monoxide was evolved and identified by its ir spectrum.

The solution was treated with water and the product isolated by ether extraction. The residue obtained on evaporating the extracts was treated with *n*-hexane and filtered giving 1.8 g (93%) of **3**, mp 190–200°. Recrystallization from ethanol-water raised the melting point to 205°, undepressed on admixture with an authentic sample.

**Preparation of *N*-Benzoyl-α,α′-dianilinostilbene (6).**—The adduct **2** was treated with 1.36 g (0.01 mol) of methyl benzoate at −60° and allowed to warm to room temperature. After 5 hr the color had changed from red to pale yellow. The product was isolated by adding water and extracting with ether. Evaporation of the extracts gave 2.1 g (91%) of a yellow solid, mp 215–219° (sealed tube). Recrystallization from degassed acetonitrile under nitrogen gave **6**, mp 222–223° (sealed tube), undepressed on admixture with an authentic sample,[8,9] whose ir spectrum was identical with that of the authentic sample: uv max (95% EtOH) 255 mμ (ε 21,300) 355 (15,800); mass spectrum (70 eV) *m/e* (rel intensity) 467 (21), 466 (53, M$^+$), 449 (37), 362 (26), 361 (88), 270 (20), 269 (90), 180 (100), 105 (26),

---

(15) E. J. MacPherson and J. G. Smith. *Chem. Commun.*. 1552 (1970).

**Preparation of *N*,*N'*-Dimethyl-α,α'-dianilinostilbene (9).**—The dianion 2 at −60° was treated with 1.42 g (0.01 mol) of methyl iodide. Rapid decolorization occurred and, after warming to room temperature, the product was isolated by quenching in water and extracting with ether. Evaporation of the ether gave 1.94 g of residue, mp 146–152°, showing a green fluorescence under uv. Recrystallization from degassed acetone under nitrogen gave 1.2 g (62%) of **9**: mp 173–175.5° (sealed tube); uv max (95% EtOH) 272 mμ (ε 18,700), 302 (16,000), 382 (10,200); ir (KBr) 2810 ($NCH_3$), 2900 and 2915 $cm^{-1}$ (aliphatic CH), no absorption for C═N; nmr ($C_6D_6$, degassed and sealed) δ 2.50 (s, 6, $NCH_3$), 6.6–7.3 (m, 20, aromatic CH); nmr ($CDCl_3$ degassed and sealed) δ 2.62 and 3.0 (singlets, 6, $NCH_3$), 6.5–7.4 (m, 20, aromatic CH); mass spectrum (70 eV) *m/e* (rel intensity) 391 (63), 390 ($M^+$, 100), 375 (34), 270 (20), 269 (57), 195 (23), 180 (70), 77 (20).

*Anal.* Calcd for $C_{28}H_{26}N_2$: C, 86.30; H, 6.72; N, 7.19. Found: C, 86.43; H, 6.55; N, 7.19.

**Preparation of *N*,*N'*-Diallyl-α,α'-dianilinostilbene (10).**—The sodium adduct 2 was treated with 1.21 g (0.01 mol) of allyl bromide at −60°. After being warmed to room temperature and stirred for 8 hr, the product was isolated by adding water and extracting with ether. Evaporation of the extracts gave 2.1 g of an oily yellowish solid which on recrystallization from *n*-hexane gave 1.55 g (70%) of **10**: mp 165–166°; uv max (95% EtOH) 278 mμ (ε 18,900), 302 (shoulder, 14,800), 382 (12,000); ir (KBr) 2860, 2905, 2920, 2980 $cm^{-1}$ (aliphatic CH); nmr (degassed $C_6D_6$) δ 3.8 (m, 4, $CH_2$), 4.9 (m, 4, $CH_2$═), 5.7 (m, 2, CH═), 6.9 (m, 20, aromatic); mass spectrum (70 eV) *m/e* (rel intensity) 443 (22), 442 (58, $M^+$), 401 (31), 372 (24), 269 (26), 180 (93), 77 (100).

*Anal.* Calcd for $C_{32}H_{30}N_2$: C, 86.82; H, 6.85; N, 6.33. Found: C, 86.99; H, 6.79; N, 6.72.

**Preparation of 1-Methyl-2,3-diphenylindole (8).**—*N*,*N'*-Dimethyl-α,α'-dianilinostilbene (9) (0.90 g, 0.0023 mol) was dissolved in 75 ml of methanol containing 1 ml of concentrated HCl and refluxed under nitrogen for 5 hr. On tlc (*n*-hexane–benzene, 10:3) the fluorescent green spot of **9** was gradually replaced by a fluorescent blue spot of lower $R_f$.

After being cooled and neutralized ($Na_2CO_3$), the product was isolated by an ether extraction. Evaporation gave an oily white solid which on recrystallization from methanol gave 0.56 g (85%) of **8**, mp 138°, undepressed on admixture with an authentic sample.[17] Evaporation of the filtrate gave an oil identified as *N*-methylaniline by its ir spectrum.

**Reaction with 1,3-Dihalopropanes.**—The dianion 2 was treated at −60° with 1.48 g (0.005 mol) of 1,3-diiodopropane. Decolorization occurred within 10 min and, after being warmed to room temperature, the product was isolated by adding water and extracting with ether. Evaporation of the solvent provided an oily solid which was triturated with anhydrous ether and the white solid filtered off giving 0.94 g (47%) of 1,2-diphenyl-2-(*N*-phenylbenzimidoyl)pyrrolidine (**14**): mp 201–202° [recrystallization from degassed diethyl ether (under $N_2$) did not raise the melting point]; no fluorescence under uv radiation; uv max (95% EtOH) 250 mμ (ε 14,100) 293 (4600); ir (KBr) 2850, 2960, 2980 (aliphatic CH), 1635 $cm^{-1}$ (C═N); nmr ($C_6D_6$) δ 1.7 (m, 2, $CH_2$), 2.4 (m, 2, $CH_2$), 3.5 (m, 2, $NCH_2$), 6.9 (m, 20, aromatics); mass spectrum (70 eV) *m/e* (rel intensity) 402 (0.5, $M^+$), 223 (74), 222 (100), 180 (52), 103 (20), 91 (35), 78 (30), 77 (66), 51 (37).

*Anal.* Calcd for $C_{29}H_{26}N_2$: C, 86.52; H, 6.52; N, 6.96. Found: C, 86.67; H, 6.56; N, 7.05.

The filtrate was evaporated and the residue chromatographed on silica gel with hexane–benzene 10:3 as eluent. The first fraction (90 mg) was crystallized from *n*-hexane to give 30 mg (1.5%) of *N*,*N'*-diallyl-α,α'-dianilinostilbene (**10**), mp 165–166°, identified by mixture melting point.

The second fraction, 0.33 g (16.5%), mp 222–224°, was 4,5,6,7-tetrahydro-1,2,3,4-tetraphenyl-1*H*-1,4-diazepine (**13**) (recrystallization from anhydrous diethyl ether did not raise the melting point): fluoresced blue in uv radiation; uv max (95% EtOH) 286 mμ (ε 20,700) 370 (30,600); ir (KBr) 2860, 2895, 2925, 2960 $cm^{-1}$ (aliphatic CH), no absorption for C═N; nmr ($C_6D_6$) δ 1.67 (quartet, 2, *J* = 5 Hz, $CH_2$), 3.85 (t, 4, *J* = 5 Hz, $NCH_2$), 6.8 (m, 20, aromatics); mass spectrum (70 eV) *m/e* (rel intensity) 403 (30), 402 (100, $M^+$), 374 (22), 180 (32), 77 (31).

*Anal.* Calcd for $C_{29}H_{26}N_2$: C, 86.52; H, 6.52; N, 6.96. Found: C, 86.25; H, 6.49; N, 7.11.

The third fraction (320 mg) proved to be a mixture (tlc) and was rechromatographed on a preparative tlc silica gel plate giving 145 mg (3.6%) of a white solid, mp 132–135°. Three recrystallizations from ethanol gave 25 mg, mp 143–144°, tentatively identified as 2-anilino-*N*-1,2-triphenyl-4-penten-1-imine (**15**): ir (KBr) 2920, 2990 (aliphatic CH), 1640 (C═N), 3350 $cm^{-1}$ (NH); nmr ($C_6D_6$) δ 1.1 (s, 1, NH), 5.2 (m, 2, CH═), 6.7 (m, 20, aromatics), and two overlapping quartets centered at 3.35 (the AB portion of an ABX pattern with $J_{AX} = J_{BX}$,[18] $J_{AB}$ = 15 Hz, 2 protons, $CH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 402 (3.5, $M^+$), 361 (12), 269 (16), 223 (33), 222 (100), 221 (33), 181 (14), 180 (75), 77 (48).

*Anal.* Calcd for $C_{29}H_{26}N_2$: C, 86.51; H, 6.52; N, 6.96. Found: C, 86.25; H, 6.62; N, 6.92.

The fourth fraction (240 mg) was crystallized with ethanol giving 200 mg (7%) of benzil monoanil, mp 98–100°, identified by a comparison of the ir spectrum with an authentic sample and by mixture melting point.

A fifth fraction was eluted from the column with chloroform and proved to be benzanilide (50 mg, mp 160°) by comparison with an authentic sample.

This reaction was repeated using the adduct from 3.6 g (0.01 ml) of benzil dianil in 200 ml of THF and 2.01 g (0.01 mol) of 1,3-dibromopropane. The reaction mixture stood overnight at room temperature before decolorization was complete. The crude reaction product was isolated by an ether extraction of the water-quenched mixture and the entire product chromatographed on silica gel. The following products were eluted: 65 mg (1.5%) of **10**, mp 167–168°; 2.32 g of yellow oil which deposited 0.42 g (10%) of **13**, mp 222–224° (on treatment with ether and cooling, no further material could be isolated from this oil which decomposed on standing); 0.30 g of an oil which yielded 50 mg (1.2%) of **15**, mp 141–142° on preparative tlc; 0.83 g of a solid which on recrystallization from ether gave 0.64 g (16%) of **14**, mp 201–202°; 0.47 g (16%) of benzil monoanil, mp 95°; 0.31 g of an oily solid which on recrystallization from benzene gave 0.12 g of benzanilide, mp 161–163°.

**Protonolysis of Disodium Adduct 2.**—Treatment of the adduct 2 at −60° with 0.5 ml (0.012 mol) of methanol (or 0.6 g, 0.01 mol of acetic acid) effected immediate decolorization. A tlc using 10:3 *n*-hexane–benzene as developing solvent showed 2 spots, the larger appearing dark blue on visualization while the smaller lead spot fluoresced blue-green. If isolation of the product was attempted using the normal procedures of extracting the water-quenched mixture with ether, only benzil dianil (1.8 g, 100%), mp 138–140°, was obtained and identified by mixture melting point.

The isolation was repeated using degassed water and degassed ether, and the ether extraction was performed under nitrogen. Drying the extracts was accomplished by filtering through a filter stick containing $MgSO_4$ into a nitrogen-filled flask. Evaporation on a vacuum line gave a yellow-green oil and a solution of this oil in degassed anhydrous ether deposited, on refrigeration, 0.20 g (11%) of **11**, identified by its ir spectrum. This material gave the same behavior on tlc as the smaller lead spot of the reaction mixture.

In a repetition of this experiment the yellow green oil was dissolved in 30 ml of 1:1 degassed ether–*n*-hexane. Cooling and filtering under nitrogen provided 1.46 g of a yellow-green solid:[19] mp 145–147° (sealed tube); ir (KBr) indicated formation of the hydroperoxide **16** during the preparation of the disk.

An attempt to purify the material by recrystallization from ether gave a solid, mp 120–121°, whose ir spectrum identified it as the hydroperoxide **16**.

**Preparation of Hydroperoxide 16.**—The adduct 2 was protonated at −60° with 0.6 g (0.01 mol) of glacial acetic acid. After being warmed to room temperature dry oxygen was bubbled through the solution for 5 hr. Water was added and the product was isolated by ether extraction, drying ($MgSO_4$), and evaporating (no heat) the extracts. The residue was triturated with *n*-hexane and the white solid filtered, 1.6 g, mp 110–120°, with

---

[17] E. Ritchie, *J. Proc. Roy. Soc. N. S. W.*, **80**, 33 (1946).

[18] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, p 364.

[19] Julian[2] described desylaniline anil of uncertain purity, mp 160–185°.

gas evolution. Titration[20] of this material showed it to be 83% hydroperoxide **16**.

It was purified by dissolving in anhydrous ether at 20°, filtering, adding *n*-hexane, and cooling to 0°. The solid, mp 119–120°, with gas evolution, analyzed as 98.6% hydroperoxide **16**: ir (KBr) 3470, 3450 (OH, NH), 1640 cm$^{-1}$ (C=N); mass spectrum (70 eV) *m/e* (rel intensity) 394 (1, M$^+$), 361 (32), 360 (80), 197 (22), 186 (32), 181 (64), 180 (100), 149 (25), 105 (35), 93 (37), 77 (72).

*Anal.*[21] Calcd for $C_{26}H_{22}N_2O_2$: C, 79.15; H, 5.63; N, 7.10. Found: C, 78.92; H, 5.84; N, 7.00.

A 100-mg sample of **16** heated under vacuum at 150° for a few minutes decomposed with gas evolution. The product, recrystallized from methanol, gave 50 mg (55%) of benzil dianil identified by mixture melting point.

A solution of 1.56 g (0.0043 mol) of $\alpha,\alpha'$-dianilinostilbene (**11**) and 0.66 g (0.0086 mol) of anhydrous sodium acetate in 75 ml of THF was stirred overnight by a stream of dry $O_2$. Isolation of the hydroperoxide **16** was accomplished as previously described, 1.3 g, mp 110–120°, with gas evolution, identified by the ir spectrum.

**Isomerization[4] of the Protonation Product.**—The adduct **2** was protonated at −60° with 0.6 g (0.01 mol) of acetic acid and warmed to room temperature, and 35 ml of anhydrous DMF containing 100 mg of sodium cyanide was added. Nitrogen was bubbled through the mixture and the THF permitted to distil. The remaining solution was stirred by the nitrogen stream for 48 hr. The reaction was monitored by tlc (1:1 benzene–*n*-hexane) and during this time the fluorescent spot increased in size relative to the nonfluorescent spot.

Addition of water and extraction with ether and evaporation of the extracts provided the crude reaction product. Methanol (50 ml) was added and after 4 hr at 0°, 0.34 g (19%) of $\alpha,\alpha'$-dianilinostilbene were deposted and identified by its ir spectrum. Attempts to isolate anything further from the filtrates by evaporation and crystallization provided only 1.2 g (67%) of benzil dianil identified by mixture melting point.

**Registry No.**—**1**, 7510-33-0; **9**, 29954-13-0; **10**, 29954-14-1; **13**, 29954-15-2; **14**, 29954-16-3; **15**, 29954-17-4; **16**, 29954-18-5.

**Acknowledgment.**—The financial support of the National Research Council of Canada is gratefully acknowledged. The award of a Province of Ontario Graduate Fellowship to one of us (E. J. M.) is also appreciated.

---

[20] R. L. Augustine, Ed., "Oxidation," Vol. 1, Marcel Dekker, New York, N. Y., 1969, p 222.

[21] We are grateful to Mr. W. Boos of the Uniroyal Research Laboratories, Guelph, Ontario, who arranged for the immediate analysis of this compound.

---

# Reactions of Aryl Azides with Carbonyl-Stabilized Sulfonium Ylides

E. VAN LOOCK, G. L'ABBÉ,* AND G. SMETS

*Department of Chemistry, Laboratory of Macromolecular Chemistry, University of Louvain, Louvain, Belgium*

*Received February 12, 1971*

Aryl azides have been found to react with 2 equiv of carbethoxymethylenedimethylsulfurane to give a mixture of aryltriazenofumarates and anilinodiazosuccinates in various amounts depending on the solvent. Reaction of aryl azides with phenacylidenesulfuranes at room temperature produces 1-anilino-1,2-dibenzoylethylenes in addition to small amounts of 1-triazeno-1,2-dibenzoylethylenes (in equilibrium with the cyclic $\Delta^2$-triazolines) and *trans*-1,2,3-tribenzoylcyclopropane. The stereochemistry of the reaction products is discussed as well as the mechanism of their formation.

Although phosphonium and sulfonium ylides are similar in structure, they have been found to react differently on several occasions. Johnson,[1] in reviewing the chemistry of both classes of ylides, clearly pointed out that the formation of a P=O bond (128 kcal/mol$^{-1}$) is the driving force in most *P*-ylide reactions, whereas *S*-ylides benefit from the sulfide leaving group. This principle is best illustrated by the synthesis of olefins and oxiranes by treating carbonyl compounds respectively with *P*- and *S*-ylides.

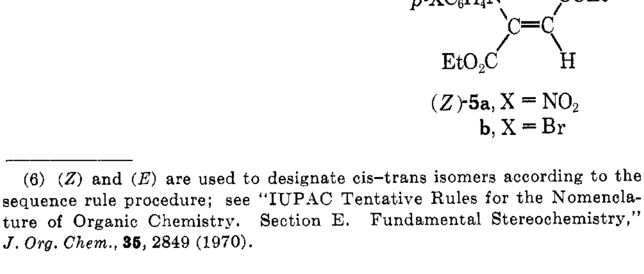
Different behavior is also observed in the reactions of nonstabilized phosphonium and oxysulfonium ylides with aryl azides, the former leading to imines[2] and the latter to triazenes and $\Delta^2$-triazolines.[3] In recent studies, the reactions of carbonyl-stabilized phosphonium ylides with aryl azides led to triazoles or diazo compounds.[4] For comparison, in this paper we have investigated the reactions of the corresponding sulfonium ylides with aryl azides.[5]

## Results

Carbethoxymethylenedimethylsulfurane (**1**) reacts smoothly with aryl azides **2a,b** at room temperature to give a mixture of aryltriazenofumarates (*Z*)-**3a,b**[6]

$$2\,EtO_2CCH{=}SMe_2 + p\text{-}XC_6H_4N_3 \xrightarrow[-2Me_2S]{}$$

**1** **2a**, X = NO$_2$; **b**, X = Br



(*Z*)-**3a**, X = NO$_2$; **b**, X = Br

**4a**, X = NO$_2$; **b**, X = Br

(*Z*)-**5a**, X = NO$_2$; **b**, X = Br

---

[1] A. W. Johnson, "Ylid Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1966, p 331.

[2] H. Hoffmann, *Chem. Ber.*, **95**, 2563 (1962).

[3] G. Gaudiano, C. Ticozzi, A. Umani-Ronchi, and P. Bravo, *Gazz. Chim. Ital.*, **97**, 1411 (1967).

[4] G. R. Harvey, *J. Org. Chem.*, **31**, 1587 (1966). P. Ykman, G. L'abbé, and G. Smets, *Tetrahedron*, **25**, 5421 (1969); **27**, 845 (1971).

[5] For a preliminary report on this topic, see E. Van Loock, G. L'abbé, and G. Smets, *Tetrahedron Lett.*, 1693 (1970); see also Y. Hayashi, T. Watanabe, and R. Oda, *ibid.*, 605 (1970). This research was presented in part at the International Symposium on Ylides, Leicester, England, July 1970.

[6] (*Z*) and (*E*) are used to designate cis–trans isomers according to the sequence rule procedure; see "IUPAC Tentative Rules for the Nomenclature of Organic Chemistry. Section E. Fundamental Stereochemistry," *J. Org. Chem.*, **35**, 2849 (1970).