

base than monoanionic phosphate. If the dissociation of I is a higher energy process compared to diethylcarbamoyl phosphate ionization, then it would be expected that if a lower energy direct nucleophilic interaction path were available, it would be taken.

In their criticism of the work of Halmann, *et al.*,⁷ Jones and Allen⁸ proposed that the method of measuring carbamoyl phosphate hydrolysis by ammonia evolution in Halmann's experiments⁷ measures the cyanate decomposition rather than carbamoyl phosphate decomposition, as supported by indirect cyanate determinations and kinetic measurements. A related erroneous concept present in Halmann's work will now be mentioned. In the pH range 5–7, the rate of production of ammonia is much lower than the rate of production of cyanate measured titrimetrically. The lowered rate of production of ammonia is not due to a lowered concentration of the monoanion in this pH range. The *observed* rate constants for the evolution of both cyanate and ammonia should be the same if both products are formed in a rate-determining step from a common precursor or set of equilibrium-related precursors. This observed rate constant should be the *sum* of the individual rate constants giving rise to each product. The individual rate constants can only be evaluated by additional data on the product ratio which is equal to the ratio of the individual rate constants. The lack of equality of the rate constants for the formation of ammonia and cyanate is a good indication that the rate constant for ammonia evolution is due to some other process unrelated to the decomposition of the carbamoyl phosphate monoanion, such as the hydrolysis of the cyanate product.

A major point of difference in ref. 7 and 8 is the interpretation of trapping experiments with azide. Hal-

mann, *et al.*,⁷ were able to isolate a 30% yield of carbamoyl azide from carbamoyl phosphate and sodium azide in the pH range 4.0–4.5. Since sodium azide has no effect upon the rate of disappearance of carbamoyl phosphate, it was proposed that azide was trapping $[H_2NC=O^+]$, which is merely a protonated form of cyanic acid. However, it seems unreasonable to us that azide could really trap a protonated species such as $[H_2NC=O^+]$ because the rate of deprotonation of such a species should be far greater than the rate of combination of azide with it in aqueous solvents.³⁰ If anything, it seems reasonable that azide should trap HCNO or CNO^- ($pK = 3.7$).³¹ Trapping experiments would be more meaningful for N,N-disubstituted carbamic acid derivatives.

In conclusion: (1) I does not undergo S_N1 hydrolysis; (2) I does undergo direct nucleophilic interactions with added nucleophiles in marked contrast to carbamoyl phosphate^{7,8} or dimethylcarbamoyl chloride⁵; (3) I does undergo a very small amount of general base catalyzed solvolysis (with a minimum β value of 0.7–0.8 indicating that specific base catalysis or direct nucleophilic reaction is of much greater importance than general catalysis), in analogy with the acetylpyridinium ion³; and (4) the nucleophilicities of neutral and anionic nucleophiles towards I are well correlated with the reactivities of the same nucleophiles toward *p*-nitrophenyl acetate.

(30) (a) The deprotonation of $H_2N^+C=O$ would be expected to be diffusion controlled^{30b} while a C–N bond-making reaction should be much slower. For example, the rate constant²⁶ for the reaction of the very strong base OH^- with the positively charged carbonyl carbon of N-acetyl-N'-methylimidazolium ion is 1.5×10^6 mole⁻¹ sec.⁻¹, while diffusion-controlled rate constants are $>10^4$ larger. (b) M. Eigen in "Techniques of Organic Chemistry," Vol. VIII, Part 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 1031.

(31) A. R. Amell, *J. Am. Chem. Soc.*, **78**, 6234 (1956).

Configurational Problems in Conjugated Systems.

I. Benzil Anion Radical and Dianion¹

Nathan L. Bauld

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. Received April 26, 1965

The *cis*–*trans* configurational distributions and configurational stabilities of benzil anion radical ($Bz_2^{\cdot-}$) and dianion (Bz_2^{2-}), formed by successive electron transfers to benzil (Bz_2), have been studied in several solvents. Alkali metal transfer agents give *cis*–*trans*- $Bz_2^{\cdot-}$ mixtures which are thermodynamically controlled owing to rapid electron exchange between the latter species and its configurationally labile parent (Bz_2). Addition of Bz_2 to various anion radicals and dianions gives a kinetically controlled $Bz_2^{\cdot-}$ composition. In either case the *cis* configuration of $Bz_2^{\cdot-}$ is favored, especially in nonpolar solvents. $Bz_2^{\cdot-}$ undergoes *cis*–*trans* isomerization but less rapidly than it is converted to Bz_2^{2-} , when sufficient electron-transfer agent is present; thus the isomer composi-

tion of Bz_2^{2-} is the same as for $Bz_2^{\cdot-}$. Unlike $Bz_2^{\cdot-}$, Bz_2^{2-} is configurationally quite stable, a contrast which is easily rationalized in terms of π -electronic rotational barriers. The enolate (Bz_3^-) formed by addition of one mole of benzoyl chloride to Bz_2^{2-} also undergoes *cis*–*trans* isomerization, but again at a rate less than that of the second benzoylation step whenever excess benzoyl chloride is present.

Introduction

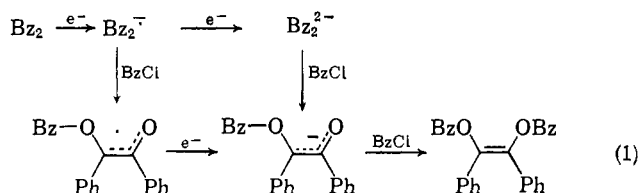
Configurational and conformational problems have been extensively investigated for conjugated dienes and diones. However, little is known about this aspect of the corresponding anion radicals and dianions. A study of some configurational aspects of the benzil

(1) A brief account of this work was published previously: N. L. Bauld, *J. Am. Chem. Soc.*, **84**, 4345 (1962).

anion radical and dianion are reported here; a similar report on diene anion radicals is planned.

Results

Configurational Analysis of $Bz_2^{\cdot-}$ and Bz_2^{2-} . Benzil (Bz_2) is converted, in discrete steps, to the anion radical ($Bz_2^{\cdot-}$) and dianion (Bz_2^{2-}) by a variety of electron transfer agents including the alkali metals² and various organic anion radicals and dianions. As indicated in eq. 1 the *cis-trans* composition of either $Bz_2^{\cdot-}$ or Bz_2^{2-}



can be found by quenching their respective solutions with excess benzoyl chloride and determining the composition of the 1,2-dibenzoyloxystilbene by infrared analysis. The crude oily ester mixture from aqueous processing is crystallized and separated from excess benzoyl chloride by adding hexane and a small amount of ethanol, heating on a steam bath, and then cooling. It was determined that these conditions caused negligible isomer fractionation of the highly insoluble esters. That the isomer distributions of $Bz_2^{\cdot-}$ and Bz_2^{2-} are carried over intact to the ester will be shown in the following section. The yields and isomer distributions in various solvents and for various electron transfer agents are given in Tables I and II.

Table I. Configurational Distributions of $Bz_2^{\cdot-}$

Electron transfer agent	Solvent	Yield, %	<i>cis</i> , %
K	THF	80	75
K	Benzene	90	100
Na	Benzene	85	100
$C_{10}H_8^{\cdot-}K^+$	THF	85	75
Stilbene $^{\cdot-}K^+$	THF	80	75

Table II. Configurational Distributions of Bz_2^{2-}

Electron transfer agent	Solvent	Yield, %	<i>cis</i> , %
Mg	Benzene	62	100
Mg	Ether	62	95
Mg	THF	79	80
Mg	Diglyme	45	80
Mg	CH_3CN	67	80
K	Benzene	60	95
K	THF	60	75
K	50% benzene-THF	85	75
K	90% benzene-DMF	80	65
K	80% THF-DMF	75	30
Na	N-Methylpyrrolidone	30	35
Na	Ammonia	30	35
$Ni(CO)_4$	Hexane + BzCl	50	95
$Ni(CO)_4$	THF + BzCl	65	40
$C_{10}H_8^{\cdot-}K^+$	THF	80	75
Stilbene $^{\cdot-}K^+$	THF	75	77
$Ph_2C=CPh_2^{2-} \cdot 2K^+$	THF	80	75

(2) H. Staudinger and A. Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

Configurational Stabilities of $Bz_2^{\cdot-}$ and Bz_2^{2-} . The solvent dependence of the configurational distributions provides a convenient means for determining configurational stability or lability. $Bz_2^{\cdot-}$ and Bz_2^{2-} were prepared in a less polar solvent, to which was subsequently added a more polar solvent. The solutions were then allowed to stand or were heated for various time intervals before addition of excess benzoyl chloride. The results (Table III) show that even after 2 hr. of refluxing the Bz_2^{2-} distribution is unchanged. This verified, additionally, that isomerization is absent in the conversion of Bz_2^{2-} to the ester. $Bz_2^{\cdot-}$, on the other hand, is stable at room temperature, but can be isomerized at reflux temperatures. Again, verification is obtained of insignificant isomerization in the trapping procedure.

The enolate ($Bz_3^{\cdot-}$), formed by addition of one mole of benzoyl chloride to Bz_2^{2-} , also undergoes isomerization when refluxed (Table III).

Discussion

The conformational energy minimum of unhindered acyclic α -diones, like that of dienes,³ seems to be located near the *trans* coplanar conformation (dihedral angle $\theta = 180^\circ$).^{4,5} In this form the carbonyl dipole-dipole repulsions are minimized and resonance energy roughly maximized. Benzil, however, is by no means an unhindered dione, and its preferred conformation, determined by several different physical methods,⁵⁻⁸ is skewed ($\theta \approx 90^\circ$).

Hückel molecular orbital (HMO) calculations (Table IV) indicate a much greater delocalization energy for the planar conformations of $Bz_2^{\cdot-}$ and Bz_2^{2-} than for the parent (Bz_2). It therefore seems likely that nonplanar forms may be safely neglected for the former two species. That this assumption is valid is also indicated by the chemical evidence on the nonisomerization of Bz_2^{2-} and $Bz_2^{\cdot-}$ presented in the previous section. The configurational analysis is thus simplified to the determination of the *cis-trans* distributions of $Bz_2^{\cdot-}$ and Bz_2^{2-} and the determination of stability or lability, *i.e.*, whether the geometric forms involved are configurations or conformations.

Both thermodynamic and kinetic $Bz_2^{\cdot-}$ distributions have been obtained. When generated by electron transfer from metals, the $Bz_2^{\cdot-}$ mixtures are thermodynamically controlled as a result of rapid electron transfers to unreacted Bz_2 . Reactions of this type are customarily quite fast⁹ and would be especially so at the *ca.* 0.5 M concentrations involved in this work. More specifically the e.s.r. spectrum of $Bz_2^{\cdot-}$ in THF in the presence of unreacted Bz_2 has lost most of its hyperfine structure at even 10^{-2} M because of such exchanges. A rapid route for equilibration of *cis-* and *trans*- $Bz_2^{\cdot-}$ is thus provided.

Kinetically controlled mixtures are obtained when Bz_2 is added to solutions of various anion radicals and

(3) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 1339 (1965), and references cited therein.

(4) J. E. Lu Valle and V. Shomaker, *ibid.*, **61**, 3520 (1939).

(5) C. C. Caldwell and R. J. W. Lefevre, *Nature*, **143**, 803 (1939). These authors find $\theta = 160^\circ$ for biacetyl.

(6) I. Bernal, *Nature*, **200**, 1318 (1965).

(7) I. E. Knaggs and K. Lonsdale, *ibid.*, **143**, 1023 (1939).

(8) P. H. Cureton, G. G. Lefevre, and R. J. W. Lefevre, *J. Chem. Soc.*, 4447 (1961).

(9) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **86**, 2537 (1964).

Table III. Configurational Stability by the Method of Solvent Additives

Species	Metal	Solvent prepared in	Final solvent	Reaction time and temperature after addition	trans, %
Bz ₂ ⁻	K	Benzene	Benzene	...	5
Bz ₂ ⁻	K	Benzene	90% benzene-DMF	15 min., reflux	30
Bz ₂ ⁻	K	Benzene	90% benzene-DMF	1 hr., reflux	45
Bz ₂ ⁻	K	Benzene	90% benzene-DMF	2 hr., reflux	60
Bz ₂ ⁻	K	THF	THF	...	25
Bz ₂ ⁻	K	THF	80% THF-DMF	1 hr., reflux	70
Bz ₂ ⁻	K	80% THF-DMF	80% THF-DMF	...	80
Bz ₂ ⁻	K	Benzene	50% benzene-THF	2 hr., reflux	25
Bz ₂ ⁻	K	50% benzene-THF	50% benzene-THF	...	25
Bz ₂ ⁻	K	Benzene	50% benzene-THF	30 min., ambient	5
Bz ₂ ⁻	K	THF	90% THF-DMF	30 min., ambient	25
Bz ₂ ²⁻	K	THF	THF	...	25
Bz ₂ ²⁻	K	THF	80% THF-DMF	1 hr., reflux	25
Bz ₂ ²⁻	K	80% THF-DMF	80% THF-DMF	...	80
Bz ₂ ²⁻	Mg	THF	THF	...	20
Bz ₂ ²⁻	Mg	THF	50% THF-DMF	2 hr., reflux	20
Bz ₃ ⁻	K	THF	90% THF-DMF	1 hr., reflux	70

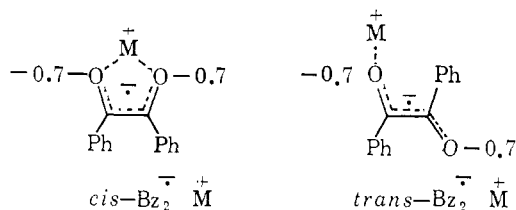
Table IV. π -Electronic Rotational Barriers

Species	Delocalization energy (Hückel) ^a	Delocalization energy (kcal.) ^b
Bz ₂	0.22	4.0
Bz ₂ ⁻	0.71	12.8
Bz ₂ ²⁻	1.20	21.6
Bz ₃ ⁻	0.7	12

^a Using $\alpha_0 = \alpha + 2\beta$ and $\beta_{CO} = \beta\sqrt{2}$ and 2Bz as a localized model. ^b Using $\beta = 18$ kcal.

dianions (e.g., naphthalene and stilbene anion radicals and tetraphenylethylene dianion). Here no excess parent is present to catalyze isomerization, and since unimolecular isomerization was shown to be slow by the method of solvent additives, the Bz₂⁻ composition must be kinetically determined.

In either case a pronounced *cis*-Bz₂⁻ preference is found—somewhat surprisingly, in view of the Coulombic repulsions between *cis* negatively charged oxygens and the steric repulsions between *cis*-phenyl groups. The results seem best interpreted in terms of ion pairs. HMO calculations indicate a large (0.7 electron) negative charge density at each oxygen atom of Bz₂⁻. In the *trans* form one of the heavily charge-laden oxygens is unable to coordinate with the metal ion, whereas in the *cis* form both oxygens, carrying essentially all of the negative charge density, may efficiently coordinate.



The foregoing picture also gives a good account of the effect of solvent polarity on configurational distribution. Since the metal ion is more efficiently coordinated to *cis*-Bz₂⁻, decreased solvent polarity should be expected to favor this form.

Since the (presumed¹⁰) unimolecular isomerization of Bz₂⁻ has been shown to be slow relative to the second electron transfer even for electron transfer from metals, the Bz₂²⁻ distributions are kinetically determined. We have been unable to equilibrate *cis*- and *trans*-Bz₂²⁻ even using large amounts of benzophenone or naphthalene to partially convert it to Bz₂⁻.

Configurational Stabilities. The finding that Bz₂⁻, but not Bz₂²⁻, is susceptible to equilibration is of interest. It may be accounted for either by the disproportionation mechanism¹⁰ available to Bz₂⁻ but not Bz₂²⁻, or by Hückel calculations of the π -electronic rotational barriers for the two species (Table IV). In the case of Bz₂⁻ the rotation must pass through a perpendicular form in which the odd electron occupies the antibonding molecular orbital ($\alpha - 0.49\beta$) of a benzoyl group instead of the nonbonding (α) molecular orbital of Bz₂⁻. This, in addition to the small (0.22 β) resonance advantage of planar Bz₂ over 2Bz, accounts for the calculated 0.71 β or 12.8-kcal. barrier for Bz₂⁻. In Bz₂²⁻ two electrons must be placed in the benzoyl ABMO; consequently the barrier is raised to 1.20 β or 21.6 kcal. for Bz₂²⁻.

The enolate (Bz₃⁻) is calculated to have a π -electronic rotational barrier of less than 0.7 β . In agreement, this species, like Bz₂⁻, undergoes isomerization at reflux temperatures.

Experimental Section

Benzil Anion Radical from Alkali Metals. Benzil (10.5 g., 50 mmoles) was added rapidly through a powder funnel to 150 ml. of solvent containing 50 mmoles + 10% excess of the desired metal while flushing the system vigorously with nitrogen. Stirring was begun and the nitrogen flow reduced to a steady trickle. The purple color of Bz₂⁻ appeared quickly. The reaction vessel was cooled in ice water sufficiently to keep the mixture at room temperature. The reaction was complete in less than 1 hr.

(10) The possibility exists that the isomerization of Bz₂⁻ in the absence of Bz₂ is a bimolecular disproportionation: $2\text{Bz}_2^- \rightleftharpoons \text{Bz}_2^{2-} + \text{Bz}_2$. Because of experimental difficulties, we have been unable to resolve this question.

Benzil Dianion from Alkali Metals. The procedure was the same as above except 100 mmoles + 10% excess of metal was used. Bz_2^{2-} is red-orange.

Benzil Anion Radical from Naphthalene and Stilbene Anion Radicals. A solution of the desired anion radical in 150 ml. of solvent was prepared from 50 mmoles of the substrate and 50 mmoles + 10% excess of alkali metal; 10.5 g. (50 mmoles) of Bz_2 was then added either at once through a powder funnel or in 100 ml. of solvent through a dropping funnel. The electron transfer is immediate, as shown by the color change to the purple of $Bz_2^{\cdot-}$.

Benzil Dianion from Naphthalene and Stilbene Anion Radicals and Tetraphenylethylene Dianion. Anion radical (100 mmoles) or 50 mmoles of dianion was prepared as above and 10.5 g. (50 mmoles) of benzil added through a powder funnel.

Reaction with Benzoyl Chloride. The solutions of $Bz_2^{\cdot-}$ or Bz_2^{2-} , prepared as above, were cooled to below room temperature in an ice bath, and 100 mmoles + 25% excess of benzoyl chloride was added through a dropping funnel. The purple or red color disappeared during the addition, but stirring was usually continued overnight to assure complete destruction of the excess alkali metal. The addition of 100 ml. of solvent at this stage facilitated stirring. The reaction mixture was then added cautiously to 300–500 ml. of water, the organics were extracted into chloroform, the chloroform was re-extracted to remove nonvolatile polar organic solvents when necessary and, after drying over sodium sulfate, the solvent was evaporated, leaving a viscous oil. Addition of ca. 50 ml. of hexane followed by 5–10 ml. of ethanol and heating crystallized the esters. The suspension was then cooled in ice and filtered. The esters thus obtained were nearly pure, as determined by infrared analysis. The pure *cis*

isomer has absorptions at 5.78, 7.92, 8.08 (sh), and 9.20 μ ; the *trans* at 5.78, 8.08, and 8.99 μ . The 9.20- μ *cis* and 8.99- μ *trans* absorptions, presumably corresponding to the respective C–OBz stretches, were used in the analysis. This consisted of comparing the product ester with prepared mixtures of the two pure isomers; it was reproducible to less than 5%. The *trans* isomer has m.p. 186°, λ_{max}^{EtOH} 261 $m\mu$ (ϵ 11,400); the *cis*, m.p. 159°, λ_{max}^{EtOH} 266 $m\mu$ (ϵ 6100).^{1,11}

Isomerizations Using Solvent Additives. The anion radical or dianion was prepared as described above, the appropriate amount of solvent additive was added, and the solution either was allowed to stand or refluxed for the desired time interval. The solution was then cooled in an ice bath and then quenched with benzoyl chloride and the reaction product was worked up as described above.

Preparation, Isomerization, and Conformational Analysis of the Enolate (Bz_3^-). Bz_2^{2-} (50 mmoles) was prepared in THF, the solution cooled, and 25 mmoles of benzoyl chloride was added, whereupon the previously red solution became a light yellow. DMF was then added to 10% (by volume) and the solution was refluxed for 1 hr., cooled, and quenched. Work-up was the same as usual.

HMO Calculations. Overlap was neglected; $\alpha_0 = \alpha + 2\beta$ and $\beta_{CO} = \beta\sqrt{2}$ were assumed. π -Electronic rotational barriers were calculated by subtracting the π -electronic energy of planar $Bz_2^{\cdot-}$ from that of one Bz (benzoyl group) and one $Bz^{\cdot-}$ and of planar Bz_2^{2-} from that of two $Bz_2^{\cdot-}$.

Acknowledgments. The author is grateful to the National Science Foundation and the University of Texas Research Institute for generous support.

(11) L. F. Fieser, *J. Chem. Educ.*, **31**, 291 (1954). These two references jointly establish the structures of the isomeric esters.

Ambident Reactivity of Thiocyanate Ion. Thiocyanate Ion Catalysis in the Isomerization of Organic Thiocyanates^{1a}

Antonino Fava,^{1b} Antonio Illiceto,^{1c} and Silvano Bresadola

Contribution from the Istituto di Chimica Organica, Università di Padova, Padova, Italy. Received July 19, 1965

Alkali thiocyanates catalyze the isomerization of benzyl thiocyanate to the isothiocyanate. The catalysis is not a salt effect as it is specific for the thiocyanate ion and the isomerization rate is first order with respect to ionic thiocyanate. The catalytic effect is interpreted as a nucleophilic displacement of thiocyanate carried out by

the N end of the thiocyanate ion: $SCN^- + RSCN \rightarrow SCNR + SCN^-$. By comparing the rate of isomerization by this mechanism with the rate of isotopic exchange: $-NCS^ + RSCN \rightleftharpoons NCS^*R + SCN^-$, which is a nucleophilic displacement of thiocyanate carried out by the S end of the SCN^- ion, the reactivity ratio, k_S/k_N , of the two "teeth," S and N, of the ambident nucleophile SCN^- , has been found to range between 10^2 and 10^3 . Temperature dependence and solvent effect on the k_S/k_N ratio have been evaluated and discussed.*

(1) (a) The financial support of C.N.R. Rome, and Shell Internationale Research Maatschappij, N. V., The Hague, Holland, is gratefully acknowledged. (b) To whom inquiries concerning this paper are to be addressed: Istituto di Chimica Generale, Università di Pisa, Pisa, Italy. (c) Deceased.