under reflux for 10 hours in a Todd micro column, as described above. No olefin was formed under these conditions.

Elimination Reactions of the *t*-Alkyl Chlorides.—The dehydrogenation of *t*-amyl bromide and chloride by potassium *t*-butoxide and of 2,4,4-trimethyl-2-pentyl bromide and chloride with 2,6-lutidine were carried out by the procedures previously described for the bromides.[2b,c]

The experimental data are summarized in Table III.

Acknowledgment.—We wish to express our appreciation to Dr. M. Nakagawa and Mr. Y. Okomoto for their assistance with several of the experiments reported in this paper.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Coördination of Polyalkylbenzenes with Silver Ion

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RECEIVED NOVEMBER 7, 1955

Argentation constants for a large number of polyalkylbenzenes have been obtained through a study of the variations in the solubilities of the aromatic substances in equimolar water–methanol solution with changes in the silver nitrate concentration of the medium. The stabilities of the silver ion complexes appear to be controlled by opposing electronic and steric effects of the alkyl substituents on the aromatic nucleus. The assumption that the unfavorable steric effects are minimized when silver ion is coördinated with the aromatic nucleus from a position above and between two unsubstituted ring carbons is in accord with the data. The results of studies of the effects of temperature changes on the magnitudes of the argentation constants indicate that as steric effects of the alkyl substituents become more pronounced the entropy losses accompanying the interactions become larger.

Thermodynamic constants for the formation of iodine and iodine monochloride complexes of polyalkylbenzenes in carbon tetrachloride solution have been reported recently.[1,2] These data indicate rather clearly that when a number of bulky alkyl substituents are present on the benzene nucleus the normally favorable electronic influences of alkyl groups on complex stability are offset by an unfavorable steric situation. The results of earlier argentation studies,[3,4] in which aqueous media were used, suggest that the formation of silver ion–alkylbenzene complexes is also subject to steric as well as electronic control by alkyl substituents. The available supporting evidence is, however, limited since the highly substituted benzenes are too insoluble in aqueous media to permit accurate evaluation of argentation constants by techniques which are appropriate for the simple alkylbenzenes.

This solubility problem has been overcome through use of an equimolar solution of water and methanol as the solvent for determination of argentation constants. This procedure was suggested by the method used by Nichols[5] to study the coördination of silver ion with unsaturated esters and has been employed successfully by Kofahl and Lucas[6] in studying the argentation of polycyclic aromatic hydrocarbons. Argentation constants for a large number of polyalkylbenzenes have now been evaluated. These and the heat, free energy and entropy changes accompanying certain of the interactions are reported here and are compared with similar data for the halogen–polyalkylbenzene interactions.

Experimental

Materials.—Commercial Solvents Corporation methanol was purified by the procedure of Morton and Mark.[7] Skellysolve C (ligroin of boiling range 85–100°) was purified for use as a solvent in spectrophotometric studies by methods described previously.[3,4]

The monoalkylbenzenes (Eastman Organic Chemicals white label grade) were washed successively with concentrated sulfuric acid, water and dilute sodium hydroxide and were dried and fractionated before use. Eastman organic chemicals *m*-xylene (b.p. 139.0–139.2°) was freed of its isomers by the procedure of Clarke and Taylor.[8] Eastman organic chemicals durene (m.p. 79–80°) and pentamethylbenzene (m.p. 51.2–52.5°) were recrystallized from ethanol. Samples of *m*-diisopropylbenzene and 1,3,5-triisopropylbenzene were furnished by Dr. A. P. Lien of the Standard Oil Co. of Indiana. 1,2,3,4-Tetraethylbenzene, b.p. 119.4–120.1° (11 mm.), was prepared by the Jacobsen reaction[9] from a mixture of tetraethylbenzenes which was obtained by alkylation of commercial triethylbenzene. All other hydrocarbons were purified as described in connection with earlier work on iodine monochloride complexes.[2] All inorganic chemicals were of reagent grade and were dried before use.

The Solubility Measurements.—Equimolar water–methanol solutions of varying concentrations of sodium and silver nitrate and of total ionic strength 0.5 were prepared and stored as described by Kofahl and Lucas.[6] To samples of these solutions contained in 125-ml. glass stoppered erlenmeyer flasks were added 0.1–1.0 g. samples of aromatic hydrocarbon. The mixtures were shaken at room temperature for 12 hours in a constant temperature bath at 25.0° to saturate the aqueous methanolic phase with hydrocarbon. Longer shaking and rotating periods did not cause further increases in the concentrations of hydrocarbons dissolved in the aqueous methanol.

After a one-half hour settling interval a 10-ml. sample of the aqueous methanol phase was removed from each mixture, and this was added to 10 ml. of Skellysolve C contained in a glass stoppered erlenmeyer flask. To this mixture was added 150 ml. of water, and the flask was shaken for two hours. The optical density of the Skellysolve C phase was then measured on the Beckman spectrophotometer against a Skellysolve C blank at some appropriate wave length in the ultraviolet region. One extraction with Skellysolve C was sufficient to remove all of the dissolved hydrocarbon from the aqueous phase as evidenced by the fact that addi-

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(1) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **77**, 2164 (1955).

(2) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

(3) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949).

(4) L. J. Andrews and R. M. Keefer, *ibid.*, **72**, 5034 (1950); **74**, 4500 (1952).

(5) P. L. Nichols, *ibid.*, **74**, 1091 (1952).

(6) R. E. Kofahl and H. J. Lucas, *ibid.*, **76**, 3931 (1954).

(7) A. A. Morton and J. G. Mark, *Ind. Eng. Chem., Anal. Ed.*, **6**, 151 (1934).

(8) H. T. Clarke and E. R. Taylor, THIS JOURNAL, **45**, 831 (1923).

(9) L. I. Smith and C. O. Guss, *ibid.*, **62**, 2625, 2631 (1940).

tional Skellysolve extracts showed negligible optical density readings. Using the separately determined molecular extinction coefficients of the hydrocarbons in Skellysolve C the concentrations of hydrocarbons in the saturated aqueous methanol solutions were then calculated.

Samples of hydrocarbon free aqueous methanol solutions, some of which contained silver nitrate or sodium nitrate, were also extracted with Skellysolve C. The extracts showed small traces of absorbing materials which could be detected by spectrophotometric measurement. The light absorbing material thus extracted by the Skellysolve apparently derived from solvent impurities, since the amount extracted did not vary with the presence or absence of nitrate salts in the aqueous methanol. The optical densities of Skellysolve C extracts obtained in the argentation studies were corrected for the slight absorption of these solvent impurities.

Argentation constants at 1.6° were determined in similar fashion. At this temperature the aqueous methanol solutions could be saturated with aromatic hydrocarbon by a 12-hour period of shaking at room temperature followed by six hours of shaking in the low temperature bath.

To check the possibility that in the argentation studies silver nitrate may have distributed to the aromatic hydrocarbon phase, 10 ml. of benzene and 30 ml. of a 0.5 M solution of silver nitrate in aqueous methanol were shaken several hours and then rotated at 25° overnight. The benzene layer then produced no measurable amount of silver chloride when it was shaken with hydrochloric acid.

To check the degree to which methanol distributed from the aqueous phase to the aromatic hydrocarbon phase 10 ml. of benzene and 30 ml. of aqueous methanol were shaken for several hours and then rotated at 25° overnight. The ultraviolet spectrum of the benzene layer was measured and compared to that measured for pure benzene over a wave length region (280–290 mμ) in which the aqueous methanol had no absorption. The blank solution in these measurements was ethanol. The optical densities of the benzene which had been equilibrated with aqueous methanol were approximately 3% less than those of pure benzene, a fact which suggests that the activity of the aromatic hydrocarbon phase in the distribution studies is essentially that of pure hydrocarbon. This conclusion is supported by an earlier study of the ternary system water–ethanol–benzene, which shows that the benzene phase which is in equilibrium with a solution approximately equimolar in water and methanol contains less than three per cent. methanol by weight.[10]

Results

The observed variations in the solubilities of the hydrocarbons in equimolar water–methanol (μ = 0.5) with changes in silver ion concentration (0–0.5 M) have all been explained on the assumption that the only equilibrium established in the solvent phase with respect to formation of a coördination compound is that given by equation 1

$$\mathrm{Ar} + \mathrm{Ag}^+ \rightleftarrows \mathrm{AgAr}^+ \quad K_1 = (\mathrm{AgAr}^+)/(\mathrm{Ar})(\mathrm{Ag}^+) \qquad (1)$$

No evidence that appreciable quantities of $\mathrm{ArAg_2}^{++}$ exist in the solutions at equilibrium has been obtained, although this ion has been encountered in previous work on the argentation of simple benzenes in aqueous media and of polycylic aromatics in aqueous ethanol.[3,4,6,11] Argentation constants, K_1, have been calculated from recorded solubility data using equation 2

$$K_1 = (\mathrm{Ar_c})/[(\mathrm{Ag_t}^+) - (\mathrm{Ar_c})](\mathrm{Ar}) \qquad (2)$$

In this equation (Ar) and (Ar$_c$) represent, respectively, the molar concentrations of free and complexed hydrocarbon in solution at equilibrium. The former is taken as equivalent to the solubility of the hydrocarbon in a 0.5 M solution of sodium nitrate in equimolar water–methanol, and the latter is calculated as the difference between the total concentration of aromatic substance in solution at equilibrium (Ar$_t$) (measured experimentally) and (Ar). The term (Ag$_t^+$) represents the total concentration of silver ion in the medium. Typical data illustrating the constancy of K_1 with changes in silver ion concentration are given in Table I.

TABLE I

THE SOLUBILITY OF AROMATIC HYDROCARBONS IN EQUIMOLAR WATER–METHANOL SILVER NITRATE SOLUTIONS AT 25.0[a]

(Ag$_t$ $^+$), mole/l.	(Ar$_t$), mole/l.	K$_1$, l./mole	(Ar$_t$), mole/l.	K_1, l./mole	(Ar$_t$), mole/l. × 100	K_1, l./mole
	Benzene		*m*-Xylene		*m*-Diethylbenzene	
0.000	0.630		0.108		6.89	
.100	...	..	.120	1.26	7.56	1.04
.200	.711	1.08	.135	1.45	8.30	1.10
.300	.752	1.09	.146	1.34	8.87	1.03
.400	.795	1.11	.159	1.35	9.57	1.04
.500	.835	1.10	.171	1.33	10.33	1.07

[a] Ionic strengths adjusted to 0.5 with sodium nitrate.

The K_1 values reported in Table II summarize all of the data recorded for the various hydrocarbons at 25.0 and 1.6°. They represent the

TABLE II

ARGENTATION CONSTANTS OF AROMATIC HYDROCARBONS IN EQUIMOLAR WATER–METHANOL AT μ = 0.5

Compound	Wave length,[a] mμ	Mol. extinction coefficient[b]	Solubility of Ar in 0.5 M NaNO$_3$, mole/l. × 100	K_1, l./mole
		Temp. 25.0°		
Benzene	273	0.602	63.0	1.10
Toluene	278	1.74	33.0	1.19
Ethylbenzene	277	2.14	17.4	0.98
Isopropylbenzene	275	4.96	9.54	1.01
t-Butylbenzene	274	5.94	6.28	0.90
o-Xylene	280	3.36	11.9	1.43
m-Xylene	281	4.42	10.8	1.35
p-Xylene	285	2.63	16.8	1.14
m-Diethylbenzene	279	4.88	6.89	1.06
m-Diisopropylbenzene	275	27.7	1.70	0.93
p-Di-*t*-butylbenzene	272	198	0.194	.62
Mesitylene	283	3.98	7.79	.80
1,2,4-Trimethylbenzene	285	7.87	5.76	1.30
1,3,5-Triethylbenzene	279	28.7	1.66	0.65
1,2,4-Triethylbenzene	282	25.0	1.92	1.18
1,3,5-Triisopropylbenzene	275	50.6	0.845	0.63
1,3,5-Tri-*t*-butylbenzene	230	333	0.120	.32
1,2,4,5-Tetramethylbenzene	286	32.0	1.22	.88
1,2,3,5-Tetramethylbenzene	285	10.8	4.54	.88
1,2,3,4-Tetramethylbenzene	285	7.30	5.02	1.69
1,2,4,5-Tetraethylbenzene	285	47.5	0.785	0.75
1,2,3,5-Tetraethylbenzene	282	62.4	.754	.74
1,2,3,4-Tetraethylbenzene	282	59.5	.871	1.05
Pentamethylbenzene	285	41.1	1.05	1.14
Pentaethylbenzene	285	94.3	0.417	0.95
Hexamethylbenzene	272	209	.109	.63
Hexaethylbenzene	238	4000	.0146	.36
p-Chlorotoluene	288	2.97	14.0	.17
		Temp. 1.6°		
Benzene	273	0.602	45.9	1.66
Toluene	278	1.74	25.1	1.76
Mesitylene	282	7.10	5.17	1.22
1,3,5-Tri-*t*-butylbenzene	228	1030	0.0477	0.52
Hexamethylbenzene	272	209	.0335	1.03

[a] Used in optical density measurements of Skellysolve extracts. [b] For the pure hydrocarbon in Skellysolve at the wave length given in the previous column.

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[10] M. J. Barbaudy, *Compt. rend.*, **182**, 1279 (1926).

[11] R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 640 (1952).

average values of K_1 recorded over a range of at least four different silver ion concentrations as typified by the data of Table I. Frequently (Ar) values at 0.1 M silver ion concentration do not deviate sufficiently from those at 0.0 M silver ion concentration to be useful in the determination of K_1. The errors of the method do not appear to be as serious as those encountered by Kofahl and Lucas[6] in the study of less soluble hydrocarbons. In general K_1 values reported in Table II agree within 5% with at least three of the individual values calculated from the data taken at varying concentrations of silver ion.

The free energies of formation of the iodine and iodine monochloride complexes of polyalkylbenzenes (except for unusual cases in which the alkyl groups constitute a strong steric barrier) vary in linear fashion with the number of alkyl groups on the aromatic nucleus.[1,2] No such uniform variations are observed in the present study as indicated by Fig. 1 in which the logarithms of the argentation constants are plotted against the number of alkyl substituents on the benzene ring. If the aromatic nucleus functions as an electron donor in coordinating with silver ion, as it apparently does in its interactions with halogens, one may anticipate from electronic considerations that the stabilities of the silver ion complexes should be favored by increasing alkylation of the donor molecule. Conversely an electron withdrawing chlorine substituent on the benzene ring should be unfavorable to the coördination. Actually K_1 for *p*-chlorotoluene (0.17) is much less than that (1.19) for toluene.

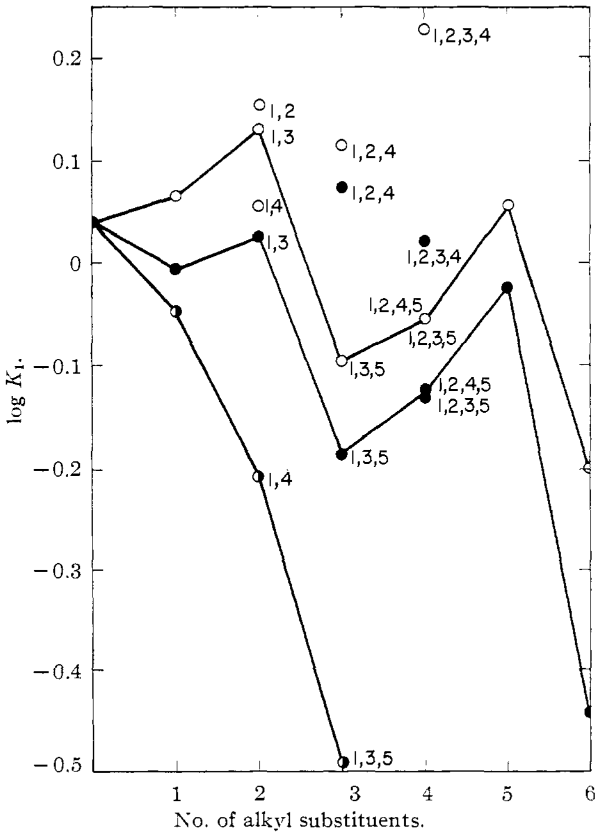

Fig. 1.—Variations in log K_1 with the number of alkyl substituents on the benzene ring: ○, methylbenzenes; ●, ethylbenzenes; ◑, *t*-butylbenzenes.

The erratic variations in log K_1 with changes in the number and positions of ring alkyl substituents are, therefore, best interpreted as reflections of opposing electronic and steric effects of the substituents. Since the solvation sphere of silver ion in a hydroxylic medium very likely includes several solvent molecules,[12] it is not surprising that the stabilities of the silver ion complexes are more susceptible to such steric influences than are those of the halogens.

For those two donors (hexaethylbenzene and 1,3,5-tri-*t*-butylbenzene) in which the alkyl groups serve as most effective shields to coördination of halogens[1,2] with the electrons of the aromatic ring the argentation constants are very small. The *t*-butyl group steric effect is apparent even in the observed argentation constant for *p*-di-*t*-butylbenzene. The effects on log K_1 of methyl and ethyl substituents both with regard to number and position are closely parallel as is shown by comparison of the lines drawn through data for similarly constituted polymethyl- and polyethylbenzenes. The methyl substituted compounds are slightly more stable than their ethyl analogs. The fact that the K_1 values for the 1,2,4-trisubstituted methyl and ethylbenzenes are more than those of their 1,3,5-isomers may be contrasted with the observation that the stabilities of HCl, HF and HF–BF_3 complexes of the trimethylbenzenes (which presumably are not subject to steric repression by methyl groups) are in the opposite order.[13–15] Similarly the hydrogen halide complexes of 1,2,3,5-tetramethylbenzene are the most stable of those of the tetramethylbenzenes whereas the 1,2,3,4-isomers show the largest argentation constants. Evidently the most favorable donor configuration for argentation is that in which ring substituents are packed together at adjacent carbons. The suggestion of Mulliken[16] that areas of the aromatic nucleus immediately adjacent to alkylated ring carbons are sterically unfavorable as coördination sites for silver ion is in accord with present observations. According to the Mulliken view, which is supported by the comments of Rundle and Goring[17] concerning the crystal structure of the silver perchlorate–benzene complex, silver ion will coördinate preferentially above and between two adjacent unsubstituted ring carbons when such positions are available. It is not clear from the present results whether this perimetric location is preferred to a more symmetric one when all positions between adjacent carbons are equivalent (as is the case with benzene and 1,3,5-trialkylbenzenes).

Isopropyl substituents on the benzene ring seem to have about the same influence on silver ion complex stabilities as do ethyl substituents. Points for log K_1 values *versus* the number of alkyl groups for

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(12) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 107.

(13) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(14) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(15) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(16) R. S. Mulliken, *ibid.*, **74**, 821 (1952).

(17) R. E. Rundle and J. H. Goring, *ibid.*, **72**, 5337 (1950).

isopropyl-, *m*-diisopropyl- and 1,3,5-triisopropylbenzenes, which have been omitted from Fig. 1 to avoid crowding of data, lie close to the points for the ethyl analogs.

Thermodynamic Constants for the Argentation Reactions.—Values of $\Delta H°$ for a few of the argentation reactions have been calculated from equilibrium constants determined at 1.6 and 25.0°. These and the changes in free energy and entropy accompanying the interactions at 25° are recorded in Table III. These values encompass the process of silver ion desolvation which accompanies complex formation,[18] and only the changes in constants resulting from changes in donor structure are significant in this discussion.

In the absence of pronounced alkyl group steric effects, $\Delta H°$ for the interaction of halogens[1,2] with polyalkylbenzenes becomes increasingly negative as the number of donor substituents increases. Parallel decreases in $\Delta F°$ and $\Delta S°$ occur, and these changes are linear with those in $\Delta H°$. With the highly hindered donors, hexaethylbenzene and 1,3,5-tri-*t*-butylbenzene, $\Delta H°$, $\Delta S°$ and $\Delta F°$ are all abnormally small in magnitude. Apparently in these two cases the complexed halogen molecules are held outside the steric barrier at a distance such that they can interact only feebly with the electrons of the donor molecule.

TABLE III

HEAT, FREE ENERGY AND ENTROPY CHANGES ACCOMPANYING AROMATIC-SILVER ION COMPLEX FORMATION IN EQUIMOLAR WATER–METHANOL SOLUTION

Compound	$-(\Delta H°)$ at 1.6, 25.0°, kcal.	$-(\Delta F°)$ at 25.0°, kcal.	$-T(\Delta S°)$ at 25.0°, kcal.	$-(\Delta S°)$ at 25.0°, cal./deg.
Benzene	2.86	0.06	2.80	9.40
Toluene	2.72	.11	2.61	8.77
Mesitylene	2.93	− .14	3.07	10.3
1,3,5-Tri-*t*-butylbenzene	3.29	− 67	3.96	13.3
Hexamethylbenzene	3.45	− .27	3.72	12.5

The $-\Delta H°$ values for argentation reported in Table III show a slight upward trend with increasing alkylation of the donor nucleus which is paralled by a corresponding increase in $-\Delta S°$ values. The variations in $\Delta F°$ with $\Delta H°$ show no regularity. The coördination of silver ion with the highly hindered donor, tri-*t*-butylbenzene, is accompanied by a larger entropy loss than is that with less hindered donors. It seems likely, therefore, that in the argentation reaction, contrary to what is observed for halogen complex formation, as steric repression to interaction becomes more pronounced, the complex components are subject to more rigid spatial requirements. There is no indication that the distance of separation of silver ion and the aromatic nucleus in the complex is greatly dependent on the number and size of alkyl substituents on the donor ring.

Acknowledgment.—The authors are indebted to Research Corporation and to the National Science Foundation for grants in support of this research.

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(18) S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Benzil–Ammonia Reaction

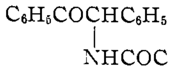
BY ERNEST WENKERT AND ARLEN B. MEKLER

RECEIVED OCTOBER 29, 1955

The reaction of benzil with ammonia is interpreted as involving the ionic cleavage of benzil–ammonia complexes containing two benzil units. The structural elucidation of imabenzil, the one as yet unknown product of the reaction, is presented.

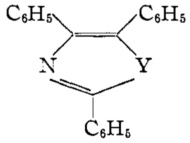
The action of ammonia on benzil, leading to a variety of products, has been known for over a century.[1] With the exception of imabenzil, a C_{35}-compound, the structures of all reaction products are well understood. Depending on the temperature, time and solvent of the reaction, various combinations of the following products have been isolated: ammonium benzoate (Ia), ethyl benzoate (Ib), benzamide (Ic), N-desylbenzamide (II), imabenzil and the three aromatic heterocycles 2,4,5-triphenyloxazole (IIIa), 2,4,5-triphenylimidazole (IIIb) and 2,3,5,6-tetraphenylpyrazine (IV).

C_6H_5COY
Ia, $Y = O^{\ominus}, NH_4^{\oplus}$
b, $Y = OEt$
c, $Y = NH_2$

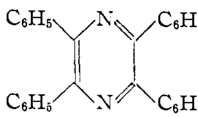


$$C_6H_5CO\underset{\displaystyle NHCOC_6H_5}{\underset{|}{C}}HC_6H_5$$

II



IIIa, $Y = O$ b, $Y = NH$



IV

In previous discussions of the mode of formation of compounds I–III, it has been suggested that a solvolytic cleavage of the central carbon–carbon bond in benzil is reponsible for the production of the benzoic acid derivatives of structure I[1a,c] and that the accompanying benzaldehyde

$$C_6H_5COCOC_6H_5 + HY \longrightarrow C_6H_5COY + C_6H_5CHO$$

becomes the precursor of II and III because of its reaction with benzil and ammonia.[1a] An alternate proposal[1b] involved the solvolytic cleavage of a carbon–carbon bond in a benzil–ammonia complex, an "internal Cannizzaro reaction" of the interme-

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[1] (a) For a complete review of the literature *cf.* R. H. Wiley, *Chem. Revs.*, **37**, 415 (1945). For the most recent contributions on this subject *cf.* (b) D. Davidson, M. Weiss and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937); (c) W. B. Leslie and G. W. Watt, *ibid.*, **7**, 73 (1942).