[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Decomposition of Diacyl Hydroxylamines and Hydrazines[1]

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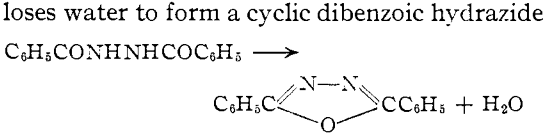
N,O-Dibenzoylhydroxylamine decomposes rapidly in refluxing toluene by a first-order process initially to phenyl isocyanate and benzoic acid. The major reaction is evidently a straightforward Lossen rearrangement, and the effect of *p*-substituents on the benzene ring and kinetic isotope effect suggest a rapid equilibrium to a zwitterion and a phenyl-bridged transition state in the decomposition. There is also a parallel radical decomposition, capable of initiating the polymerization of methyl methacrylate, which accounts for about 1% of the total reaction. The photochemical decomposition of dibenzoylhydroxylamine involves homolytic scission of the N–O bond, gives rise to quite different products, and serves as an efficient initiating process for polymerization. Evidence has also been obtained for some radical production in the thermal and photochemical decomposition of a number of other hydroxylamine and hydrazine derivatives.

The bond dissociation energies D(HO–OH) and $D(H_2N–NH_2)$ are reported as 54 and 60 kcal., respectively,[2] and $D(HO–NH_2)$ might be expected to have an intermediate or similar value. Diacylation of hydrogen peroxide reduces the bond dissociation energy to approximately 30 kcal., and benzoyl peroxide is widely used as a source of free radicals in the temperature range of 60–100°. A similar radical dissociation of diacylhydroxylamines and hydrazines at slightly higher temperatures should be anticipated. In support of this view, the bond dissociation energy of *sym*-dibenzoylhydrazine has been estimated as 36.2 kcal.[3] although the basis of the calculation seems open to some question, and the compound has been disclosed as an initiator for ethylene polymerization at 200–240°.[4] Further evidence for the weakness of the N–N bond in highly substituted hydrazines is the reversible dissociation of tetraarylhydrazines near room temperature first described by Wieland.[5]

In contrast to these observations, the products obtained on the decomposition of diacylhydroxylamines and hydrazines are generally considered to arise *via* polar paths. In 1872, Lossen[6] reported that N,O-dibenzoylhydroxylamine, heated above its melting point, yields phenyl isocyanate. A complex mixture of other products including benzoic acid, benzanilide, carbanilide (*sym*-diphenylurea) and CO_2 are formed as well.[7] This "Lossen rearrangement" occurs more cleanly and at a lower temperature when a salt of the diacylhydroxylamine (or O-acylhydroxylamine acid) is heated in alkaline solution, and it is under these conditions that the reaction has usually been studied.[8] When dibenzoylhydrazine is heated to 350°, it loses water to form a cyclic dibenzoic hydrazide[9]



$$C_6H_5CONHNHCOC_6H_5 \longrightarrow C_6H_5C\langle N{-}N \rangle CC_6H_5 \text{ (via O) } + H_2O \quad (1)$$

but, on sudden heating to 450°, it decomposes to benzonitrile, aniline and carbon dioxide, products for which a path analogous to the Lossen rearrangement is suggested.[9] As will be remarked later, certain diacyl peroxides[10,11] also undergo Lossen type rearrangements at rates which compete with their thermal decomposition into radicals. In order to clarify the situation, we have reinvestigated the decomposition of a series of diacylhydroxylamines and hydrazines and some related compounds. In non-polar solvents diacylhydroxylamines decompose by what kinetics and products indicate to be a straightforward Lossen rearrangement, but there is evidently a small amount of radical scission as well, since the systems initiate vinyl polymerization. In contrast, photochemical decomposition gives products anticipated from a radical decomposition and serves as an efficient photoinitiator of vinyl polymerization. Evidence for radical formation from series of hydrazine derivatives (with the exception of tetraphenylhydrazine) is less conclusive and apparently thermal dissociation occurs only at higher temperatures.

Products and Kinetics of the Decomposition of Diacylhydroxylamines. — Dibenzoylhydroxylamine has been found to decompose quite rapidly in refluxing toluene. Table I lists products isolated after various times of heating. Evidently the starting material has almost completely disappeared in four hours and the initial products are those of the Lossen rearrangement

$$C_6H_5CONHOCOC_6H_5 \longrightarrow C_6H_5NCO + C_6H_5COOH \quad (2)$$

as shown both by their isolation, and the high yield of *o*-methoxycarbanilide when the reaction is carried out in the presence of *o*-anisidine. On longer heating, both phenyl isocyanate and benzoic acid disappear, and the more complex products formed are those expected from their interaction, presumably *via* the formation of the mixed anhydride

$$C_6H_5NCO + C_6H_5COOH \longrightarrow C_6H_5NHCOOCOC_6H_5 \quad (3)$$

and its subsequent decomposition.[12] Since phenyl isocyanate is relatively stable under the reaction conditions employed, the rate of the initial rearrangement can be followed conveniently by an isocyanate titration. The technique employed involves adding excess aniline to an aliquot of the re-

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[1] Taken from the Ph.D. Dissertation of Anthony N. Naglieri, Columbia University, 1959. Support of this work by a contract with the Office of Ordnance Research, U. S. Army is gratefully acknowledged.

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 48.

[3] L. G. Cole and E. C. Gilbert, THIS JOURNAL, **73**, 5423 (1951).

[4] J. R. Roland and J. Harmon, U. S. Patent 2,433,015, December 23, 1947.

[5] H. Wieland, *Ann.*, **381**, 200 (1911).

[6] W. Lossen, *ibid.*, **161**, 347 (1872).

[7] F. Pieschel, *ibid.*, **175**, 305 (1875).

[8] H. L. Yale, *Chem. Revs.*, **33**, 209 (1943).

[9] E. C. Gilbert, THIS JOURNAL, **49**, 286 (1927).

[10] J. E. Leffler, *ibid.*, **72**, 67 (1950).

[11] P. D. Bartlett and F. D. Green, *ibid.*, **76**, 1088 (1954).

[12] W. Dieckmann and F. Breest, *Ber.*, **39**, 3052 (1906); C. Naegeli and A. Tyabayi, *Helv. Chim. Acta*, **17**, 931 (1934); **18**, 142 (1935); A. Fry, THIS JOURNAL, **75**, 2686 (1953).

TABLE I

PRODUCTS FROM THE DECOMPOSITION OF DIBENZOYLHYDROXYLAMINE IN REFLUXING TOLUENE

	Mole % based on hydroxylamine			
Time, hours	4	4[a]	48	48
Starting material	1	..	..	..
Benzoic acid	91.5	89	[b]	6.1
Phenyl isocyanate	89.5	..	[c]	[c]
Carbanilide	[b]	..	20.3	30
Benzanilide	..	..	23	1
Triphenylbiuret	..	..	25	14
CO_2	2.2	0	30.6	..
Benzoic anhydride	..	..	[b]	..

[a] In presence of 0.98 equivalent *o*-anisidine; in addition 91% *o*-methoxycarbanilide was isolated. [b] Qualitatively isolated and identified. [c] Odor detected, but material not isolated.

action mixture and determining the aniline not consumed by the reaction

$$C_6H_5CO + C_6H_5NH_2 \longrightarrow C_6H_5NHCONHC_6H_5 \quad (4)$$

by titration with perchloric acid in acetic acid. Results obtained in this way showed the decomposition to be cleanly first order over at least two half-lives, and the data of a typical experiment are shown in Fig. 1.

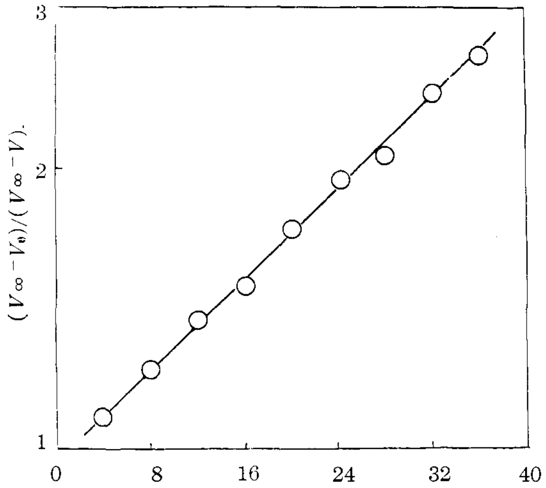


Fig. 1.—Decomposition of N-benzoyl-O-(*p*-nitrobenzoyl)-hydroxylamine. Ordinate scale is in ml. of acid used in titration (see text).

First-order constants for dibenzoylhydroxylamine and some of its *p*-substituted derivatives are listed in Table II. Qualitatively, the variations in rate with structure and experimental conditions are consistent with former data on the decomposition of the dibenzoylhydroxylamine anion in basic solution[13,14] and the accepted formulation of the Lossen rearrangement. However, they show a number of features which give further insight into the detailed path of the reaction in non-polar solvents: 1. The reaction is quite rapid, with a half-life of the hydroxylamine of approximately one hour at 114° and forty-two hours at 83°. If the change from one aromatic hydrocarbon solvent to another can be ignored, this temperature coefficient corresponds to an activation energy of 33 kcal. The activation energy for decomposition of the anion in aqueous solution, in comparison, is 26.5 kcal., and extrapolation of data at 30–40°[14] to 83° indicates $k_{83} = 0.017$ sec.$^{-1}$ (Hauser's data are in min.$^{-1}$), some 3700 times our value in benzene. 2. The decomposition is accelerated 2.3-fold by the presence of aniline, presumably by a moderate base catalysis. 3. Substitution of deuterium for hydrogen on nitrogen only slightly retards the decomposition, $k_H/k_D = 1.29$. 4. Electron-supplying substituents on the N-benzoyl group strongly accelerate the decomposition, while electron-withdrawing groups retard. The magnitude of the effect is about 40% of that noted by Hauser[13] for the anion where the Hammett ρ-value of the reaction has been calculated[15] as −2.6. However, it should be noted that our experiments are at a higher temperature. 5. Substituents on the O-benzoyl group have a negligible effect on rate, significantly less than in the case of the anion decomposition[13] where $\rho = 0.865$.[15]

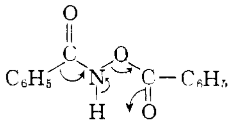
TABLE II

FIRST-ORDER RATE CONSTANTS FOR DECOMPOSITION OF DIBENZOYLHYDROXYLAMINES $RC_6H_5CONHOCOC_6H_5R'$ IN TOLUENE

Run	R	R'	*T*, °C.	*k*, sec.$^{-1}$ × 10^4
1	H–	H–	114	1.94
2	H–	H–	113	1.72
3	H–	H–	112	1.51
4	*p*-CH_3O–	H–	114	5.26
5	H–	*p*-CH_3O–	115	2.29
6	*p*-CH_3O–	*p*-NO_2–	114	10.3
7	H–	*p*-NO_2–	114	2.70
8	*p*-NO_2–	H–	113	0.311
9	*p*-NO_2–	*p*-CH_3O–	112	.317
10[a]	H–	H–	83	.046
11[b]	H–	H–	114	4.45
12[c]	H–	H–	114	1.50

[a] Benzene solvent. [b] Excess aniline present during decomposition. [c] Deuterated compound, $C_6H_5CONDOCOC_6H_5$.

The electronic shifts considered to be involved in the Lossen rearrangement are



(5)

The hydrogen transfer is here shown as intramolecular to the carbonyl oxygen, since Leffler[16] has suggested that hydrogen bonding between these atoms provides some of the driving force for the reaction.

Points 1–5 above suggest something about the timing of the different shifts. The large effect on rate of substituents on the N-benzoyl group indicate that phenyl migration contributes considerable driving force to the reaction and must be well underway by the time the transition state is reached. On the other hand, the negligible effect of O-acyl substituents and the small isotope effect taken to-

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(13) W. B. Renfrow, Jr., and C. R. Hauser, THIS JOURNAL, **59**, 2308 (1937).

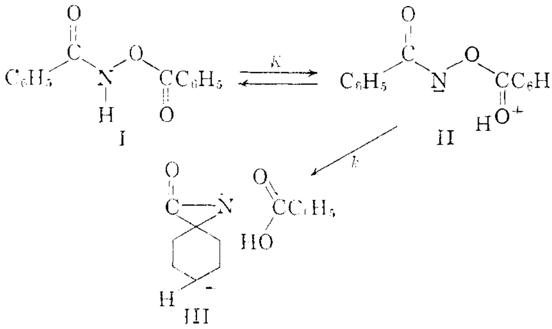
(14) R. D. Bright and C. R. Hauser, *ibid.*, **61**, 618 (1939).

(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 190–191.

(16) J. E. Leffler, THIS JOURNAL, **72**, 4294 (1950).

gether are harder to account for. At first glance they suggest that N–O and N–H bond breaking occur at a later stage in the reaction. However, no plausible phenyl-bridged intermediate in which these bonds are intact can be drawn.

The most plausible alternative which we can suggest is that proton transfer is a rapid prior equilibrium between I and II, and II then undergoes N–O bond scission to give a bridged transition state III. The small isotope effect is consistent with such an equilibrium, and one would have to assume that the effect of electron supply and withdrawal at the O-benzoyl group on the equilibrium constant K and the rate constant k essentially cancel out. In alkaline media, on the other hand, where the anion of which I and II are conjugate acids is involved, only the rate of N–O bond breaking is important.



(6)

Photochemical Decomposition of Diacylhydroxylamines.—The photolysis of dibenzoylhydroxylamine at 25° was investigated in acetone and chloroform solution using an internal low pressure mercury arc delivering most of its radiation at 2537 Å.[17] The hydroxylamine shows a strong absorption in this region with a maximum at 2338 Å. The choice of solvents was dictated by the low solubility of dibenzoylhydroxylamine in the solvents used for the thermal decomposition, although the acetone experiments are complicated by the simultaneous photolysis of solvent. Typical experiments are summarized in Table III.

TABLE III

PHOTOLYSIS OF DIBENZOYLHYDROXYLAMINE AND N-*p*-ANISOYL-O-*p*-NITROBENZOYLHYDROXYLAMINE AT 25°

	Yields in mole % of starting material			
Run	1[a]	5	6	7[e]
Solvent	Acetone	Acetone	$CHCl_3$	Acetone
Molarity	0.141	0.199	0.045	0.023
Time, hr.	48	48	120	120
Recovd. hydroxylamine	[b]	[b]	31	59
Benzoic acid	33.4	71	27	34.6
Benzamide	45	44	34	22
CO_2	17.4	8[d]	[c]	[c]
Benzene	[c]	[b]	40	23
CO	[c]	[c]	.....	[c]
C_2Cl_6	.....	.....	35	.....

[a] Experiment at approximately 80% light intensity of other runs. [b] Not determined. [c] Identified qualitatively. [d] From separate duplicate run. [e] N-*p*-Anisoyl-O-*p*-nitrobenzoylhydroxylamine at 15°; products reported as benzoic acid, benzamide and benzene are *p*-nitrobenzoic acid, *p*-methoxybenzamide and nitrobenzene.

Plainly the products of photolysis are quite different from those of the thermal decomposition. No phenyl isocyanate or carbanilide is produced; some of the O-benzoyl group appears as benzene, and, in chloroform, attack on solvent leads to hexachloroethane. In acetone, the parallel photolysis of solvent also produces carbon monoxide and considerable tar not reported in Table III. These results are consistent with an initial photolytic scission of the N–O bond

$$C_6H_5CONHOCOC_6H_5 \longrightarrow C_6H_5CO\dot{N}H + C_6H_5COO\cdot \quad (7)$$

followed by

$$C_6H_5CO\dot{N}H + RH \longrightarrow C_6H_5CONH_2 \quad (8)$$

$$C_6H_5COO\cdot + RH \longrightarrow C_6H_5COOH + R\cdot \quad (9)$$

$$C_6H_5COO\cdot \longrightarrow C_6H_5\cdot + CO_2 \quad (10)$$

$$C_6H_5\cdot + RH \longrightarrow C_6H_6 + R\cdot \quad (11)$$

where RH represents solvent. In chloroform $R\cdot = CCl_3$, and the trichloromethyl radicals, as would be expected, dimerize to C_2Cl_6. The sequence 7–11 is certainly in keeping with accepted formulations of other radical processes, but the possibility of some induced decomposition involving additional steps is not excluded. On the other hand, the incomplete reaction in run 6, in spite of long exposure to intense radiation and the good yield of hexachloroethane, a chain termination product, certainly shows that the photolysis is not a long-chain process.

Two further points are worth mentioning. Our results give no evidence for decomposition of the benzoylamino radical into isocyanic acid and phenyl.

$$C_6H_5CO{-}\dot{N}H \longrightarrow C_6H_5 + HNCO \quad (12)$$

Also, the highly polar substituted dibenzoylhydroxylamine which shows the most rapid thermal Lossen rearrangement undergoes the same sort of homolytic photolysis as dibenzoylhydroxylamine itself.

Polymerization Experiments.—Initiation of vinyl polymerization provides one of the most convincing and sensitive tests for free radical production in a chemical reaction. Table IV summarizes a series of experiments testing the ability of dibenzoylhydroxylamine to initiate the polymerization of

TABLE IV

POLYMERIZATION INITIATION BY DIBENZOYLHYDROXYLAMINE

Monomer	*T*, °C.	Time, hr.	[Initiator]	% polym./hr.	Blank
Methyl methacrylate	60	20	0.01	0.61[a]	0
Methyl methacrylate	80	7	.01	1.58	0
Methyl methacrylate	100	5	.005	1.70	0
Methyl methacrylate	100	5	.001	0.73	0
Methyl methacrylate	100	5	.01	2.02	0
Methyl methacrylate	160	1	.01	24.8	1.06
Methyl methacrylate	28	5	.01	>20[b,c]	0.85
Styrene	80	7	.01	0.56	0.56
Styrene	100	5	.005	2.14	2.11
Styrene	100	5	.01	2.32	2.11
Styrene	25	6.4	.005	0.49[b]	0.35
Styrene	25	6.4	.01	0.48[b]	0.35
1:1 styrene Methyl methacrylate	100	3	.1	3.76	2.36

[a] Initial rate. [b] Samples in Corex-D ampules irradiated with GE-RS sun-lamp. [c] Sample completely polymerized.

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(17) C. Walling and R. Rabinowitz, THIS JOURNAL, **81**, 1137 (1959).

methyl methacrylate and styrene. Reactions were run in sealed degassed ampules and polymerization measured by change in index of refraction. Photoinitiation of methyl methacrylate is seen to be very rapid, in keeping with our interpretation of the photolysis of the hydroxylamine as a radical process, and there also appears to be significant thermal initiation by the hydroxylamine at 60–160°. Results with styrene are less obvious, perhaps because of the competing thermal initiation by styrene itself, and the well-known fact that k_p^2/k_t (which is a measure of the amount of polymer produced per initiating radical) is considerably smaller for this monomer.[18] The final copolymerization experiment provides further evidence for the radical nature of the initiated reaction, for analysis of the product showed it to be essentially a 1:1 copolymer as anticipated for radical initiation.[19]

Plots of % polymerization *vs.* time for methyl methacrylate were linear at 80 and 100°, during the times indicated in the table, although there was considerable scatter in rate between runs at initiator concentrations below 0.01 *M*. At 60°, conversion increased linearly for approximately eight hours and then leveled off. The origin of this observation is obscure, for, unless the Lossen rearrangement of the hydroxylamine is enormously faster in methacrylate that in hydrocarbon solvents, it cannot arise from exhaustion of initiator by this path.

Providing the hydroxylamine does not act as an inhibitor as well as initiator, the actual rate of initiation in the above experiment can be calculated from the relation

$$R_i = A'R_p^2/[M]^2 \qquad (13)$$

and the values of A' for methyl methacrylate reported by Tobolsky and Ferington.[20] The experiments using 0.01 *M* initiator give R_i = 5.9 and 12.2 × 10^{-10} mole/l. sec. at 80 and 100°, respectively. Assuming two radicals per initiator and a 50% initiator efficiency, these correspond to rate constants for radical decomposition of 5.9 and 12.2 × 10^{-8} sec.$^{-1}$. While the poor reproducibility noted above makes these values only approximate, they are only about 1% of the rates of the Lossen rearrangement of the hydroxylamine given in Table II, and only 0.1% of the rate of thermal decomposition of benzoyl peroxide.[21] In short, dibenzoylhydroxylamine actually appears to decompose thermally by two parallel paths: the polar Lossen rearrangement which is the faster and accounts for the products isolated, and a radical scission, detectable only when its effect is multiplied by the initiation of some sort of chain process.

Although the order of reaction rate is reversed so that generally the radical scission is the faster process, as was noted earlier, a polar rearrangement

$$\text{RCO—O—O—COR} \longrightarrow \text{R—O—CO—O—COR} \qquad (14)$$

is also observable with some diacyl peroxides. With triptoyl peroxide, it accounts for some 16% of the decomposition, while, in the case of *p*-methoxy-*p'*-nitrobenzoyl peroxide,[10] the polar reaction becomes the dominant one in polar solvents and also shows acid catalysis.

We have also investigated more briefly the ability of some other hydroxylamines and hydrazines to act as polymerization initiators, and results with methyl methacrylate are listed in Table V. All the compounds tested, with the exception of tetraphenylhydrazine, show some activity as photoinitiators, although they are less effective than dibenzoylhydroxylamine.

TABLE V

POLYMERIZATION INITIATION OF METHYL METHACRYLATE BY OTHER HYDRAZINE AND HYDROXYLAMINE DERIVATIVES

Initiator	Mole/ l.	*T*, °C.	Time, hr.	% polymer/hr.	Blank
sym-Dimethyldiben-	0.2	30[a]	5	1.33	0.90
zoylhydroxylamine	.2	160	8	2.27	1.06
	.2	150[b]	20	1.04	0.54
	.05	150[b]	6	0.75	.54
Dibenzoylhydrazo-	.1	28[a]	5	1.13	.85
benzene	.1	60	18	0	0
	.1	160	1	6.82	1.06
N-Phthalimido-					
phthalimide	.05	150	6	0.74	0.54
Trichloroacetyl-	.1	28[a]	5	5.17	0.85
hydrazobenzene	.1	160	1	~1[c]	1.06
Tribenzoylhydrazine	.1	28[a]	5	3.34	0.85
	.1	160	1	4.89	1.06
N-Phenyldibenzoyl-					
hydroxylamine	.1	80	3	1.23	0
Tetraphenylhydrazine	.05	28[a]	5	.18	0.85
	.05	160	1	>50	1.06

[a] Photoinitiation with Ge-RS sunlamp in Corex-D ampule. [b] In presence of 0.1% hydroquinone. [c] Black solution of approximately same viscosity as blank.

N-Phenyldibenzoylhydroxylamine at 80° shows some initiation, while tetraphenylhydrazine produces rapid polymerization at 160°, a temperature at which its dissociation into radicals is known to be very rapid and reversible.[5,22] The remainder of the hydrazines (with the exception of the trichloroacetyl compound which decomposes rapidly to dark products) give a small amount of initiation at 150–160°. Evidently their decomposition into radicals is slow even at this temperature, and one is led to the conclusion that the bond dissociation energy of this class of compounds must be considerably higher than that estimated by Cole and Gilbert.[8] We believe, however, that the small differences in polymerization rate between the samples containing initiator and the blanks are real, and note that the polymerization rates of the blanks are reproducible and in good agreement with the thermal polymerization rate for methyl methacrylate reported some years ago by Walling and Briggs.[23]

Experimental

Solvents and monomers were commercial materials, dried and distilled before use.

Dibenzoylhydroxylamines were prepared as described by Hauser[13,14] and melting points agreed with those which he reports.

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[18] *Cf.* reference 2, pp. 83–85.

[19] C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950).

[20] A. V. Tobolsky and T. E. Ferington, *J. Colloid Sci.*, **10**, 536 (1955).

[21] *Cf.* reference 2, p. 478.

[22] C. K. Cain and F. Y. Wiselogle, THIS JOURNAL, **62**, 1163 (1940).

[23] C. Walling and E. R. Briggs, *ibid.*, **68**, 1141 (1946).

N-Trichloroacetylhydrazobenzene, which has not previously been reported, was obtained in an unsuccessful attempt to synthesize the bis-trichloroacetyl compound. Hydrazobenzene (5.0 g., 0.027 mole) was dissolved in 60 ml. of pyridine and 13.0 g. (0.071 mole) of trichloroacetyl chloride added dropwise under nitrogen to the cooled, stirred solution. Pyridine hydrochloride precipitated immediately and the solution turned deep red in color. After an hour, the mixture was poured into 500 ml. of cold water, and the red oil taken up in 50 ml. of benzene, dried over $CaCl_2$ and chromatographed on 200 g. of acid-washed alumina. Elution with benzene removed 0.6 g. of azobenzene. Further elution with 1:3 ether–benzene gave a brownish-yellow solid which, on recrystallization three times from 95% ethanol, yielded 2.9 g. (32%) of white crystalline N-trichloroacetylhydrazobenzene, m.p. 126.5–127° dec.

Anal. Calcd.: C, 51.01; H, 3.36; N, 8.50; Cl, 32.27. Found: C, 51.09; H, 3.60; N, 8.65; Cl, 32.47.

Other hydrazine derivatives and reference compounds were prepared by standard literature methods, and melting points were in agreement with those reported previously.

Thermal Decomposition of Dibenzoylhydroxylamines.—Workup of a typical 4-hour run was as follows: Dibenzoylhydroxylamine (0.704 g., 2.92 mmoles) was added to 60 ml. of dry toluene in a 100-ml. two-neck round-bottom flask. After the system was flushed with nitrogen, a preweighed Ascarite absorption tube was attached to the reflux condenser and the system was refluxed for four hours. An increase in weight of the Ascarite tube due to carbon dioxide was found to be 5.8 mg. (0.13 mmoles). Toluene was distilled from the solution under reduced pressure leaving an amorphous residue having a strong phenyl isocyanate odor. The residue was quickly dissolved in ether and extracted with 2% sodium hydroxide to give 0.330 g. (2.70 mmoles) of benzoic acid which was recrystallized from water and identified by mixed melting point and infrared spectrum. The ether solution was dried with magnesium sulfate and evaporated to a liquid residue containing a very small amount of white solid. The solid was separated by filtration and recrystallized from 95% ethanol, m.p. 239–242°; m.p. of authentic carbanilide, 240–242°, mixed m.p. 238–242°.

The 0.240 g. of liquid residue had a strong phenyl isocyanate odor. Its infrared spectrum in chloroform showed a strong peak at 4.5 μ indicative of an isocyanate group. Addition of aniline to the residue gave a white solid which when recrystallized from alcohol melted at 238–241°. A mixed melting point with carbanilide was 239–241°. The ultraviolet absorption spectra of both were identical with a maximum at 2570 Å.

In a typical 48-hour run, dibenzoylhydroxylamine (3.367 g., 13.9 mmoles) was suspended in 50 ml. of dry toluene. The system was flushed with nitrogen and then a preweighed Ascarite absorption tube was attached to the reflux condenser. After the solution was refluxed for 48 hours, 0.187 g. (4.25 mmoles) of carbon dioxide was obtained. When the toluene solution was cooled, 0.680 g. (2.82 mmoles) of carbanilide precipitated and was filtered and identified as previously described. A faint odor of phenyl isocyanate was noted. Addition of the above solution to 200 g. of acid-washed alumina (Fisher) and elution with benzene resulted in the isolation and identification of the following compounds in the order they appeared.

1. Traces of **benzoic anhydride**, $\text{ultraviolet}_{\text{max}}$ 2350 Å. (crude product); $\text{ultraviolet}_{\text{max}}$ of an authentic sample of benzoic anhydride is 2370 Å. Infrared spectra were identical. Two drops of aniline was added to the residue and then heated on a steam-bath for a few minutes. When the derivative was cooled, it was identified as benzanilide, m.p. 162–163°, mixed m.p. with benzanilide 161–162°.
2. **γ-Triphenylbiuret** (0.955 g., 3.47 mmoles) was recrystallized from 95% ethanol; m.p. 148–149° $\text{ultraviolet}_{\text{max}}$ 2500 Å.; authentic sample: m.p. 147–148.5°; $\text{ultraviolet}_{\text{max}}$ 2500 Å., mixed m.p. 147–148°.
3. A trace of **benzoic acid** was recrystallized from water and identified by infrared and a mixed melting point.
4. **Benzanilide** (0.648 g., 3.29 mmoles) was recrystallized from 95% ethanol; m.p. 160–163°, $\text{ultraviolet}_{\text{max}}$ 2670 Å.; authentic sample of benzanilide: m.p. 160–161°, $\text{ultraviolet}_{\text{max}}$ 2670 Å., mixed m.p. 161–163°.
5. A trace of **carbanilide** was identified as described previously.

The experiment in the presence of *o*-anisidine was worked up by removing the toluene under reduced pressure, taking up the residue in ether, and separating benzoic acid and *o*-anisidine by successive extraction with aqueous alkali and acid. The remaining ether solution, on drying and evaporation, yielded 1.38 g. (5.69 mmoles) 2-methoxycarbanilide, identified by mixed m.p. and ultraviolet spectrum.

Photochemical Decompositions.—The ultraviolet irradiation apparatus was identical to lamp No. 4 used by Rabinowitz,[17,24] except for some cases in which a larger irradiation vessel was used. The lamp was a quartz coil (8 mm. outside diameter) cold electrode type filled with approximately 4 mm. of argon and a few drops of very pure mercury. It was operated by means of a General Electric 51 G high voltage transformer. The radiation emitted is confined to the mercury resonance lines at 1849 and 2537 Å.

The reaction vessels used had volumes of approximately 160 and 750 ml. (with the lamp in them). Calibration of lamp No. 4 at 25° and a Variac setting of 70 in the 160-ml. vessel shows an intensity of 1.35×10^{20} photons/min.[24]

Nitrogen was slowly bubbled through a sintered glass disk located at the bottom of the vessel during all irradiation. The vessel was surrounded by a jacket through which water at constant temperature was circulated at high speed by means of a circulating thermostat. A condenser was attached to the system to minimize the loss of volatile materials.

In a typical acetone run, dibenzoylhydroxylamine (4.772 g., 19.8 mmoles) was photolyzed in 140 ml. of acetone. A pre-weighed Ascarite absorption tube and a trap containing 0.5% aqueous palladium chloride were attached to the system. After 48 hours irradiation at a Variac setting of 70 and 25°, the Ascarite tube had absorbed 0.151 g. (3.45 mmoles) of carbon dioxide and the palladium chloride solution contained precipitated palladium indicating the presence of carbon monoxide.

The light yellow acetone solution was distilled under reduced pressure collecting the distillate in a Dry Ice trap. The residue was an amber oil which slowly solidified. The acetone distillate was distilled through a 10″ helix packed column. A number of fractions was collected and each was examined by ultraviolet absorption in 95% ethanol. The ultraviolet spectra of the later fractions showed strong absorption peaks in the region 2300–2800 Å., identical to the ultraviolet spectrum of pure benzene in 95% ethanol. The residue was dissolved in 75 ml. of chloroform and extracted three times with 30-ml. portions of 2.5% hydrochloric acid. The combined extracts were neutralized with sodium hydroxide. After saturating the solution with salt, it was extracted with chloroform, which was then dried over sodium sulfate. The evaporation of solvent resulted in 1.08 g. (8.92 mmoles) of benzamide. The latter was recrystallized from water, m.p. 126–127°, m.p. with an authentic sample 126–128°. The infrared spectra of both were identical.

The original chloroform solution was next extracted three times with 30-ml. portions of saturated sodium bicarbonate. The combined extracts were neutralized with hydrochloric acid and extracted with chloroform. The latter was dried over sodium sulfate and upon evaporation of the solvent gave 0.806 g. (6.61 mmoles) of benzoic acid, identified by m.p., mixed m.p., and infrared spectra.

Further extraction of the chloroform solution with NaOH and evaporation of the residue gave only unidentifiable tars. Photolysis and workup of N-anisoyl-O-(*p*-nitrobenzoyl)-hydroxylamine in acetone was carried out in essentially the same manner except that the residue remaining after the removal of solvent was taken up in ether, and the nitrobenzene was finally isolated from the ether fraction and identified by infrared spectrum and its behavior on gas chromatography.

In a typical photolysis in chloroform (33.6 mmoles in 750 ml. of $CHCl_3$), CO_2 but no CO was detected. In work-up approximately 100 ml. of *n*-heptane was added to the chloroform solution which was then distilled through a 10″ helix packed column. The distillate was collected until the boiling point reached 96° (boiling point of *n*-heptane). From the optical density of the distillate at 2550 Å. it contained 13.4 mmoles of benzene. Addition of 75 ml. of

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[24] R. Rabinowitz, Thesis, Columbia University, 1958.

ether to the residue from the distillation precipitated 1.73 g. (7.17 mmoles) of dibenzoylhydroxylamine.

Extraction of the filtrate with 5% hydrochloric acid gave 1.40 g. (11.5 mmole) of benzamide. Extraction with saturated sodium bicarbonate gave 1.09 g. (9.0 mmoles) of benzoic acid and 0.80 g. (3.32 mmoles) of dibenzoylhydroxylamine. They were separated by dissolving benzoic acid in hot water and filtering. Both were identified by mixed melting points and infrared spectra. Finally the extracted ether solution was dried over sodium sulfate and evaporated. A residue of 2.80 g. (11.7 mmoles) of hexachloroethane was identified. Hexachloroethane was immediately suspected because it sublimed readily into colorless rhombic crystals. The m.p. and mixed m.p. of sublimed material in a sealed tube was 185–187°.

Kinetics of Lossen Rearrangement.—Solutions of approximately 2.0×10^{-3} *M* hydroxylamine in toluene (or benzene) were prepared in a 200-ml. three-neck round-bottom flask to which were attached a thermometer, a reflux condenser and a sampling device with a capacity of 5.55 ml. The system was flushed with nitrogen and a Drierite drying tube was attached to the condenser. As soon as the solution started to reflux (heating mantle), a sample was taken. Subsequent samples were taken at known time intervals. The refluxing temperature was controlled to ±0.2°.

The samples or aliquots were quickly poured into 250-ml. iodine flasks which contained 1.0-ml. aliquots of 2.2×10^{-3} mole/l. aniline in toluene stock solution. To each flask 35 ml. of toluene was immediately added and with occasional shaking allowed to stand for more than 15 minutes. After five drops of methyl violet (0.2 g. of methyl violet in 100 ml. of chlorobenzene) was added, the excess aniline was titrated, with magnetic stirring, to a blue end-point with standard 0.1 *N* perchloric acid in glacial acetic acid.[25] A typical rate curve, obtained by plotting the difference between the acid used in titration and that calculated as required for complete reaction, appears in Fig. 1.

Polymerization experiments were carried out in 5-ml. sealed degassed ampoules, using aliquots of standard solution of initiator in monomer, or, where the initiator showed a low room temperature solubility, by pipetting a standard solution of initiator in acetone into the ampule, evaporating the acetone, and adding a measured amount of monomer. In general, reactions were followed by opening the ampoules and determining the change in index of refraction, 1% polymerization corresponding to 9.4×10^{-4} and 5.7×10^{-4} unit, respectively, for methacrylate and styrene. The value for methacrylate is that of Walling and Briggs[23]; that for styrene was determined from a series of solutions of commercial polystyrene in monomer. The actual physical presence of polymer was demonstrated in many cases by adding some of the reacted mixture to methanol.

The copolymerization experiment (Table IV) was carried out on a larger sample containing 1:1 styrene-methyl methacrylate by volume. After 3 hours, the product was worked up essentially as described by Lewis and Mayo.[26] Analysis of the polymer showed C, 75.3; H, 7.67. The carbon analysis corresponds to 57 wt. % styrene, 43% methacrylate.

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[25] J. S. Fritz, "Acid–Base Titrations in Nonaqueous Solvents," the G. Frederick Smith Chemical Co., Columbus, Ohio, 1952, p. 9.

[26] F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

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[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Preparation and Characterization of Salts Which Contain the $B_{10}H_{13}$ Anion

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The $B_{10}H_{13}$ anion has been characterized by spectrophotometric means. Absorption maxima arise at two wave lengths, 267 and 335 mμ. Salts which contain this anion and alkali metal, tetraalkylammonium, alkyl-triphenylphosphonium, diethylammonium or triethylammonium cations have been prepared and their interconversion reactions examined.

The acidic behavior of decaborane in aqueous solution was recently recognized by Guter and Schaeffer[1] and ascribed to the operation of two distinct processes: direct ionization of decaborane as in (1) and the formation of an ion–dipole decaborane hydrate which is a strong acid(2).

$$B_{10}H_{14} + H_2O \rightleftarrows B_{10}H_{13}^{\ominus} + H_3O^{\oplus} \qquad (1)$$

$$B_{10}H_{14} + H_2O \rightleftarrows B_{10}\overset{\ominus}{H}_{14}\overset{\oplus}{O}H_2 \qquad (2)$$

$$B_{10}\overset{\ominus}{H}_{14}\overset{\oplus}{O}H_2 + H_2O \rightleftarrows B_{10}\overset{\ominus}{H}_{14}OH + H_3O^{\oplus}$$

Rationalization for the existence of the $B_{10}H_{13}$ anion may be found in the topological arguments of Lipscomb.[2]

Most recently Schaeffer and co-workers[3] have prepared the $B_{10}H_{13}$ anion in aqueous dioxane and aqueous acetonitrile by treatment of decaborane with sodium hydroxide and morpholine, respectively. These authors report two absorption maxima in the ultraviolet region which are characteristic of the $B_{10}H_{13}$ anion: 265 and 330 mμ. These results are in substantial agreement with our own. In addition to the $B_{10}H_{13}$ anion, Schaeffer, *et al.*,[3] have identified, by spectrophotometric means, the anion $B_{10}H_{15}O$ produced by the removal of a proton from the ion–dipole hydrate of decaborane as in (2) above. Under special circumstances we have also observed this species at 249 mμ.

Results and Discussion

Tetraalkylammonium Salts.—The addition of a diglyme solution of decaborane to an aqueous solution of tetramethylammonium hydroxide results in the immediate precipitation of a bright yellow, water-insoluble solid in essentially quantitative yield. Extension of this reaction to other tetraalkylammonium hydroxides gave similar insoluble materials whose elemental analyses (see Experimental) were in agreement with the following formulation where R = alkyl.

$$B_{10}H_{14} + R_4\overset{\oplus}{N}\overset{\ominus}{O}H \longrightarrow R_4\overset{\oplus}{N}B_{10}\overset{\ominus}{H}_{13} + H_2O$$

The ultraviolet absorption spectra of freshly prepared solutions of these salts in dry acetonitrile

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[1] G. A. Guter and G. W. Schaeffer, THIS JOURNAL, **78**, 3546 (1956); Abstracts of Papers, 131st Meeting, Am. Chem. Soc., Miami, Fla., p. 3R, 1957.

[2] W. N. Lipscomb, *J. Phys. Chem.*, **62**, 381 (1958), suggests the possible removal of a bridge proton to produce a two center B–B bond. Some evidence for this is to be found in deuterium exchange studies of M. F. Hawthorne and John J. Miller, THIS JOURNAL, **80**, 754 (1958).

[3] G. W. Schaeffer, J. J. Burns, T. J. Klingen, L. A. Martincheck and R. W. Rozett, Abstracts of Papers, 135th Meeting, Am. Chem. Soc., Boston, Mass., 1959 p. 44M.