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The Synthesis and Stability of Acyl Radicals; Some Reactions of Diacyl Diimides

BY RICHARD CRAMER

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Acyl radicals appear to react as units below about 100° rather than disintegrating to carbon monoxide and alkyl radicals. There is also evidence that carbon monoxide rapidly combines with simple alkyl radicals to yield acyl radicals. These conclusions are based on an examination of acyl radicals derived by: (1) disintegration of some diacyl diimides, (2) hydrogen abstraction from aldehydes by alkyl radicals and (3) carbon monoxide addition by alkyl radicals. Support is also given by theoretical and experimental work which has been reported in the literature.

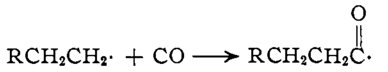
Benson[1] has estimated that in the gas phase the enthalpy change in reaction (1) is 15 ± 3 kcal. and a number of investigators have found the activation energy for this reaction to be about 16 ± 3 kcal.[2] Consequently, the reverse reaction, addition of carbon monoxide to a methyl radical, would be expected to have little or no activation energy.[1,3]

$$CH_3CO \longrightarrow CH_3\cdot + CO \quad \Delta H = 15 \pm 3 \text{ kcal.} \qquad (1)$$

If these conclusions may be projected to acyl radicals in general, then (1) acyl radicals should be easily formed from alkyl radicals and carbon monoxide and (2) acyl radicals should have sufficient stability at moderate temperatures to react as a unit instead of undergoing decarbonylation to alkyl radicals and carbon monoxide.

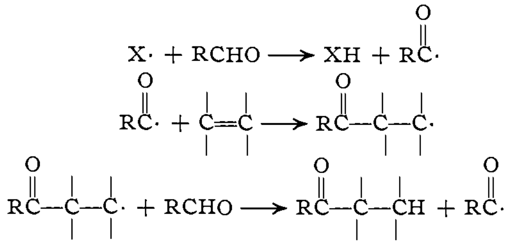
Several syntheses reported recently support these projections.

(a) It has been shown[4] that carbon monoxide and ethylene copolymerize to give polyketones. This polymerization evidently proceeds through reaction 2. The composition of these polyketones changes with the pressure applied to the gas mixture from which they are synthesized, and Walling[5] has pointed out that this can be explained on the assumption that during copolymerization equilibrium is attained in reaction 2. Apparently, carbon monoxide adds to alkyl radicals faster than ethylene does and reaction 2 probably has a lower activation energy than reaction of alkyl radicals with ethylene (about 2–3 kcal.).[6]



$$RCH_2CH_2\cdot + CO \longrightarrow RCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}\cdot \qquad (2)$$

(b) Acyl radicals obtained by removal of an aldehyde hydrogen will, under appropriate conditions, add to an olefinic bond with little or no loss of carbon monoxide.[7] This reaction is one step of a chain reaction which with certain aldehydes and ethylenic compounds gives good yields of acylated products.[8] The steps involved in the synthesis are



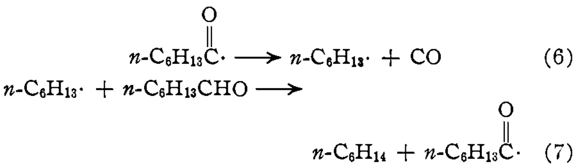
$$X\cdot + RCHO \longrightarrow XH + R\overset{\overset{\displaystyle O}{\|}}{C}\cdot \qquad (3)$$

$$R\overset{\overset{\displaystyle O}{\|}}{C}\cdot + \overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot \qquad (4)$$

$$R\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot + RCHO \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}H + R\overset{\overset{\displaystyle O}{\|}}{C}\cdot \qquad (5)$$

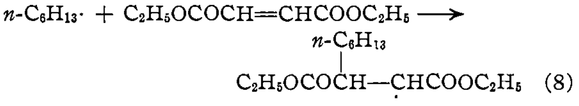
An examination, in this Laboratory, of the addition of heptaldehyde to diethyl maleate to give diethyl heptanoylsuccinate according to the reactions of equations 3 to 5 showed that at 85°, following Patrick's procedure[8] with benzoyl peroxide as initiator, about 70 molecules of ester and aldehyde reacted per molecule of benzoyl peroxide. No carbon monoxide was evolved, indicating that under these conditions acyl radicals derived from heptaldehyde are relatively stable.

When attempts were made to add heptaldehyde to diethyl maleate at 135° with di-*t*-butyl peroxide as initiator, decarbonylation occurred. Carbon monoxide was evolved, and *n*-hexane was formed. Probably reactions 6 and 7 were involved in the decarbonylation. About 30 molecules of heptaldehyde were decarbonylated for each molecule of di-*t*-butyl peroxide used. There was little addition of hexyl radicals to diethyl maleate indicating reaction 7 is faster than reaction 8 under these conditions.



$$n\text{-}C_6H_{13}\overset{\overset{\displaystyle O}{\|}}{C}\cdot \longrightarrow n\text{-}C_6H_{13}\cdot + CO \qquad (6)$$

$$n\text{-}C_6H_{13}\cdot + n\text{-}C_6H_{13}CHO \longrightarrow n\text{-}C_6H_{14} + n\text{-}C_6H_{13}\overset{\overset{\displaystyle O}{\|}}{C}\cdot \qquad (7)$$



$$n\text{-}C_6H_{13}\cdot + C_2H_5OCOCH{=}CHCOOC_2H_5 \longrightarrow C_2H_5OCO\underset{}{\overset{\overset{\displaystyle n\text{-}C_6H_{13}}{|}}{C}}H{-}\underset{\cdot}{C}HCOOC_2H_5 \qquad (8)$$

Likewise, Winstein and Seubold[9] found that the acyl radical obtained by abstracting the aldehyde hydrogen of 3-methyl-3-phenylbutyraldehyde decarbonylated at 130° but was relatively stable at 80°.

(c) The carboxylation of organic compounds with carbon monoxide and hydroxyl radicals[10] ap-

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[1] S. W. Benson, Bulletin from Armed Services Technical Information Agency at Knott Bldg., Dayton 2, Ohio, First Technical Report on Project "Energy Transfer Processes in Reaction Kinetics," AD 19167.

[2] E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939); D. S. Herr and W. A. Noyes, THIS JOURNAL, **62**, 2052 (1940); S. W. Benson and G. S. Forbes, *ibid.*, **65**, 1399 (1943); A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1811 (1952); D. H. Volman and W. M. Graven, THIS JOURNAL, **75**, 3111 (1953).

[3] G. B. Porter and S. W. Benson, *ibid.*, **75**, 2773 (1953).

[4] (a) M. M. Brubaker, U. S. Patent 2,495,286, Jan. 24, 1950; (b) M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952); (c) D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood and H. S. Young, *ibid.*, **74**, 3391 (1952).

[5] C. Walling, *J. Polymer Sci.*, **16**, 315 (1955).

[6] M. J. Roedel, THIS JOURNAL, **75**, 6110 (1953); H. W. Melville and J. C. Robb, *Proc. Roy. Soc. (London)*, **202A**, 198 (1950).

[7] C. H. Stiteler and J. R. Little, U. S. Patent 2,517,732, Aug. 8, 1950; M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949); T. M. Patrick, *ibid.*, **17**, 1009 (1952).

[8] *Organic Syntheses*, **34**, 51 (1954).

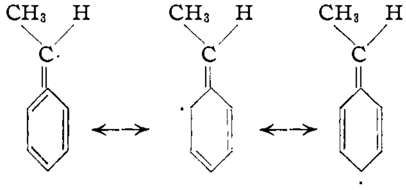
[9] S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947).

[10] D. D. Coffman, U. S. Patent 2,687,432, Aug. 24, 1954.

parently involves the very fast addition of carbon monoxide to alkyl radicals. Since carboxylation proceeds rapidly at room temperature, a low energy of activation is indicated for formation of acyl radicals.

(d) The combination of methyl radicals and carbon monoxide has been noted by Faltings[11] in the irradiation of ethane–carbon monoxide mixtures at ordinary temperatures and pressures to yield acetone.

Although acyl radicals lose carbon monoxide at 130°, this reaction can be reversed, at least with some structures, if carbon monoxide is supplied at a sufficiently high pressure. Thus, ethylene and carbon monoxide copolymerize at 260° when pressures around 600 atm. are used.[4b] Likewise, in experiments described in this paper, ethyl radicals obtained by pyrolysis of tetraethyllead at 200° have been found to combine with carbon monoxide at a pressure of 1000 atm. to give diethyl ketone. On the other hand, α-phenylethyl radicals did not combine with carbon monoxide under the same pressure and at a somewhat lower temperature (150°). α-Phenylethyl radicals were prepared by abstraction of hydrogen from ethylbenzene with alkyl radicals obtained through thermal decomposition of di-*t*-butyl peroxide. α-Phenyl ethyl radicals are known to have been formed because 2,3-diphenylbutane was isolated from the reaction mixture. It may be that the α-phenylethyl radical is stabilized through resonance and so does not add carbon monoxide readily.



However, if the α-phenylethyl radical is resonance stabilized, the stabilization is not so great as to bring about easy decarbonylation of the α-phenylpropionyl radical at temperatures near 60°. α-Phenylpropionyl and propionyl radicals were obtained from the corresponding diacyl diimides, and some of the properties of the imides and acyl radicals were studied.

Chemistry of Diacyl Diimides.—Diacyl diimides were prepared through a series of reactions similar to that employed by Stolle[12] and summarized in equations 9 to 11.

$$2RCOCl + H_2NNH_2 \longrightarrow (RCONH)_2 \qquad (9)$$

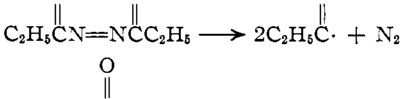
$$(RCONH)_2 + HgCl_2 \longrightarrow (RCON)_2Hg \qquad (10)$$

$$(RCON)_2Hg + Br_2 \text{ or } I_2 \longrightarrow RCON{=}NCOR \qquad (11)$$

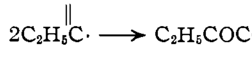
Bis-(α-phenylpropionyl)-diimide was obtained as a red oil containing about 70% diimide as determined by the volume of nitrogen liberated when samples were heated.[13] The gas evolved in thermal decomposition of crude bis-(α-phenylpropionyl)-diimide, which occurs smoothly at 60°, is nitrogen. Absence of carbon monoxide indicates that α-phenylpropionyl radicals are stable under these conditions. Since bis-(α-phenylpropionyl)-diimide catalyzes the polymerization of styrene, and the resulting polymer after repeated solution and reprecipitation absorbs infrared radiation in the carbonyl region, there appears little doubt that α-phenylpropionyl radicals are formed in thermal decomposition of the diimide.

Dipropionyldiimide was obtained as yellow crystals which melted to a red liquid at −25 to −24°. It decomposed (1) within an hour when heated at 140°, (2) in the presence of such compounds as water, alcohols and acetic acid or (3) when treated with bromine. In the course of all these decompositions the amount of nitrogen evolved approached but did not exceed 0.5 mole per mole of dipropionyldiimide, but no carbon monoxide was obtained.

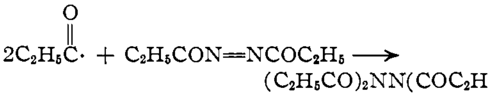
The probable primary reaction is formation of propionyl radicals and nitrogen (equation 12).



$$C_2H_5\overset{O}{\overset{\|}{C}}N{=}N\overset{O}{\overset{\|}{C}}C_2H_5 \longrightarrow 2C_2H_5\overset{O}{\overset{\|}{C}}\cdot + N_2 \qquad (12)$$



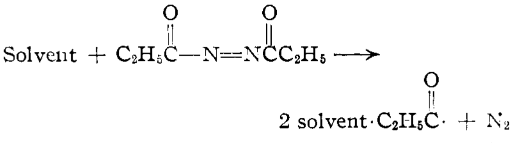
$$2C_2H_5\overset{O}{\overset{\|}{C}}\cdot \longrightarrow C_2H_5COCOC_2H_5 \qquad (13)$$



$$2C_2H_5\overset{O}{\overset{\|}{C}}\cdot + C_2H_5CON{=}NCOC_2H_5 \longrightarrow (C_2H_5CO)_2NN(COC_2H_5)_2 \qquad (14)$$

The propionyl radicals may dimerize (equation 13) or add to dipropionyldiimide (equation 14). The ability of acyl radicals to add to doubly bonded nitrogen atoms has been demonstrated by Huisgen and Jacob[14] in the radical-catalyzed additions of aldehydes to azodiformic ester.

Dipropionyldiimide resembles dibenzoyldiimide[15] in its rapid reaction with certain nucleophilic solvents. This is illustrated in Table I in which the time for reaction with several compounds is given. The detailed course of the reaction is uncertain. However, 1,2-dipropionylhydrazine, a volatile substance containing the propionyl group (probably propionic acid or methyl propionate), and nitrogen were obtained in the reaction with methanol. Further, the reaction apparently proceeds by a free radical mechanism since acrylonitrile polymerizes when added to the reaction mixture, and the polymer formed contains carbonyl groups. Leffler and Bond[15] have suggested that for dibenzoyldiimide the initial step is the formation of solvated acyl radicals. Application of this hypothesis to dipropionyldiimide would give the reaction of equation (15). The complexed radical might then



$$\text{Solvent} + C_2H_5\overset{O}{\overset{\|}{C}}{-}N{=}N\overset{O}{\overset{\|}{C}}C_2H_5 \longrightarrow 2\ \text{solvent}\cdot C_2H_5\overset{O}{\overset{\|}{C}}\cdot + N_2 \qquad (15)$$

react with solvent (for example, methanol) to form an acylated product and hydrogen (equations 16a and/or 16b) which could combine with the diacyl diimide (17).

When dipropionyldiimide is decomposed by reaction with bromine in carbon tetrachloride solu-

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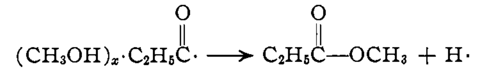
[11] K. Faltings, *Ber.*, **72B**, 1207 (1939).

[12] R. Stolle, *ibid.*, **45**, 273 (1912).

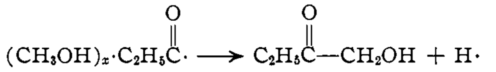
[13] In the thermal decomposition of dipropionyldiimide or bis-(α-phenylpropionyl)-diimide only half of the nitrogen is evolved.

[14] R. Huisgen and F. Jacob, *Ann.*, **590**, 37 (1954).

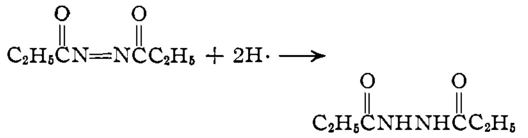
[15] J. E. Leffler and W. B. Bond, THIS JOURNAL, **78**, 335 (1956).



$$(\mathrm{CH_3OH})_x\cdot\mathrm{C_2H_5}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot \longrightarrow \mathrm{C_2H_5}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OCH_3} + \mathrm{H}\cdot \quad (16a)$$



$$(\mathrm{CH_3OH})_x\cdot\mathrm{C_2H_5}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\cdot \longrightarrow \mathrm{C_2H_5}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}CH_2OH} + \mathrm{H}\cdot \quad (16b)$$



$$\mathrm{C_2H_5}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{N{=}N}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{C_2H_5} + 2\mathrm{H}\cdot \longrightarrow \mathrm{C_2H_5}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHNH}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{C_2H_5} \quad (17)$$

tion, a propionyl halide, identified *via* propionanilide, is a reaction product. Although less than half of the diimide nitrogen was evolved as gas, no nitrogen-containing fragment was identified in the residues. It seems likely that decomposition occurred through a radical mechanism and that propionyl halide was formed through reaction of a propionyl radical with either bromine or carbon tetrachloride. There was apparently no loss of carbon monoxide from propionyl radicals.

TABLE I

REACTION OF DIPROPIONYLDIIMIDE WITH SOLVENTS

Solvent	Time[a] for decolorization
Methanol	5 min.
Ethyl alcohol	5 min.
Water	10 min.
Acetic acid	15 min.
Chloroform	30 min.
Acetone	3 hr.
Styrene[b]	3 hr.
Toluene	20 hr.
Vinyl acetate	20 hr.
Bromobenzene	20 hr.

[a] The time given is for disappearance at room temperature of the red color due to dipropionyldiimide following mixing of equal volumes of a 0.08 *M* solution of dipropionyldiimide in bromobenzene and the solvent in question. [b] Decolorization by styrene may occur through a different mechanism, *viz.*, copolymerization. Under conditions permitting easier isolation of the product, polymerization of styrene in the presence of diimides gave a nitrogen-containing polymer. Vinyl acetate did not yield a nitrogen-containing polymer.

The production of radicals in the thermal decomposition of dipropionyldiimide is indicated by the catalysis of polymerization of vinyl monomers summarized in Table II. Catalysis of methyl methacrylate and acrylonitrile polymerization is especially evident. The infrared spectra of the polymers of acrylonitrile and styrene contained strong absorption bands attributed to carbonyl groups from propionyl radicals which initiated polymerization. The styrene polymer also contained bands characteristic of the amide grouping. A possible explanation, that dipropionyldiimide copolymerized with styrene, would also account for the fact that the color of dipropionyldiimide faded in styrene polymerization in about one-quarter the time required with the other vinyl monomers, although the amount of polymer formed was less. Apparently the diimide was consumed both as monomer and initiator. Copolymerization of vinyl monomers with azodiformic ester was noted earlier by Joyce.[16]

TABLE II

POLYMERIZATION OF VINYL MONOMERS WITH PROPIONYL RADICALS

Reaction mixtures contained 5 ml. of vinyl monomer and 0.18 g. of dipropionyldiimide in 10 ml. of benzene. The polymerization at 20° contained 3 ml. of methanol. Controls contained no diimide.

Vinyl monomer	Temp., °C.	Conversion to polymer, % With catalyst	Control
Acrylonitrile	80	3.4	0
Acrylonitrile	20	18.6	0
Methyl methacrylate	80	15	1
Styrene	80	2	0.5

Propionyl radicals from dipropionyldiimide also catalyzed the polymerization of ethylene at 1000 atm. in the temperature range 60–100° to give a low molecular weight, carbonyl-containing polymer.

Experimental

Decarbonylation of Heptaldehyde. A reaction mixture containing 182 g. (1.6 moles) of heptaldehyde, 138 g. (0.8 mole) of diethyl maleate and 0.5 g. of di-*t*-butyl peroxide was heated in a bath of boiling xylene (135–140°) using the apparatus of Patrick.[8] Gas was evolved from the reaction mixture and after 1.75 hr. the rate and total evolution from that time on were measured. The reaction mixture refluxed at an accelerating rate and after 3.25 hr. the reflux condenser was replaced with a 6″ Vigreux column. Five hours after the reaction was started, 0.5 g. of di-*t*-butyl peroxide was added and 15.5 hr. later, 0.5 g. more was added, but there was only 60 ml. of gas evolved following the last addition of peroxide.

The total amount of gas evolved (including a conservative estimate of 1.8 l. during the first 1.75 hr.) was 11.7 l. (corrected to 0°, 1 atm.). Absorption analysis indicated this gas was 91% carbon monoxide.

Hexane was the first liquid to distil from the reaction mixture, b.p. 68–69°, refractive index n^{25}_{D} 1.3720, yield 22.6 g. (0.26 mole). The residual reaction product was distilled through a 12″ glass helix-packed column. Heptaldehyde (51 g.) was recovered at 56° (22 mm.). The pressure was then reduced to 2 mm. and the distillation continued at a reflux ratio of 4/1 and a distillation rate of 5–10 ml./hr. Diethyl maleate (74 g.) was recovered at 74–77° followed by 3 g. of a liquid product which appeared to be diethyl hexylsuccinate. This material boiled at 104–105° (2 mm.) and had a refractive index, n^{25}_{D} 1.4319.

Anal. Calcd. for $C_{14}H_{26}O_4$: C, 65.2; H, 10.10. Found: C, 65.59; H, 10.33.

The distillation residue weighed 74 g. It did not distil at 150° (1 mm.) and was not identified.

Diethyl Ketone from Tetraethyllead and Carbon Monoxide.—A 400-ml., silver-lined pressure vessel was swept out with nitrogen and charged with 33.2 g. of tetraethyllead and 80 ml. of benzene. The vessel was closed and heated to 200° for 18 hr. while a carbon monoxide pressure of 1000 atm. was maintained.

Products from this and four similar experiments run at temperatures between 220 and 250° were combined and distilled through a 12-inch column packed with glass helices. The following fractions were collected.

Fract.	Boiling range, °C.	Press.	n^{25}_{D}	Wt., g.
1	80–82	Atm.	1.4978	325
2	82–97	Atm.	1.4910	23
3	97–104	Atm.	1.3942	10
4	104–136	Atm.	1.4058	5
5	128–151	49 mm.	1.4677	8
6	155–173	35 mm.	1.4795	5
7	115	6 mm.	1.4909	7
Residue				5

The first fraction was substantially all benzene. By partially freezing and decanting the unfrozen portion, repeated several times, a 10-ml. fraction was obtained which

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[16] R. M. Joyce, U. S. Patent 2,507,718, May 16, 1950.

had a refractive index of 1.4972 at 25°, indicating little impurity in the concentrate.

Fraction 3 was diethyl ketone as indicated by boiling point, refractive index and melting point of a 2,4-dinitrophenylhydrazone (154°). The mixed melting point of this derivative was not depressed. Fraction 4 also yielded a 2,4-dinitrophenylhydrazone of diethyl ketone.

Samples of 5, 6 and 7 were oxidized with alkaline permanganate and all yielded diethyl ketone identified as the 2,4-dinitrophenylhydrazone. It is suggested that these fractions contain condensation products which may be homologs of mesityl oxide or phorone formed by thermal polymerization of diethyl ketone. If this is true the yield of diethyl ketone or products derived from it is 35 g. and the conversion from tetraethyllead is about 50%.

Attempt to Add Carbon Monoxide to α-Phenylethyl Radicals.—A 400-ml., silver-lined pressure vessel was charged with 1 ml. of di-*t*-butyl peroxide and 25 ml. of ethylbenzene. It was heated to 150° for 2.3 hr. under a carbon monoxide pressure of 3000 atm. The colorless liquid obtained did not absorb infrared radiation in the carbonyl region. Evaporation left 0.5 g. of needle-shaped crystals which upon recrystallization melted at 122.6°. Klages[17] reports a melting point of 126° for 2,3-diphenylbutane.

Bis-(α-phenylpropionyl)-diimide.—A modification of Stolle's[12] procedure was used. 1,2-Bis-(α-phenylpropionyl)-hydrazine was prepared by slow addition of 10 g. (0.29 mole) of anhydrous hydrazine dissolved in 200 ml. of dioxane to a stirred solution of 96 g. (0.57 mole) of α-phenylpropionyl chloride in 100 ml. of dioxane at 10°. The mixture was then warmed to 40°, and 25 g. (0.63 mole) of sodium hydroxide was added, the temperature rising further to 70°, but after 0.5 hr. the mixture remained acidic. A 50% aq. sodium hydroxide solution was added in 1–2-ml. portions until the mixture became alkaline. After standing 16 hr., the solution was poured into water and the solid which separated was washed with water. The product was recrystallized from dioxane, m.p. 194°, yield 52.5 g. (63%).

Anal. Calcd. for $C_{18}H_{20}O_2N_2$: N, 9.54. Found: N, 9.52.

The mercury salt was obtained by dissolving 37.5 g. (0.127 mole) of 1,2-bis-(α-phenylpropionyl)-hydrazine in a solution of sodium ethoxide prepared from 6 g. (0.26 mole) of sodium metal in 150 ml. of ethyl alcohol and adding 34.6 g. (0.127 mole) of mercuric chloride dissolved in 150 ml. of ethyl alcohol. The yellow mercury salt which precipitated was washed with water, ethyl alcohol, then with ether and dried.

Bis-(α-phenylpropionyl)-diimide was obtained by the reaction of bromine with the mercury salt of the hydrazine suspended in various media. Typically, 2 g. of the mercury hydrazide (0.0035 mole) in 100 ml. of liquid was treated with 0.56 g. (0.0035 mole) of bromine. When benzene was used as reaction medium, 35 to 38 ml. of nitrogen (0.0015 to 0.0017 mole) was evolved at room temperature in about 40 min. The reaction mixture was then colorless. If ether was used, nitrogen evolution was complete in about 15 min. When, however, the reaction was carried out in dioxane, only about 6 ml. of nitrogen was evolved during the first 20 min. Evolution of nitrogen then stopped and the reaction mixture retained an intense red color. By removing dioxane in a current of nitrogen at a temperature below 40°, a deep red liquid was obtained which appeared to be crude bis-(α-phenylpropionyl)-diimide. When this substance was heated to 110°, it evolved nitrogen and left a residue from which 1,2-bis-(α-phenylpropionyl)-hydrazine could be recovered.

Benzene solutions in which bis-(α-phenylpropionyl)-diimide had been prepared contained an alkali-soluble material from which α-phenylpropionanilide was obtained by reaction with thionyl chloride and aniline. Accordingly this material was probably α-phenylpropionyl bromide. In addition, an unidentified neutral liquid boiling at 125° (3 mm.) was isolated which contained 71.67% C, 7.41% H and no nitrogen and had a molecular weight of about 220.

Bis-(α-phenylpropionyl)-diimide as a Catalyst for Styrene Polymerization.—Ten-ml. samples of styrene were warmed with: (a) 0.5 g. of crude bis-(α-phenylpropionyl)-diimide, (b) the residue left from thermal decomposition of 0.5 g. of crude bis-(α-phenylpropionyl)-diimide, (c) alone as blank.

After 10 min. at 100° the red color of diimide in the first sample had faded. The products were poured into 50 ml. of methanol. Polymer precipitated from the sample which had contained the diimide.

Dipropionyldiimide.—Mercury 1,2-dipropionylhydrazine was prepared by the addition of an ethyl alcohol solution of 42 g. (0.29 mole) of dipropionylhydrazine (obtained from propionic anhydride and hydrazine) to a solution of 13.4 g. (0.58 mole) of sodium metal in ethyl alcohol, followed by addition of a solution of 78.6 g. (0.29 mole) of mercuric chloride in ethyl alcohol. The white precipitate was washed with water, then with ethyl alcohol and dried, yield 98 g. (0.29 mole), m.p. 240° dec.

Anal. Calcd. for $C_6H_{10}O_2N_2Hg$: C, 21.0; H, 2.92; N, 8.16. Found: C, 20.88; H, 3.00; N, 7.87.

Reaction of Bromine with Mercury 1,2-Dipropionylhydrazine.—This reaction was typically run at room temperature by the addition of 0.80 g. (0.005 mole) of bromine to 1.72 g. (0.005 mole) of mercury dipropionylhydrazine in 50 ml. of liquid. When benzene was used as reaction medium, 40 ml. (0.0018 mole) of nitrogen was evolved. A further addition of 0.8 g. of bromine resulted in the further evolution of 17 to 18 ml. of nitrogen indicating that bromine had been consumed in some reaction other than oxidation of mercury dipropionylhydrazine. When a benzene solution of bromine was used and added over a period of about 45 min., only 2.5 ml. of nitrogen was evolved indicating that oxidation of the mercury salt is a faster reaction than the reaction of bromine with diimide which results in nitrogen evolution. However, in nitrobenzene medium 51.9 ml. (0.0023 mole) was evolved even when bromine was added slowly to the mercury hydrazide. In bromobenzene medium with slow addition of bromine, 7 ml. (0.0003 mole) of nitrogen was evolved during oxidation; when the reaction mixture was heated to 140°, 48.5 ml. (0.002 mole) more nitrogen was evolved through thermal decomposition of dipropionyldiimide. When carbon tetrachloride was used as reaction medium, 21 ml. (0.001 mole) of nitrogen was evolved. Addition of aniline to the reaction mixture gave propionanilide, apparently through reaction with propionyl chloride or bromide. These results are summarized in Table III.

TABLE III

EFFECT OF SOLVENT ON PREPARATION OF DIPROPIONYLDIIMIDE

Solvent	Mole of N_2/mole of mercury 1,2-dipropionylhydrazine
Benzene	0.01
Bromobenzene	.06
Carbon tetrachloride	.20
Nitrobenzene	.50

Reaction of Iodine with Mercury 1,2-Dipropionylhydrazine.—When iodine is used in place of bromine in the synthesis of dipropionyldiimide, evolution of nitrogen does not occur during oxidation even when nitrobenzene is employed as the medium and the halogen is not added slowly. With iodine oxidation and methylene chloride as the reaction medium, fairly pure samples of dipropionyldiimide were obtained. A mixture of 100 ml. of methylene chloride, 8.60 g. (0.025 mole) of mercury 1,2-dipropionylhydrazine and 6.35 g. (0.025 mole) of iodine were stirred together at room temperature for 10 minutes. Mercuric iodide was filtered from the mixture and solvent removed at 0° (10 mm.). The diimide could be distilled at about 25° (1 mm.) onto a solid CO_2-cooled cold finger where it crystallized as yellow needles which melted to a red liquid at −25 to −24°.

Anal. Calcd. for $C_6H_{10}O_2N_2$: C, 50.7; H, 7.04; N, 19.7. Found: C, 49.56; H, 6.45; N, 16.18.

If it is assumed that the contaminant contains no nitrogen, then the nitrogen analysis indicates 82% dipropionyldiimide. Since 1.00 g. of the diimide is equivalent to 118 ml. of 0.0993 *N* $Na_2S_2O_3$, titration indicates 83% diimide in the sample.

Thermal Decomposition of Dipropionyldiimide.—A 2.2-g. sample of distilled dipropionyldiimide melting at −25° to −23° was heated to 125° until no more gas was evolved (2.8 hr.). The gas was nitrogen and amounted to 127 ml. or 37% of the nitrogen present. Distillation of the residue gave about 1 g. of yellow liquid, b.p. 70–84° (45 mm.),

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[17] A. Klages, *Ber.*, **35**, 2693 (1902).

which gave a positive test for carbonyl group with 2,4-dinitrophenylhydrazone reagent, but a crystallizable derivative was not obtained.

Reaction of Dipropionyldiimide with Compounds Containing an Active Hydrogen.—A solution of dipropionyldiimide was prepared by the addition over 45 min. of 0.80 g. (0.005 mole) of bromine in 10 ml. of bromobenzene to a stirred suspension of 1.72 g. (0.005 mole) of mercury dipropionylhydrazine in 40 ml. of bromobenzene. Only 7 ml. (0.0003 mole) of nitrogen was evolved, so it was assumed that the solution contained 0.004 mole of dipropionyldiimide in 50 ml. of bromobenzene (0.08 molar). The red solution was filtered and 5-ml. portions added to each of the 10 liquids listed in Table I. The time required for the disappearance of color is listed in that table.

A 2.2-g. (0.015) sample of distilled dipropionyldiimide was added to 30 ml. of methanol. Nitrogen (142 ml., 42%) was evolved and the mixture retained a faint pink color. Distillation left a residue which after recrystallization melted at 130–133° and weighed 0.6 g. Its melting point was not depressed by authentic 1,2-dipropionylhydrazine.

Anal. Calcd. for $C_6H_{12}O_2N_2$: C, 50.0; H, 8.35; N, 19.4. Found: C, 49.88; H, 8.67; N, 19.2.

The distillate was hydrolyzed with aqueous alkali and volatile products removed. The residue was taken up in water, acidified, extracted with ether and the ether extract exactly neutralized with 0.0029 mole of alkali. The residue left from evaporation of this solution yielded *p*-methylpropionanilide when heated with *p*-toluidine.

Catalysis of Vinyl Polymerization by Dipropionyldiimide.—Solutions containing 0.18 g. (0.0012 mole) of distilled dipropionyldiimide and 5 ml. of styrene, acrylonitrile or methyl methacrylate in 10 ml. of benzene were warmed in a water-bath at 75–80° for 2 hr. together with solutions of the vinyl monomers containing no dipropionyldiimide. The solution containing styrene and dipropionyldiimide was decolorized in 1 hr. The others remained pink throughout the experiment. The mixtures were poured into 30 ml. of methanol and the polymer which separated was filtered and dried. A sample of polyacrylonitrile also was prepared by allowing a solution containing 0.18 g. of dipropionyldiimide, 5 ml. of acrylonitrile, 5 ml. of methanol and 10 ml. of benzene to stand at 20° for 18 hr. The yields of polymer are summarized in Table II.

Both polyacrylonitrile samples absorbed strongly at 5.8 μ indicating the presence of a carbonyl group in the product, while the sample of polystyrene prepared in the presence of dipropionyldiimide absorbed strongly at 5.96 μ indicating an amide structure obtained through copolymerization of dipropionyldiimide with styrene.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A New Synthesis of a Dioxadiene

BY R. K. SUMMERBELL AND GREGORY J. LESTINA

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An alkyl substituted dioxadiene has been made for the first time. When *trans*-2,5-bis-(iodomethyl)-*p*-dioxane was treated with hot base, the elimination of the elements of hydrogen iodide produced a diolefin, 2,5-bis-(exomethylene)-*p*-dioxane. This substance was isomerized by means of a palladium-on-charcoal catalyst to a stable diolefin, 2,5-dimethyl-*p*-dioxadiene. Treatment of either diolefin with methanol in the presence of a trace of acid produced the dimethoxyacetal of dimeric hydroxyacetone, thus supporting a dioxane structure for that compound.

Introduction

In most respects, a dioxadiene acts as an aliphatic vinyl ether, but certain of its properties are those of a resonance-stabilized system.[1–6] Prior to the present work, only two methods of synthesizing dioxadienes have been available. Symmetrical tetraphenyldioxadiene[5] is prepared readily by condensing benzoin with methanol and heating the adduct in refluxing acetic anhydride. Although this synthesis is convenient, the resulting compounds have all of the dioxadiene hydrogens substituted by aryl groups, thus preventing the study of many important types of reactions. The simple parent compound, dioxadiene, is formed by the action of the magnesium iodide–magnesium–butyl ether system on symmetrical tetrachlorodioxanes.[1,4] To prepare homologs of dioxadiene by this method would require unavailable starting materials, since no preparation of the necessary chlorinated substituted dioxanes has been reported, and the isolation of the requisite compounds from chlorination of alkyl dioxanes will probably occasion considerable difficulty. In a recent study, the pyrolysis of 2,5-dimethoxy-*p*-dioxane[7] failed to yield the expected dioxadiene.

The structure of 2,5-bis-(iodomethyl)-*p*-dioxane recently has been proved,[8] and the compound is prepared readily in quantity. It occurred to us that this compound might serve as a convenient starting material for the synthesis of a dialkyldioxadiene, if the elements of hydrogen halide could be removed to form a diexomethylene dioxane and the latter could be rearranged to form a dioxadiene. The probable intermediate, the diexomethylene compound, is of interest in relation to the general problem of preparing such types as potential monomers for polymerization studies.[9] A closely related compound, 2-exomethylenetetrahydrofuran, had been prepared by Paul and Tchelitcheff[10] from 2-bromomethyltetrahydrofuran by elimination of hydrogen bromide with base. Essentially the same reaction was used by us recently in the preparation in good yield of 2,3-bis-(exomethylene)-*p*-dioxane.[11]

This general method of preparing a dioxadiene was attempted in our laboratories some years ago

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(1) R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, **61**, 3020 (1939).

(2) G. R. Lappin and R. K. Summerbell, *J. Org. Chem.*, **13**, 671 (1948).

(3) G. R. Lappin and R. K. Summerbell, THIS JOURNAL, **78**, 2600 (1948).

(4) L. W. Pickett and E. L. Sheffield, *ibid.*, **68**, 216 (1946).

(5) W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 201 (1931); **526**, 195 (1936).

(6) J. Y. Beach, *J. Chem. Phys.*, **9**, 53 (1941).

(7) W. E. Parham and H. E. Reiff, THIS JOURNAL, **77**, 6391 (1955).

(8) R. K. Summerbell and J. R. Stephens, *ibid.*, **76**, 731, 6401 (1954).

(9) W. J. Bailey and Robert L. Hudson, *ibid.*, **78**, 670 (1956).

(10) R. Paul and S. Tchelitcheff, *Bull. soc. chim.*, **17**, 520 (1950).

(11) R. K. Summerbell and Gregory J. Lestina, THIS JOURNAL, **79**, 3878 (1957).