Hydrazinedicarboxylic Anhydrides and Their Reactions

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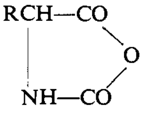
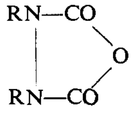
Abstract: 1,2-Dialkylhydrazine-1,2-dicarboxylic anhydrides (II) were synthesized along with several derivatives of 1,2-dialkylhydrazines. Alkylation of ethyl hydrazinedicarboxylate with both methyl and ethyl sulfate afforded the ethyl 1,2-dialkylhydrazinedicarboxylates which on hydrolysis produced the 1,2-dialkylhydrazines. Treatment with ethyl chloroformate yielded the ethyl 1,2-dialkylhydrazinecarboxylates, and these, on reaction with phosgene, gave 2-carbethoxy-1,2-dialkylhydrazinecarbonyl chlorides. Pyrolysis of the latter yielded II and ethyl chloride. The isopropyl analog was made in comparable steps from 1,2-diisopropylhydrazine which, in turn, was made by reduction of acetone azine. These anhydrides were less reactive than the analogous azasuccinic anhydrides. The methyl compound could be polymerized to a polycarbohydrazide, H(NMeNMeCO)$_n$NMeNHMe, by heating in water, ethanol, or pyridine. The ethyl and isopropyl compounds failed to react with ethanol or pyridine, which suggests steric blocking of carbonyl groups in these anhydrides. Reaction with aniline induced no polymerization but gave rise to hydrazinecarboxanilides, RNHNRCONHC$_6$H$_5$. On heating *in vacuo* all three anhydrides sublimed without decomposition. When 2-carbethoxyhydrazinecarbonyl chloride was heated in toluene, hydrogen chloride was evolved instead of ethyl chloride. The resulting solid seemed to be a dimer (VII) of carbethoxyamino isocyanate. Pyrolysis in the molten state at 125 or 145° caused evolution of both hydrogen chloride and ethyl chloride. The exact nature of these solid products is in doubt. No hydrazinedicarboxylic anhydride was obtained as such.

Azasuccinic anhydrides[2] (I), or Leuchs' anhydrides,[3] have been studied extensively as precursors of polypeptides.[4] In such polymerizations, I may be first isolated as such or it may have a transient existence. A synthesis from α-amino acids uses acidic reagents, first ethyl chloroformate and then thionyl chloride. Acid-sensitive amino acids (tryptophan, serine) do not lend themselves to this approach.



I



IIa, R = CH$_3$
b, R = C$_2$H$_5$
c, R = (CH$_3$)$_2$CH
d, R = H

A synthesis on the basic side, which permits the formation of polytryptophan, uses malonic ester or a substituted malonic ester as the starting substance. After conversion to a hydroxamic acid, this is subjected to a Lossen rearrangement[5]

$$\text{EtOOC-CHR-COOEt} \longrightarrow \text{HOOC-CHR-CONHOH} \longrightarrow \text{HOOC-CHR-NCO} \rightleftarrows \text{I} \longrightarrow \text{polypeptide}$$

The general availability of substituted malonic esters makes this a particularly general approach.

The present study concerns itself with 1,2-hydrazinedicarboxylic anhydrides (II), hitherto unreported. These would be "diazasuccinic anhydrides." To synthesize II, it was planned to acylate a hydrazine first with chloroformic ester, then with phosgene to form the ester acyl chloride which was to be pyrolyzed

$$\text{RNHNHR} \longrightarrow \text{RNHNRCOOEt} \longrightarrow \text{ClCONRNRCOOEt} \longrightarrow \text{II} + \text{EtCl}$$

This plan worked well when R = CH$_3$, C$_2$H$_5$, (CH$_3$)$_2$CH.

A good synthesis of 1,2-dimethylhydrazine has been reported by Hinman[6]

$$\text{H}_2\text{NNH}_2 \xrightarrow{\text{ClCOOEt}} \underset{\text{III}}{\text{C}_2\text{H}_5\text{OOCNHNHCOOC}_2\text{H}_5} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{NHNHCH}_3$$

but we prepared it instead by a new method which also worked well, namely, methylation of III with methyl sulfate (NaOH, 20°), followed by acid hydrolysis.

$$(\text{-NHCOOEt})_2 \longrightarrow (\text{-NMeCOOEt})_2 \xrightarrow{\text{HCl}} (\text{-}\overset{+}{\text{N}}\text{H}_2\text{Me})_2 \xrightarrow{\text{NaOH}} (\text{-NHCH}_3)_2$$

We made 1,2-diethylhydrazine also from III by comparable treatment with ethyl sulfate, but this ethylation was less successful than the methylation. A preferable route would appear to be the reduction of acetaldehyde azine, (—N=CHEt)$_2$, by LiAlH$_4$ as described by Renaud and Leitch.[7] 1,2-Diisopropylhydrazine was synthesized by reduction of acetone azine.[7]

Synthesis of ethyl 1,2-dialkylhydrazinecarboxylate was accomplished successfully by reaction of the hydrazine with ethyl chloroformate

$$\text{RNHNHR} + \text{ClCOOC}_2\text{H}_5 \longrightarrow \text{RNHNRCOOC}_2\text{H}_5$$

It was hoped that ethyl carbonate could be used in this synthesis, since it is known[8] to work well at 25° in converting hydrazine into ethyl hydrazinecarboxylate, but the yield of product with the dimethylhydrazine was so poor, even at 135° in a sealed tube, that the plan was abandoned. This lack of reactivity is probably the result of a steric effect since the conformation of dimethylhydrazine undoubtedly places the alkyl groups on opposite sides of the molecule and interferes with the approach of ethyl carbonate.

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[1] Tee Pak Foundation Fellow, 1959–1960.

[2] The name "N-carboxyglycine anhydride" that is often seen for such compounds (R = H) is misleading, for it really designates (HOOC-NHCHRCO)$_2$O. The second word of a two-word name (as ether, ketone, anhydride) should not depend on a substituting prefix ("carboxy") in the first word.

[3] H. Leuchs, *Ber.*, **39**, 857 (1906).

[4] C. H. Bamford, A. Elliott, and W. E. Hanby, "Synthetic Polypeptides," Academic Press Inc., New York, N. Y., 1956.

[5] C. D. Hurd and C. M. Buess, *J. Am. Chem. Soc.*, **73**, 2409 (1951); C. D. Hurd and L. Bauer, *ibid.*, **73**, 4387 (1951).

[6] R. L. Hinman, *ibid.*, **78**, 1648 (1956).

[7] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

[8] O. Diels, *Ber.*, **47**, 2186 (1914).

Reaction of the above ethyl esters with phosgene was smooth

$$\mathrm{RNH\text{-}NR\text{-}COOC_2H_5 + COCl_2 \longrightarrow ClCO\text{-}NR\text{-}NR\text{-}COOC_2H_5 + HCl}$$

When R was methyl or ethyl, and with a fivefold excess of phosgene, yields were about quantitative. When R was isopropyl, and with only a 0.4-mole excess of phosgene, the yield was 72.5%. More phosgene probably would have raised this yield.

Hydrazobenzene differed from the three dialkylhydrazines since it yielded ethyl *p,p'*-biphenylylenedicarbamate, $(\text{-}C_6H_4NHCOOC_2H_5)_2$, on reaction with ethyl chloroformate in boiling dioxane solution. This benzidine rearrangement was promoted by the hydrogen chloride of the reaction. A similar rearrangement occurs with benzoyl chloride as acylating agent.[9]

A good yield of ethyl 1,2-diphenylhydrazinecarboxylate, $C_6H_5NHN(C_6H_5)COOC_2H_5$, resulted from the reaction of hydrazobenzene, ethyl chloroformate, and pyridine at 20°, but there was essentially no reaction of this substance with phosgene.

The three substituted carbamyl chlorides that were made from phosgene, all liquids, reacted smoothly with aniline to give crystalline anilides, $C_6H_5NHCONRNRCOOEt$.

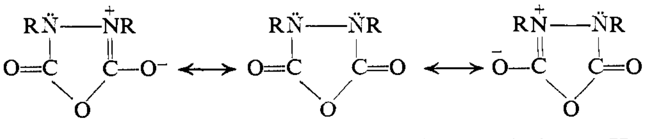
Pyrolysis of these three acyl chlorides at 150–180° gave rise to the anhydrides II in approximately quantitative yields. Ethyl chloride was evolved. Alkaline hydrolysis of IIa yielded 1,2-dimethylhydrazine, which was characterized as the picrate. IIa is soluble in water, whereas IIb and IIc are insoluble.

It was stated above that the anhydrides of structure I were of interest because of the polymerization reactions that may be induced by water, alcohol, amines, or heat. Polypeptides, formed in this way, possess repeating amide units. If anhydrides of structure II polymerized analogously the polymer should contain repeating carbohydrazide units

$$\mathrm{II \xrightarrow{H_2O} (HOOCNRNRCOOH) \xrightarrow{-2CO_2} RNHNHR \xrightarrow{II}}$$
$$\mathrm{(HOOCNRNRCONRNHR) \xrightarrow{-CO_2} CO(NRNHR)_2 \xrightarrow{II}}$$
$$\mathrm{CO_2 + RNHNRCONRNRCONRNHR}$$

Continued reaction of the latter with II would result in the polymer $\mathrm{H(NRNRCO)}_n\mathrm{NRNHR}$ (IV). The polymer from II, differing from the polymer from I, would have no terminal carboxyl group.

One can predict that II should be more sluggish than I because of delocalization of electrons involving both carbonyl groups



Reaction with water confirms this prediction. IIa lost no weight on standing in moist air for 21 days, and the loss in 61 days was only 2.9% of the total carbon dioxide available. Also, there was a negligible change in melting point. In contrast, I (R = H) lost almost the theoretical weight of carbon dioxide in 4 days.[10] As a matter of fact, there was no apparent reaction when IIa was dissolved in an equal weight of warm water. After standing for a time, however, a slow evolution of carbon dioxide was noted. Then the reaction was hastened by heating to 100°. The polycarbohydrazide (IV) resulting from this treatment appeared to have 11 repeating units, $\mathrm{H(NMeNMeCO)_{11}NMeNHMe}$, based on elemental analysis and its reaction with *p*-bromophenyl isocyanate.

We refluxed II with 16 times the weight of water used in the previous experiment and measured the volume of carbon dioxide evolved. That from IIa was 59% of the possible amount; IIb, 69%; and IIc, 75.5%. Thus, IIa gives rise to more extensive polymerization than IIb which, in turn, is greater than IIc. According to the steps given above leading to IV, n moles of II would yield $n + 1$ moles of CO_2. The ratio $(n + 1)/n$ is 2 if $n = 1$, or 1.50 if $n = 2$, or 1.20 if $n = 5$. Since 2 is the total CO_2 possible, or 100%, then 1.50 represents 75% of this total, and 1.20 represents 60%. From such calculations, 59% for IIa shows $n = 5.5$, 69% for IIb shows $n = 2.64$, and 75.5% for IIc shows $n = 1.96$. The percentage of C, H, and N in these polymers was in reasonable agreement with these n values. Since n apparently drops from 11 to 5.5 (for IIa) when a large excess of boiling water is used, this suggests that the higher concentration of water competes better for the acid anhydride with the incipient hydrazino acid or hydrazine in the chain-propagating step.

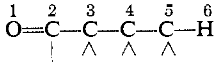
IIa was unchanged by refluxing for 9 days either in dry benzene or in ordinary benzene. In contrast, Woodward and Schramm[11] brought about polymerization of I (R = benzyl, isobutyl) by allowing a solution of it in ordinary benzene to stand for 2 weeks.

IIa, IIb, and IIc were all soluble in absolute alcohol, but the last two were unchanged after 24 hr of refluxing. IIa, however, underwent polymerization presumably to V in part, but evidence pointed to IV as well, which could be explained by traces of water in the alcohol.

$$\underset{\mathrm{V}}{\mathrm{C_2H_5OOC(NMeNMeCO)}_n\mathrm{NMeNMeCOOC_2H_5}}$$

Thus, the analytical values were low for C and H but high for N. Also, the infrared spectrum showed a peak for NH.

The reactivity of IIa toward water or alcohol and the sluggishness of IIb and IIc indicate that a steric hindrance to nucleophilic attack on the anhydride carbonyl exists in IIb or IIc that is absent in IIa. This may be regarded as a consequence of the "rule of six"[12] which states that in reactions involving addition to a double bond the greater the number of atoms in position 6 the greater will be the steric effect. Thus, the arrangement



$$\overset{1}{\mathrm{O}}{=}\overset{2}{\mathrm{C}}{-}\overset{3}{\mathrm{C}}{-}\overset{4}{\mathrm{C}}{-}\overset{5}{\mathrm{C}}{-}\overset{6}{\mathrm{H}}$$

is present in IIb and IIc but not in IIa.

Aniline reacted with IIa or IIc to yield the hydrazinecarboxanilides, $RNHNRCONHC_6H_5$. Any polymerization effect must have been slight. Since 1,2-dimethylhydrazine is a stronger base than aniline ($pK_a = 7.52$ *vs.* 4.58), this suggests that the reaction of II with aniline is faster than the decarboxylation of the intermediate

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[9] D. Stern, *Ber.*, **17**, 379 (1884).

[10] F. Wessely, *Z. Physiol. Chem.*, **146**, 72 (1925).

[11] R. B. Woodward and C. H. Schramm, *J. Am. Chem. Soc.*, **69**, 1551 (1947).

[12] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p 206.

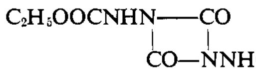
carbamic acid PhNHCONRNRCOOH, implying some stabilization of the latter as the salt by reaction with the bases present.

No polycarbohydrazides resulted from the heating of II under diminished pressure. Instead, the anhydrides sublimed unchanged. This is interesting since heating is a well-known technique[13] for producing polypeptides from I. If Kopple's suggestion[14] that thermal polymerization of I proceeds *via* an α-isocyanato acid, RCH(NCO)COOH, is correct, this might explain this nonpolymerization of IIa–c since the latter can form no such isocyanate.

The carbamyl chlorides, ClCONRNRCOOEt, that give rise to IIa–c have no proton on the nitrogen atoms. The analog, ClCONHNHCOOEt (VI), that would be the precursor of IId does have such protons and thus becomes aligned structurally with the conventional carbamyl chlorides that pyrolyze into isocyanates by losing hydrogen chloride: RNHCOCl → RNCO + HCl. If VI behaved in this way the product would be EtOOCNHNCO rather than IId.

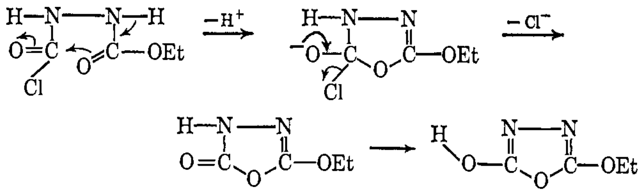
2-Carbethoxyhydrazinecarbonyl chloride (VI), a crystalline solid, was prepared in nearly quantitative yield by reaction of ethyl hydrazinecarboxylate,[8] NH_2NH-$COOC_2H_5$, and phosgene. It behaved normally toward water, alcohol, and *p*-bromoaniline forming, respectively, $NH_2NHCOOC_2H_5$ (+ CO_2 + HCl), (-NHCO-$OC_2H_5)_2$, and *p*-$BrC_6H_4NHCONHNHCOOC_2H_5$.

Heating of VI did not yield IId, at least not pure, nor did it produce the monomeric isocyanate. A chlorine-free, uncrystallizable glass was formed when the pyrolysis was performed in refluxing toluene, and HCl (96 mole %) was eliminated to the exclusion of observable ethyl chloride. Based on elemental analyses, molecular weight data, and two strong infrared carbonyl absorption peaks at 5.48 and 5.70 μ (with none at 4.5 μ as would be required for a monomeric isocyanate), this product may be regarded as a dimer of the isocyanate of structure[15] VII. The infrared absorption at 5.48 μ strongly supports the four-membered ring in VII, since this is the position for β-lactams. An isocyanate trimer would not absorb at 5.5 μ.


$$\begin{array}{l} C_2H_5OOCNHN\text{——}CO \\ \qquad\qquad\quad\;\; | \qquad\;\; | \\ \qquad\qquad\quad\;\; CO\text{—}NNHCOOC_2H_5 \end{array}$$

VII

Conceivably, VI might also pyrolyze into HCl by involvement of the hydrogen that is β to the -COCl group. A 1,2,4-oxadiazole (VIII) would result. However, VIII would explain neither the infrared absorption at 5.48 μ nor the molecular weight which is about double that of VIII.



VIII

Although infrared and analytical evidence supported structure VII, its glassy, uncrystallizable nature casts doubt on its purity. Also, no good chemical evidence could be obtained in support of VII (or VIII). The substance reacted with hot water, aniline, and aryl isocyanates to form solid or crystalline derivatives, but none was identifiable except the one from refluxing aniline which was carbanilide. Carbon dioxide was evolved in the reaction with hot water, but only three-fifths as much as would be expected from VII by hydrolytic opening of the ring and decarboxylation. These reactions need nore study before they can be evaluated with certainty.

If VI was heated at 0.1 mm to 125°, a glassy solid also was obtained but of higher nitrogen and lower carbon content than the above residue. The band at 5.48 μ in the infrared spectrum was still present, but weak. As judged by the loss in weight on heating, both HCl and C_2H_5Cl were eliminated.

When VI was heated at atmospheric pressure in a nitrogen atmosphere to 145°, it was established that about equal amounts of HCl and C_2H_5Cl were evolved. The glassy residue was of still higher nitrogen and lower carbon content than the preceding. The infrared absorption at 5.48 μ was reduced to a weak shoulder on an intense band at 5.7–5.8 μ.

The residues from the three modes of heating were similar in appearance. All dissolved in water to give quite acidic solutions that contained no chloride ion and that produced a deep amber color with ferric chloride solution.

Experimental Section

Combustion analyses were performed by Hilda Beck.

Hydrazinedicarboxylic Esters. Ethyl 1,2-Dimethylhydrazinedicarboxylate. To ethyl 1,2-hydrazinedicarboxylate,[16] mp 135°, were added simultaneously in four portions with stirring 1.75 moles each of methyl sulfate and 10% sodium hydroxide solution at 20–25°. The mixture was stirred 15 min between each addition and finally for 2 extra hr. During this time the original solid had changed to an oil which was ether extracted, dried (Drierite), and distilled. The fraction that was collected at 78–88° (0.5 mm) represented a 62% yield; redistillation, bp 74.5° (0.2 mm), n^{25}D 1.4309. The colorless liquid had a minty odor. It had major infrared peaks at 3.38 (none at 3.0), 4.64, 5.80, 6.61, 6.92, 7.25, 7.48, 8.3–8.7, 9.08, 9.40, 9.55, 10.6, 11.3, 12.8, 13.1, and 15.0 μ. *Anal.* Calcd for $C_8H_{16}N_2O_4$: C, 47.0; H, 7.90; N, 13.7. Found: C, 46.6; H, 7.62; N, 14.1.

Ethyl 1,2-Diethylhydrazinedicarboxylate. The above directions were modified, using for 0.475 mole of ethyl hydrazinedicarboxylate 2.38 moles each of ethyl sulfate and alkali. The temperature was held at 95° during addition and then at 60° for 1 extra hr. The fraction collected at 70–100° (0.2 mm) was stirred again with 0.75 mole each of ethyl sulfate and 10% sodium hydroxide solution at 60–90° for 2.5 hr. The resulting oil, bp 84–86° (0.2 mm), was obtained in 42% yield; n^{25}D 1.4330. Its infrared peaks were at 3.40, 4.65, 5.86, 6.49, 6.87, 7.11, 7.30, 7.75, 7.91, 8.50, 8.69, 8.80, 9.15, 9.30, 9.62, 9.82, 12.90, and 13.15 μ. *Anal.* Calcd for $C_{10}H_{20}N_2O_4$: C, 51.7; H, 8.68; N, 12.0. Found: C, 51.6; H, 8.26; N, 11.7.

1,2-Dialkylhydrazines. 1,2-Dimethylhydrazine *via* Acid Hydrolysis. Ethyl 1,2-dimethylhydrazinedicarboxylate (150 g) was refluxed with 500 ml of 37.7% hydrochloric acid for 72 hr, since some ester persisted after 64 hr. After evaporation under reduced pressure to remove alcohol, the dihydrochloride was dissolved in 190 ml of water and added dropwise to 200 g of sodium hydroxide pellets in a flask equipped with a reflux condenser. When all was

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(13) H. Leuchs and W. Manasse, *Ber.*, **40**, 3235 (1907); F. Sigmund and F. Wessely, *Z. Physiol. Chem.*, **157**, 91 (1926); E. Katchalski, I. Grosfeld, and M. Frankel, *J. Am. Chem. Soc.*, 70, 2094 (1948).

(14) K. D. Kopple, *ibid.*, **79**, 6442 (1957).

(15) Helpful discussion by correspondence with J. B. Hendrickson is gratefully acknowledged.

(16) N. Rabjohn, *Org. Syn.*, **28**, 58 (1948).

added, the solution was distilled up to 101°. The distillate weighed 43 g and contained 38.8 g (88.0%) of dimethylhydrazine as determined by titration with 0.1 *N* hydrochloric acid with methyl orange as indicator. A sample was converted to the picrate, mp 149–151° dec; lit.[17] 147–150° dec.

Via **Alkaline Hydrolysis.** The ethyl 1,2-dimethylhydrazinedicarboxylate (110 g) was refluxed for 1 hr with an excess of 50% aqueous potassium hydroxide solution, after which the mixture was distilled to a temperature of 101°. The clear liquid (61 g) of ammoniacal odor was 39.3% dimethylhydrazine by titration, yield 73%. The alkaline hydrolysis is faster and would be the method of choice if there is no objection to the presence of alcohol in the hydrazine.

1,2-Diethylhydrazine. Ethyl 1,2-diethylhydrazinedicarboxylate (82 g) and an excess of 50% aqueous potassium hydroxide was heated under reflux for 24 hr. The two-phase system was distilled into concentrated hydrochloric acid. The resulting dihydrochloride, after vacuum evaporation, was made up to 125 ml with water and added dropwise with cooling onto 200 g of sodium hydroxide pellets. Then the mixture was distilled to dryness, and to the 71 g of distillate was added 100 g of sodium hydroxide pellets. The hydrazine was taken up in ether, dried with potassium hydroxide pellets, separated, and distilled, bp 103–105°, yield 22.1 g (72%). Its reported[7] boiling point is 106–107°.

1,2-Diisopropylhydrazine. This was prepared from acetone azine (0.42 mole) and lithium aluminum hydride (0.44 mole) of 95% purity (rather than the recommended 64%) according to published directions,[7] yield 78%, bp 122–122.5°.

Hydrazinecarboxylic Esters. Ethyl hydrazinecarboxylate, mp 43–45, was made in 80.5% yield from hydrazine hydrate and ethyl carbonate by Diels procedure.[8]

1,2-Dialkylhydrazinecarboxylic Esters. General Procedure. Three solutions were prepared: (1) the dialkylhydrazines (0.2–0.3 mole), dissolved in 25 ml of methanol, cooled to −30°; (2) ethyl chloroformate in 50 ml of methanol, also at −30°, using slightly less than the identical molar amount taken in solution 1, (3) methanolic potassium hydroxide, using the same number of moles as in solution 2. Solution 2 was added dropwise into solution 1, with stirring, during 20 min. Solution 3 was also added dropwise after one-third to one-half of solution 2 had been added. When addition was complete the mixture was allowed to warm to room temperature and was stirred for 2 hr, then filtered to remove KCl. Methanol was distilled off, ether added, the ether layer dried over Drierite, and the ether removed by distillation. The residue was distilled under reduced pressure. Details follow for the dimethyl, diethyl, and diisopropyl compounds.

Methyl: bp 64° (17 mm), $n^{25}\text{D}$ 1.4272, yield 61%, minty odor, infrared carbonyl absorption at 5.92 μ. *Anal.* Calcd for $C_5H_{12}N_2O_2$: C, 45.42; H, 9.15; N, 21.20. Found: C, 45.95; H, 9.56; N, 21.65.

Ethyl: bp 81° (18 mm), $n^{25}\text{D}$ 1.4257, yield 59%, infrared carbonyl absorption at 5.95 μ. *Anal.* Calcd for $C_7H_{16}N_2O_2$: C, 52.47; H, 10.07; N, 17.49. Found: C, 51.80; H, 9.71; N, 17.68.

Isopropyl: bp 90° (14 mm), $n^{25}\text{D}$ 1.4270, yield 47%, infrared carbonyl absorption at 5.85 μ. *Anal.* Calcd for $C_9H_{20}N_2O_2$: C, 57.41; H, 10.71; N, 14.88. Found: C, 58.20; H, 10.65; N, 14.94.

Ethyl 1,2-Diphenylhydrazinecarboxylate. To a solution of 11 g of hydrazobenzene and 50 ml of dry pyridine, cooled to 10°, was added 11.4 ml of ethyl chloroformate dropwise and with stirring. The temperature was held at 15–20°. The mixture was kept overnight at 10° and was filtered to remove pyridine hydrochloride. To the filtrate was added 150 ml of water. The insoluble orange oil was separated, dissolved in ether, washed with dilute hydrochloric acid and water, and then dried (Na_2SO_4). The 12 g of oil remaining after removal of ether solidified after a time. It was recrystallized from ethanol at −20° to give 9 g (60%) of pale yellow solid, mp 64.5°. *Anal.* Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.25; N, 10.93. Found: C, 69.96, 70.20; H, 5.99, 6.26; N, 11.19.

Ethyl 1,2-Dimethylhydrazinecarboxylate Hydrochloride, Cl^--$^+NH_2MeNMeCOOC_2H_5$. The above dimethyl compound was treated with cold concentrated hydrochloric acid. Excess acid and water were removed under diminished pressure. The residue was crystallized from 1:5 ethanol–ethyl acetate, and again from 1:4 acetonitrile–ether, mp 106°. *Anal.* Calcd for $C_5H_{13}ClN_2O_2$: C, 35.62; H, 7.77; N, 16.62. Found: C, 36.16; H, 7.62; N, 16.87.

Ethyl *p,p'*-Biphenylylenedicarbamate. A solution of 5.5 g of hydrazobenzene and 11.4 ml of ethyl chloroformate in dry dioxane was refluxed for 45 min and then left overnight. The 1.2 g of gray solid that had separated was crystallized from ethanol, yielding 0.8 g of crystals, mp 230–232°. Analysis, mixture melting point with an authentic sample (mp 230°) of the title compound, and identical infrared spectra confirmed its identity.

Acyl Chlorides. General Procedure for Synthesis of $ClCONRNRCOOC_2H_5$, R = H, CH_3, C_2H_5, $(CH_3)_2CH$. About 0.75 mole of phosgene was dissolved in 80 ml of absolute ether at 0° contained in a flask equipped with condenser, magnetic stirrer, inlet tube, and outlet tube leading to an alkali trap. Then a solution of 0.15 mole of the hydrazinecarboxylic ester, $HNRNRCOOC_2H_5$, in 80 ml of absolute ether was added dropwise with cooling and stirring. This was continued for 1 hr, and then the excess of phosgene and ether was distilled off. When R = H, the residue was a soft, white, crystalline solid, very sensitive to moisture, that was dissolved in ether and crystallized therefrom, by addition of pentane; mp 78–80°, yield 96%. It readily yielded ethyl 1,2-hydrazinedicarboxylate (2 g from 2 g), mp 135°, on reaction with ethanol.

When R was alkyl, the products were liquids, and, when R was methyl, it was distilled at 80–85° at 0.1–0.6 mm, yield 100%. When R was ethyl or isopropyl, the products were used in the subsequent step without final purification since it was found that the 1,2-diethyl compound decomposed somewhat during vacuum distillation (at 82–83° and 0.18 mm). Infrared spectra for the dimethyl, diethyl, and diisopropyl compounds were similar. In the synthesis of the 1,2-diisopropyl compound only 0.21 mole of phosgene was taken (rather than 0.75), with a resultant drop in yield to 72.5%.

There was no apparent reaction between phosgene and ethyl 1,2-diphenylhydrazinecarboxylate even on standing overnight. The original ester was recovered and identified by melting point, mixture melting point, and infrared spectrum.

2-Carbethoxyhydrazinecarbonyl Chloride. Infrared peaks were seen at 2.99, 3.11, 3.28, 5.60, 5.85, 6.05, 6.52, 6.66, 7.75, 7.92, 9.51, 11.60, and 12.90 μ. *Anal.* Calcd for $C_4H_7ClN_2O_3$: C, 28.88; H, 4.23; N, 16.82. Found: C, 28.58; H, 4.17; N, 17.23.

2-Carbethoxy-1,2-dimethylhydrazinecarbonyl Chloride. Infrared peaks were seen at 3.44, 5.75, 5.85, 7.09, 7.35, 7.57, 7.86, 8.51, 8.85, 9.38, 9.80, 10.45, 11.45, 11.70, 13.10, and 15.15 μ. *Anal.* Calcd for $C_6H_{11}ClN_2O_3$: C, 37.03; H, 5.69. Found: C, 36.98; H, 5.48.

Derivatives of Acyl Chlorides with Arylamines. Ethyl N-*p*-Bromophenyl-1,2-hydrazinedicarboxamate, $BrC_6H_5NHCONHNHCOOC_2H_5$. Addition of 2 g of *p*-bromoaniline in 15 ml of toluene to 1 g of 2-carbethoxyhydrazinecarbonyl chloride caused immediate precipitation of a white solid. It was separated, rinsed, and recrystallized from absolute alcohol, yield 1.2 g, mp 216–217°. *Anal.* Calcd for $C_{10}H_{12}BrN_3O_3$: C, 39.42; H, 4.00; N, 13.91. Found: C, 39.40; H, 3.87; N, 14.37.

The acyl chloride (2.1 g) also reacted with absolute ethanol (10 ml, refluxing, 10 min) to form 2.1 g of ethyl hydrazinedicarboxylate, mp 135°.

Ethyl N-Phenyl-1,2-dimethyl-1,2-hydrazinedicarboxamate, $C_6H_5NHCONMeNMeCOOC_2H_5$. Mixing 2-carbethoxy-1,2-dimethylhydrazinecarbonyl chloride (1 g) with 2–4 ml of aniline (no solvent) caused a mild exotherm. After 10 min of heating at 100° the mixture was cooled and treated with dilute hydrochloric acid. The resulting solid (1 g) was recrystallized from 50% aqueous alcohol to produce 0.5 g of white needles, mp 124.5–125°. *Anal.* Calcd for $C_{12}H_{17}N_3O_3$: C, 57.34; H, 6.82; N, 16.72. Found: C, 57.61; H, 6.74; N, 17.04.

Ethyl N-Phenyl-1,2-diethyl-1,2-hydrazinedicarboxamate. The same directions were followed as for the dimethyl analog. From 1 g of the acyl chloride there was obtained 1 g of product after crystallization from aqueous alcohol, mp 77–78°. *Anal.* Calcd for $C_{14}H_{21}N_3O_3$: C, 60.19; H, 7.58; N, 15.04. Found: C, 59.30; H, 7.53; N, 15.29.

Ethyl N-Phenyl-1,2-diisopropyl-1,2-hydrazinedicarboxamate. Using the same directions, we obtained 1.1 g of crude product from 1 g of acyl chloride. After recrystallization from aqueous ethanol 0.5 g of white needles resulted, mp 87–89°. *Anal.* Calcd for $C_{16}H_{25}N_3O_3$: C, 62.52; H, 8.20; N, 13.67. Found: C, 62.23; H, 7.73; N, 13.97.

1,2-Hydrazinedicarbox-*o*-toluidide, $(-NHCONHC_6H_4CH_3)_2$, *via* 1,2-Hydrazinedicarbonyl Chloride. A solution of 6.0 g of anhydrous hydrazine, prepared by treatment of hydrazine hydrate with barium oxide,[18] in 20 ml of dry chloroform was added dropwise

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[17] L. Knorr and A. Kohler, *Ber.*, **39**, 3257 (1906).

[18] C. F. Hale and F. F. Shetterly, *J. Am. Chem. Soc.*, **33**, 1071 (1911).

with cooling to an excess of phosgene (130 g) in 100 ml of absolute ether. A white solid separated. After 2.5 hr the excess of phosgene was removed and the solution was filtered to remove the solid. A sample of the filtrate rapidly became cloudy when exposed to air. That it contained the dicarbonyl chloride was established by reaction with alcohol, forming ethyl 1,2-hydrazinedicarboxylate, mp 130–132°.

One-third of the filtrate was mixed with 3 ml of *o*-toluidine. After a few hours, the solution was separated from the precipitated amine salt and evaporated. The 0.6 g of off-white solid was twice crystallized from alcohol to give white crystals which melted at 224–225°. *Anal.* Calcd for $C_{16}H_{18}N_4O_2$: C, 64.41; H, 6.08; N, 18.78. Found: C, 64.17; H, 5.70; N, 18.86.

Dicarboxylic Anhydrides. General Directions. The 2-carbethoxy-1,2-dialkylhydrazinecarbonyl chloride (0.05–0.10 mole) was placed in a dry, 25-ml, round-bottom flask attached to a trap cooled to −78°. The system was flushed with dry nitrogen. The flask was heated by an oil bath. The dimethyl compound decomposed at 160–175°, the diethyl homolog at 170–180°, and the diisopropyl compound at 140–155°, as judged by evolution of gas. The evolution of gas ceased in 10–20 min. A quantitative yield of ethyl chloride was collected in the cold trap from each run. Its identity was confirmed by its boiling point (13°). Also, it burned with a green flame. The weight of residue was quantitatively what was expected by detachment of C_2H_5Cl. Tetrahydrofuran was a good crystallizing solvent. All three anhydrides sublimed readily without decomposition, IIa at 50–120° (0.005–0.01 mm), IIb at 60° (0.05 mm), and IIc at 70° (0.05 mm). IIa melted at 88–89°, IIb at 111–112°, and IIc at 80–81°.

Anal. Calcd for $C_4H_6N_2O_3$ (IIa): C, 36.93; H, 4.65; N, 21.53. Found: C, 37.38; H, 4.64; N, 21.94. Calcd for $C_6H_{10}N_2O_3$ (IIb): C, 45.56; H, 6.37; N, 17.71. Found: C, 44.95; H, 6.07; N, 18.18. Calcd for $C_8H_{14}N_2O_3$ (IIc): C, 51.60; H, 7.58; N, 15.04. Found: C, 52.30; H, 7.15; N, 15.27.

Infrared. The spectrum of IIa showed strong absorption bands at 5.48, 5.69, 7.44, and 10.25 μ, and medium bands at 8.90, 10.65, and 13.80 μ. IIb absorbed strongly at 5.42, 5.65, and 10.38 μ and had medium bands at 3.32, 6.83, 7.25, 7.60, 9.21, and 9.86 μ. The strong bands for IIc were at 5.41, 5.65, 7.53, and 10.26 μ and the medium bands were at 3.33, 6.81, 7.24, 8.10, 8.45, and 8.78 μ.

Reactions of 1,2-Dimethyl-1,2-hydrazinedicarboxylic Anhydride. With Water. A clear solution resulted without evident reaction when 1.017 g of IIa was mixed with 1 ml of warm water. Heating the solution caused a vigorous evolution of carbon dioxide ($Ba(OH)_2$). If left at 25° a very slight evolution of gas commenced in 2 hr, and after 20 hr the mixture solidified to a white opaque mass. This redissolved at 100°. After 24 hr at 25° the mixture was heated under reflux for 2 hr and was again left at 25° for 12 hr. The white solid, after desiccation at 100° (0.1 mm) for 24 hr, weighed 0.653 g. It softened at 150° and was all melted at 190°. It was soluble in warm water and warm pyridine. *Anal.* Calcd for $H[N(CH_3)N(CH_3)CO]_{11}N(CH_3)NHCH_3$: C, 41.7; H, 7.43; N, 33.4. Found: C, 40.3; H, 6.98; N, 35.0. Strong bands appeared in the infrared spectrum at 5.95, 6.74, 6.92, and 7.32 μ and medium bands at 2.86, 3.05 (sh), 3.40, 8.92, 9.25, and 13.35 μ.

To 0.3 g of this polymer in 3 ml of dry pyridine at 100° was added 0.3 g of *p*-bromophenyl isocyanate. After evaporation of the pyridine, 0.5 g of brown solid remained, part of which dissolved in boiling water. The insoluble part (dried) was dissolved in warm dimethylformamide and precipitated therefrom by addition of dry ether to give 0.15 g of an off-white solid. Both the isocyanate and N,N′-bis-*p*-bromophenylurea are soluble in dimethylformamide and unprecipitated by ether. The same infrared peaks were present as before as well as an additional weak band at 6.25 μ and a medium one at 6.55 μ. Bromine analysis by the Schöninger method was helpfully performed by the analytical department of Armour and Co. *Anal.* Calcd for $BrC_6H_4NHCO[N(CH_3)N(CH_3)CO]_{11}N(CH_3)N(CH_3)CONHC_6H_4Br$: Br, 11.4. Found: Br, 11.7.

When 0.3067 g of IIa was refluxed for 2 hr with 5 ml of water, 0.1226 g of carbon dioxide was evolved, as measured in an attached Ascarite tube with a nitrogen sweep. This represents 59.2% of the total possible CO_2. The residual product was a viscous, colorless oil, but it had about the same infrared pattern as the previous one, the peak at 2.85 μ being shorter and broader, those at 9.25 and 11.35 μ being absent, and a new peak at 8.0 μ. *Anal.* Calcd for $H(NMeNMeCO)_{5.5}NMeNHMe$: C, 41.5; H, 7.76; N, 34.2. Found: C, 40.2; H, 7.46; N, 34.4.

With Alcohol. A mixture of 1.01 g of IIa and 1 ml of absolute ethanol was refluxed for 22 hr. Evaporation left 0.74 g of white solid, changing to 0.5 g of mp 218–222° after being extracted with boiling tetrahydrofuran (to remove unused IIa). *Anal.* Found: C, 42.5; H, 7.08; N, 32.4.

With Aniline. A mixture of 1.0 g of IIa and 1.0 g of aniline was warmed briefly. The clear solution evolved carbon dioxide and continued to do so for some time. After 72 hr at 25° a clear, viscous solution resulted from which aniline was removed by vacuum heating to 70°. The residual solid (1.4 g) was crystallized from tetrahydrofuran to yield 0.8 g of 1,2-dimethylhydrazinecarboxanilide, $CH_3NHN(CH_3)CONHC_6H_5$, mp 107–108°. *Anal.* Calcd for $C_9H_{13}N_3O$: C, 60.31; H, 7.30; N, 23.45. Found: C, 60.12; H, 7.18; N, 23.40.

When 0.72 g of IIa, 20 ml of dry benzene, and only 0.1 g of aniline was refluxed for 41 hr, half of the IIa was recovered. A small amount of oil was formed also which was not investigated.

With Hot Pyridine. Two grams of IIa was heated under reflux with 15 ml of dry pyridine for about 25 hr, after which pyridine was removed leaving an oily solid. Tetrahydrofuran dissolved the oil. The pale brown, undissolved solid (0.55 g), mp 231–234°, was soluble in hot water. Treatment of 0.4 g of this with 0.5 g of *p*-bromophenyl isocyanate in pyridine yielded a product which, after extraction with boiling water and drying, was dissolved in dimethylformamide and precipitated therefrom with ether. The product (0.2 g) was analyzed by chemists at Armour and Co. *Anal.* Calcd for $BrC_6H_4NHCO(NMeNMeCO)_{13}NMeNMeCONHC_6H_4Br$: Br, 10.2. Found: Br, 10.2.

With Aqueous KOH. To 20 ml of 50% aqueous potassium hydroxide was added 1.3 g of IIa. The mixture was distilled until 10 ml was collected. The distillate had an ammoniacal odor. To it was added 10 ml of a saturated solution of picric acid in ethanol. The mixture was heated for 5 min and then cooled to obtain 1.0 g of yellow needles of mp 150–151°. This is 1,2-dimethylhydrazinium picrate.

Reactions of 1,2-Diethyl-1,2-hydrazinedicarboxylic Anhydride. With Water. When equal weights (2 g each) of IIb and water were mixed and left for 67 hr, then refluxed for 6 hr, much of the acid anhydride still persisted. On cooling the aqueous solution, 0.9 g of white needles separated. That this was essentially IIb was established by melting point (100–104°), mixture melting point (109–110°), and the infrared spectrum which were the same as authentic IIb.

When a large excess of water (10 ml) was mixed with IIb (0.308 g) and heated under reflux for 3 hr until carbon dioxide was no longer evolved, the original two-phase system gradually became homogeneous. A total of 0.118 g of CO_2 was released, or 68.9% of the possible amount. Evaporation of the water and diethylhydrazine left a pale yellow oil, less viscous than its counterpart from IIa. The infrared spectrum showed a strong peak at 5.97 μ and medium peaks at 2.91, 3.05, 3.31, 6.85, 7.20, 7.34, 7.88, 8.95, 12.7–13.8, and 15.0 μ. *Anal.* Calcd for $H(NEtNEtCO)_{2.64}NEtNHEt$: C, 53.1; H, 9.94; N, 26.2. Found: C, 52.2; H, 9.62; N, 26.4.

With Ethanol. From an original 1.50 g of IIb, refluxed for 24 hr with 1.5 ml of absolute ethanol, was recovered 1.45 g (mp 108–112°, mmp 111–112°).

With Hot Pyridine. After refluxing a mixture of 0.496 g of IIb and 15 ml of dry pyridine for 42 hr, then removing the pyridine, a solid residue was obtained. Hot tetrahydrofuran dissolved it readily, and on cooling the solution 0.26 g of pure IIb separated (mp 111°). Evaporation of the filtrate yielded another 0.20 g (mp 100–109°). Thus, any polymerization was negligible.

Reactions of 1,2-Diisopropyl-1,2-hydrazinedicarboxylic Anhydride. With Water in Large Excess. Refluxing 0.3475 g of IIc with 10 ml of water for 5.5 hr caused separation of an oil and liberation of 0.184 g of CO_2. The oil changed to a white solid on cooling. On drying it for analysis at 70° (0.05 mm), about one-fourth of it sublimed to give clear crystals of mp 68°. Infrared absorption bands appeared at 2.82, 3.00, 3.31, 6.00, 7.21, 7.59, 8.80, 9.36, 11.38, and 12.25 μ. *Anal.* Calcd for $H[N(C_3H_7)N(C_3H_7)CO]_{1.96}N(C_3H_7)NHC_3H_7$: C, 60.0; H, 11.1; N, 21.0. Found: C, 60.3; H, 11.2; N, 22.2.

With Ethanol or Pyridine. No reaction occurred on refluxing IIc with an equal weight of absolute ethanol or with 25 parts of dry pyridine, both for 22 hr. The original compound, mp 77–79° and mmp 79–80°, was obtained from both on evaporation of solvents.

With Aniline. The same directions were followed as for IIa plus aniline, and also with 1-g quantities of reagents. The solution was deep red in color and quite fluid (in contrast to the viscid solution from IIa). After vacuum removal of aniline (25–70°), a red oil resulted which gradually changed to a brown solid, mp 70–75°, 1.2 g. It was crystallized from aqueous ethanol, but with difficulty, to obtain light brown crystals (0.5 g) of 1,2-diisopropylhydrazinecarboxanilide, mp 79.5°. *Anal.* Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 8.97; N, 17.86. Found: C, 66.89; H, 8.41; N, 17.83.

Pyrolysis of 2-Carbethoxyhydrazinecarbonyl Chloride. Heating in Toluene. A solution of 3.5 g of this acyl chloride in 15 ml of dry toluene was refluxed under anhydrous conditions for 17 hr. Hydrogen chloride was evolved, and in duplicate experiments it was absorbed in water and titrated with 0.1 *N* base, showing a total that was 94–96% of theoretical. After evaporation of the toluene there remained 2.5 g of a glassy solid (solid A) that softened at 50–55° and became molten at 63°. It was hygroscopic and failed to crystallize from common solvents. The infrared spectrum showed strong peaks at 5.48, 5.70, and 8.00 μ and medium bands at 3.00, 3.34, 6.60, 6.78, 7.00, 7.24, 7.65, 9.38, and 12.90 μ. *Anal.* Calcd for $C_8H_{12}N_4O_6$: C, 36.95; H, 4.65; N, 21.54; mol wt, 260. Found: C, 36.91; H, 4.56; N, 21.61; mol wt, 276 (Rast).

Solid A dissolved in warm water. The solution was strongly acidic (pH about 2). A trace of carbon dioxide was given off. The solution tested negatively for chlorine ($AgNO_3$) and gave a deep amber-red color with ferric chloride. During a 17-hr reflux period with 0.5715 g of solid A and 10 ml of water there was evolved 0.066–0.070 g of CO_2 (theory 0.097 g for one carbonyl of VII). The resulting solid, after distilling off water and desiccation at 70° (0.05 mm) for 2 hr, looked like the starting material. It softened at 45°, fused at 55°, and had a similar infrared spectrum, except the peak at 5.70 μ was broader and the one at 5.48 μ was absent. *Anal.* Found: C, 34.5; H, 5.14; N, 26.45.

One gram of solid A gradually dissolved in 3 ml of aniline at 100°. After it was cooled, some dilute hydrochloric acid was added. The insoluble brown material (0.12 g) was crystallized from ethanol (Norit) to yield an off-white solid, mp 170–172°. *Anal.* Found: C, 61.3; H, 5.40; N, 16.8. If, instead, the aniline solution was refluxed for 2.5 hr before adding the dilute HCl, then 1.0 g of carbanilide resulted (mp and mmp 236–238°).

One gram of solid A, 2 ml of phenyl isocyanate, and 2 drops of pyridine were warmed at 100° for a few mixtures, cooled, and mixed with ether. The precipitated white solid (0.7 g) was crystallized from dimethylformamide to give 0.4 g of substance, insoluble in camphor at 190°, and melting above 300°. *Anal.* Found: C, 59.7; H, 2.95; N, 19.2.

Heating at Atmospheric Pressure. Ten grams of 2-carbethoxyhydrazinecarbonyl chloride (0.060 mole) was slowly heated to 145° by an oil bath. The flask was connected in series to a trap at −78° and a water trap. A flow of nitrogen gas was maintained. The cold trap collected 2 ml of ethyl chloride (0.03 mole) and the water trap collected 0.033 mole of hydrogen chloride. The glassy residue (6.3 g), solid B, melted higher than solid A; it softened at 100° and melted at 110–115°. Its infrared spectrum was similar to that of solid A except that the peak at 5.48 μ was reduced to a shoulder, and those at 6.60 and 6.78 μ were somewhat stronger. *Anal.* Found: C, 30.9; H, 4.38; N, 28.8.

Potentiometric titration of a solution of 0.4062 g of solid B in water with 0.1 *N* alkali gave a neutral equivalent of 336. Long refluxing (22 hr) of 0.5629 g of an aqueous solution of solid B liberated 0.043 g of carbon dioxide.

Heating at Low Pressure. Nine grams of the acyl chloride lost 2.6 g during 2 hr of heating at 125° (oil bath) and 0.1-mm pressure. The glassy solid residue (solid C) looked like solids A and B. Its infrared spectrum resembled that from solid B except for a strong band at 5.48 μ as from solid A. Its neutral equivalent, determined as for solid B, was 345. *Anal.* Found: C, 34.3; H, 4.54; N, 25.4.

Refluxing a solution of 0.5648 g of solid C in 10 ml of water for 24 hr caused the evolution of 0.067 g of CO_2. The residue, after evaporation of the water, softened at 45° and was molten at 62°. The only significant change in the infrared spectrum was loss of the band at 5.48 μ. *Anal.* Found: C, 32.8; H, 4.85; N, 28.5.

To a solution of 1.0 g of solid C in 5 ml of warm pyridine was added 1.1 ml of 1-naphthyl isocyanate. The white precipitate (2.1 g) that formed during an hour was crystallized from dimethylformamide, yield 0.8 g, mp >300°. *Anal.* Found: C, 65.73, 65.11; H, 4.43, 4.27; N, 14.32, 14.44.

The Free-Radical Chemistry of Fluoro Ketones. I. Reaction with Saturated Substrates

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Abstract: Polyfluoro ketones participate in free-radical, chain-addition reactions with the carbon–hydrogen bond. With many types of substrate R–H, addition to the fluoro ketone carbonyl group proceeds readily to give good yields of alcohol $R(R_F)_2COH$ and ether $ROCH(R_F)_2$. A mechanism is suggested to account for the results, including the observed preference for alcohol formation.

The carbonyl group is resistant to free-radical attack; products formed by the addition of free radicals to carbonyl groups have only occasionally been observed.[1a–e] Moreover, in the case of ketones these reactions are nonchain processes. Even with aldehydes the sole known exception is the addition of cyclopentane to formaldehyde[1b] where the kinetic chain length is 2. It is known that radicals are capable of adding to the carbonyl function of molecules like chloranil by a nonchain mechanism to yield products which are mainly ethers of the corresponding hydroquinones or copolymers.[2] In contrast with even such special cases, we find that fluoro ketones will undergo efficient radical chain addition of R–H.

Fluoro ketones are characterized by the electron-withdrawing inductive effect exerted by highly electronegative fluoroalkyl groups. This results in a weakly polarized, electron-deficient carbonyl function, direct

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