tion was in progress. After approximately 24 hr of irradiation, the solvent was removed and the reaction products were separated and collected by glc. A 20% bis(β-cyanoethoxy)ethane on Chromosorb W column (85°) was utilized for the separation. In addition to *trans*-8,9-dihydroindene (6%), tricyclo[3.3.1.$0^{8,9}$]nonadiene (30%) and cis-fused I (18%) were obtained. Trans-fused compound (164 mg) was collected (11%): uv (EtOH) λ_{max} 311 nm (ϵ 4500); nmr (neat) τ 4.1 (s, 6, vinyl H) and 9.0 (m, 4, allylic and cyclopropyl H). Analysis of the compound on an analytical glc instrument prior to reduction with potassium showed it to be >99.9% pure.

9,9-Dideuterio-*trans*-bicyclo[6.1.0]nona-2,4,6-triene. Using similar conditions as described in the previous experiment, 0.7 g of 9,9-D_2-I in methanol was irradiated with a low-pressure Hg lamp for 18 hr. After concentrating the reaction mixture, the following compounds were separated and collected by gas chromatography on the column used above: 5,5-dideuterio-*trans*-dihydroindene (22%); 5,5-dideuterio-*cis*-dihydroindene (3%); 2,2-dideuteriotricyclo[3.3.1.$0^{8,9}$]nonadiene (52%); 5,5-dideuterioindene (8%); and 9,9-D_2-II, 105 mg (15%), nmr (neat) τ 4.1 (s, 6, vinyl H) and 9.0 (s, 2, allylic H).

cis^4-Cyclononatetraene[16] **(III).** *anti*-9-Chloro-*cis*-bicyclo[6.1.0]-nona-2,4,6-triene[28] (7.5 g, 0.01 mol) and 4 ml of THF, previously distilled from lithium aluminum hydride, were placed in a 25-ml round-bottomed Schlenk flask equipped with a mechanical stirring bar and a micro condenser, while maintaining a nitrogen atmosphere in the flask. Lithium metal (180 mg), cut in small pieces, was then added to the solution. The reaction was allowed to proceed at room temperature under a nitrogen atmosphere for 24 hr, after which time it turned dark brown in color. The mixture was then cooled to 0° and 10–15 ml of water (0°) was quickly added with stirring. The quench of the lithium cyclononatetraenide and the work-up were conducted in a cold room at −20 to 0°. The CNT produced from the quench was quickly extracted with three 3-ml portions of chilled pentane (0°), and the combined pentane extracts were dried over $MgSO_4$. After filtration and concentration of the pentane solution, it was chromatographed by glc on a 3% bis(β-cyanoethoxy)ethane on 60–80 Chromosorb W column ($^3/_8$ in. × 1.3 ft) at 0°. The preparative gas chromatographic instrument was placed in the cold room in order to maintain low-temperature conditions for the collection. When a sufficient amount (100 mg) of III was collected, the chromatography was stopped and the collected material was analyzed on an analytical PE-800 gas chromatograph (employing the same column as above) and it showed the following composition: 4.0% *cis*-8,9-dihydroindene; 4.8% *trans*-8,9-dihydroindene; and 91.2% III, nmr (D_8-THF) τ 4.3 (s, 8, vinyl H), 7.1 (t, 2, allylic H).

9-Deuterio-cis^4-cyclononatetraene. Lithium cyclononatetraenide[15] (0.01 mol) in THF solution was quenched with D_2O (15 ml) at 0°. The product was worked up in the same manner as described above. Analytical glc showed the following composition for the material which was purified by preparative gas chromatography: 4.2% *cis*- and 5.0% *trans*-8,9-dihydroindene; 90.8% 9-D_1-III, nmr (D_8-THF) τ 4.3 (s, 8, vinyl H) and 7.1 (broad s, 1, allylic H).

Acknowledgments. We thank Professor D. Kivelson for making his esr facilities available to us. We also thank Drs. G. Petrowski and J. Dirlam for providing aid in the synthesis of some of the compounds and for helpful discussions. Also, we wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

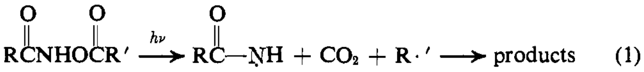
Diacylamino and Diacyl Nitroxide Radicals from Triacylhydroxylamine Photolyses[1]

Frank R. Stermitz* and David W. Neiswander

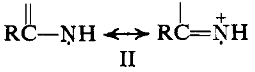
Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521. *Received August 12, 1972*

Abstract: Irradiation of *N,N,O*-tripropionylhydroxylamine, *N,N,O*-triacetylhydroxylamine, and *N*-acetoxysuccinimide causes photolysis to produce mainly CO_2, the corresponding imide, and the *N*-alkylimide. A mechanism is proposed which involves formation of a diacylamino radical which undergoes hydrogen abstraction, coupling, and in one case disproportionation. Thus, photolysis of triacylhydroxylamines will provide a simple method for producing both cyclic and acyclic diacylamino radicals. A strong epr signal was observable during photolysis of the triacylhydroxylamines, but this signal proved identical with that obtained during $Pb(OAc)_4$ oxidation of the corresponding *N*-hydroxy compounds or the triacylhydroxylamines themselves and was thus assigned to the diacyl nitroxide rather than the diacylamino radical. A minor photolytic pathway yielding CO and the diacyl nitroxide was proposed to account for the epr signal which occurred during photolysis.

Some time ago, the photolysis of *N,O*-diacylhydroxylamines was found[2,3] to produce products shown to arise from the acylamino radical I. It was suggested[3] that the chemical evidence was in favor of I existing as a σ radical II (with the unpaired electron in a σ orbital), rather than as a π radical III (with the unpaired electron in a π orbital). Epr spectra were not reported as supporting evidence. More recently, results[4] of a diacyldimethyltetrazene photolysis to yield IV were

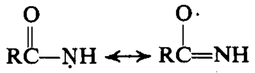


$$\mathrm{R\overset{O}{\overset{\|}{C}}NHO\overset{O}{\overset{\|}{C}}R'} \xrightarrow{h\nu} \underset{\mathrm{I}}{\mathrm{R\overset{O}{\overset{\|}{C}}{-}\dot{N}H}} + \mathrm{CO_2} + \mathrm{R\cdot'} \longrightarrow \text{products} \qquad (1)$$



$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}\dot{N}H} \longleftrightarrow \mathrm{R\overset{O^-}{\overset{|}{C}}{=}\overset{+}{\dot{N}}H}$$

II



$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}\dot{N}H} \longleftrightarrow \mathrm{R\overset{O\cdot}{\overset{|}{C}}{=}NH}$$

III

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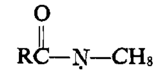
(1) This work was supported in part by Grant GM-15425 from the National Institute of General Medical Sciences and by a BSSG grant from NIH to Colorado State University.

(2) B. Danieli, P. Manitto, and G. Russo, *Chem. Ind.* (*London*), 329 (1969).

(3) B. Danieli, P. Manitto, and G. Russo, *ibid.*, 203 (1971).

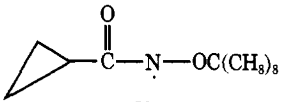
(4) P. Tordo, E. Flesia, and J. M. Surzur, *Tetrahedron Lett.*, 183 (1972).



$R\overset{\overset{O}{\|}}{C}-\dot{N}-CH_3$

IV

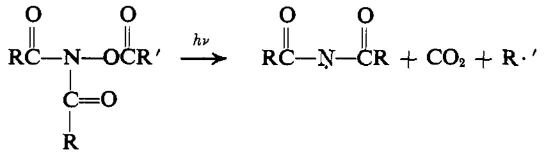
suggested to indicate a π structure for IV because of the 7-G a_N value obtained from an epr spectrum observable during the reaction. In addition, the radical V was reported[5] to be a π radical, based upon an epr



V

spectrum whose g value was 2.006 G with an a_N value of 10.5 G. Predictions based upon chemistry and/or theoretical considerations have been that acylamino (or diacylamino) radicals are σ[6] or are π.[7]

We recently developed[8] a convenient synthesis for a variety of triacylhydroxylamines and considered that these should photolyze to produce diacylamino radicals, such as VIa and VIIa, whose structure and chemistry could be explored.



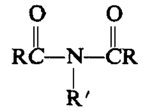
$$R\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{\underset{C=O}{\underset{|}{N}}}-O\overset{\overset{O}{\|}}{C}R' \xrightarrow{h\nu} R\overset{\overset{O}{\|}}{C}-\dot{N}-\overset{\overset{O}{\|}}{C}R + CO_2 + R\cdot' \quad (2)$$

VI, R = R′ = CH_3 VIa, R = CH_3
VII, R = R′ = CH_2CH_3 VIIa, R = CH_2CH_3
VIII, R = CH_2CH_2;
R′ = CH_3

Results

Photochemistry. Photolyses were carried out on *N*,*N*,*O*-triacetylhydroxylamine (VI), *N*,*N*,*O*-tripropionylhydroxylamine (VII), and *N*-acetoxysuccinimide (VIII). A major portion of the work was conducted with VII, mainly because of its superior solubility characteristics in a variety of solvents. The absorption spectra of the triacylhydroxylamines were similar and showed a maximum at 205–210 nm, trailing to no absorption at approximately 280 nm. Molar extinction coefficients at 254 nm (the major intensity line of the irradiation source) in cyclohexane were: VI, 180; VII, 210; and VIII, 68. Of the three, only VIII showed some fine structure with shoulders at 257 nm (ϵ 55), 251 (105), 243 (130), 227 (240), and 225 (350). Molar extinction coefficients for VI and VII at 208–209 nm were 12,000 and 16,000, respectively, while the maximum for VIII was at about 205 nm with molar extinction coefficient about 1,600. Irradiations in cyclohexane solvent through a Pyrex filter gave no photolysis after several hours, nor were VI–VIII thermally sensitive. However, irradiation of VII with 254-nm light in a variety of solvents caused rapid photolysis. VI underwent photolysis in diethyl ether, cyclohexane, and ethanol. Due to insolubility, VIII was not studied in cyclohexane. It did photolyze in diethyl ether, but was inert in benzene. The results with VII will be described in detail.

The major products from VII irradiation were CO_2, propionimide (IX), and *N*-ethylpropionimide (X). Photolysis of VII was carried out in solvents contain-



$R\overset{\overset{O}{\|}}{C}-\underset{R'}{\underset{|}{N}}-\overset{\overset{O}{\|}}{C}R$

IX, R = CH_2CH_3; R′ = H
X, R = R′ = CH_2CH_3
XI, R = CH_3; R′ = H
XII, R = R′ = CH_3

ing hydrogens of differing ease of abstraction and in each case the two major products were IX and X, but in differing ratios. The results are given in Table I.

Table I. Nongaseous Products from Photolysis of Tripropionylhydroxylamine in Various Solvents[a]

Solvent	% total yield[b]	% propionimide (IX)	% *N*-ethylpropionimide (X)	IX/X ratio
2-Propanol	42	25	17	3:2
Ethanol	42	20	20	1:1
Cyclohexane	39	20	19	1:1
Benzene	17	3	14	1:5

[a] Solutions 0.1 *M* in VII irradiated 2 hr at 254 nm. [b] The remainder was unreacted starting material.

Because the genesis of IX could be presumed to have involved hydrogen abstraction from solvent, we examined the photolysis solutions in the cases of irradiations in cyclohexane and benzene for bicyclohexyl and biphenyl, respectively. No biphenyl was found in the benzene solution, but significant quantities of bicyclohexyl were detected in irradiations conducted in cyclohexane. Mechanistically, a radical disproportionation could account for production of IX in benzene, so the gaseous products from an irradiation of VII in benzene were scrubbed through a bromine solution. From this solution, 1,2-dibromoethane was isolated and thus ethylene was shown to be an additional product from the photolysis of VII in benzene.

For the photolysis of VII in cyclohexane we also determined CO_2 evolution quantitatively in comparison with disappearance of VII. Two determinations showed 93 and 91% of the theoretical CO_2 was formed based upon the amount of VII which had disappeared. For reasons discussed later, we also found it necessary to check for CO as a photolysis product and, indeed, discovered that 4% CO (again based upon VII disappearance) was formed during an irradiation of VII in cyclohexane. Thus, the total CO + CO_2 production was about 96% of the theoretical. Our methods of quantitation probably could not differentiate this from 100%.

Although we did not at this point have elucidation of the photochemical mechanisms as a goal, we did measure quantum yields for disappearance of VII during irradiations in cyclohexane and ethanol. These were determined to be 0.62 in cyclohexane and 0.72 in ethanol. The quantum yields were identical in freeze–thaw degassed and in nondegassed solutions.

Photolysis of *N*,*N*,*O*-triacetylhydroxylamine (VI) was studied qualitatively in diethyl ether, cyclohexane, and ethanol. In each solvent, the products were the

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(5) T. Koenig, J. A. Hoobler, and W. R. Mabey, *J. Amer. Chem. Soc.*, **94**, 2514 (1972).

(6) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *ibid.*, **89**, 4875 (1967).

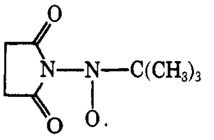
(7) M. C. R. Symons, *J. Chem. Phys.*, **55**, 1493 (1971).

(8) F. R. Stermitz and F. A. Norris, *J. Org. Chem.*, **35**, 527 (1970).

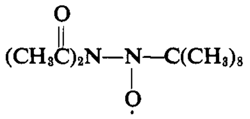
imide XI and the *N*-methylimide XII in approximately equal amounts. The photolysis of VI in cyclohexane produced a CO_2/CO ratio of about 100, bicyclohexyl in quantity somewhat greater than in the case of VII photolysis, and considerable methane. Although quantitative measurement of these products was not accomplished, each (with the exception of CO) represented major products.

Irradiation of *N*-acetoxysuccinimide (VIII) in diethyl ether produced succinimide and *N*-methylsuccinimide in a 2:1 ratio, along with CO_2. The quantum yield of photolysis was not measured, but was qualitatively similar to that of VII. Irradiation of VIII in benzene resulted in no photoproducts even after prolonged (8 hr) irradiation.

Radical Trapping and Epr Results. The succinimidyl radical has been successfully trapped[9] with nitroso-*tert*-butane to produce XIII. The epr spectrum of XIII showed[9] a triplet of triplets analyzable as being due to $a_N{}^1$ (nitroxide nitrogen) = 16.4 G and $a_N{}^2$ (imidyl nitrogen) = 1.8 G. We, therefore, conducted a similar experiment on VI photolysis in methylene chloride and obtained an epr spectrum showing a triplet of triplets ($a_N{}^1$ = 16.0 G and $a_N{}^2$ = 1.8 G) in excellent agreement with the expected spectrum for the diacetylamino-*tert*-butyl nitroxide XIV.



XIII

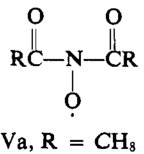


$$(CH_3\overset{O}{\overset{\|}{C}})_2N\text{—}\underset{\dot{O}}{N}\text{—}C(CH_3)_3$$

XIV

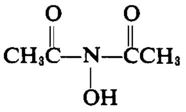
Thus encouraged, we attempted to observe the presumed intermediate diacylamino radicals directly by epr examination during photolysis. VI and VIII were nearly insoluble in cyclopropane (a usual choice for such work) so photolysis of VII in freeze–thaw degassed cyclopropane at −100° in the epr cavity was conducted. A 1 : 1 : 1 three-line spectrum was obtained which showed an a_N value of 6.3 G and a *g* value of 2.007. VI was soluble in CH_2Cl_2 and a similar experiment, but in that solvent, yielded a nearly identical spectrum with a_N = 6.1 G. A suitable solvent was not found for photolysis work with VIII in the epr cavity.

Although the diacylamino radicals VIa and VIIa could account for the observed epr spectra (compare the quoted a_N and *g* values for IV and V), the possibility also existed that the spectra could be due to the corresponding nitroxide radicals XVa and XVb.[10] Many acyl nitroxides have been reported[11] with a_N values and *g* values close to those of our observed spectra. Similar nitroxides have been prepared[12] by $Pb(OAc)_4$ oxidation of *N*,*N*-disubstituted hydroxylamines. We therefore synthesized XVI and treated it with $Pb(OAC)_4$ in an epr tube and examined the epr spectrum. The spectrum obtained proved to be identical with that observed during VI photolysis. It was also found that we were able to generate the same spectrum by direct treatment of VI with $Pb(OAc)_4$ and thus the more easily prepared triacylhydroxylamines can serve as sources of diacyl nitroxide radicals. This was confirmed with VII which yielded, upon treatment with $Pb(OAc)_4$, an epr spectrum identical with that from VII photolysis. The $Pb(OAc)_4$ generated spectra had half-lives of several minutes at room temperature and were still visible after several hours.



$$R\overset{O}{\overset{\|}{C}}\text{—}\underset{\dot{O}}{N}\text{—}\overset{O}{\overset{\|}{C}}R$$

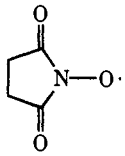
XVa, R = CH_3
XVb, R = CH_2CH_3



$$CH_3\overset{O}{\overset{\|}{C}}\text{—}\underset{OH}{N}\text{—}\overset{O}{\overset{\|}{C}}CH_3$$

XVI

We also oxidized VIII and *N*-hydroxysuccinimide with $Pb(OAc)_4$ and obtained identical epr spectra from both sources. The resulting cyclic nitroxide XVII gave a nine-line spectrum interpreted as arising from hyperfine interactions of the nitrogen triplet (a_N = 3.6 G) and four equivalent hydrogen nucleus interactions (a_N = 1.8 G). We briefly looked at the similarly prepared nitroxide of glutarimide and again hyperfine interactions were observable. However, resolution was not sufficiently good to allow assignments to be made. Thus, hydrogen hyperfine interactions are observable in the case of the cyclic diacyl nitroxides, but not in the acyclic diacyl nitroxides.



XVII

Discussion

The present results are explicable by Scheme I, where VII photolysis in cyclohexane is used as an example. Thus, a major photolytic pathway yields a diacylamino radical which undergoes hydrogen abstraction from solvent and radical coupling reactions. A minor pathway involves photolysis to yield the nitroxide, carbon monoxide, and the ethyl radical. The scheme is somewhat modified when benzene is employed as a solvent. Firstly, the solvent itself is absorbing the light, and hence, we are dealing with a sensitized (by benzene) photolysis. Secondly, no biphenyl was found as a by-product and hence, the source of the hydrogen necessary to form IX is not the solvent.

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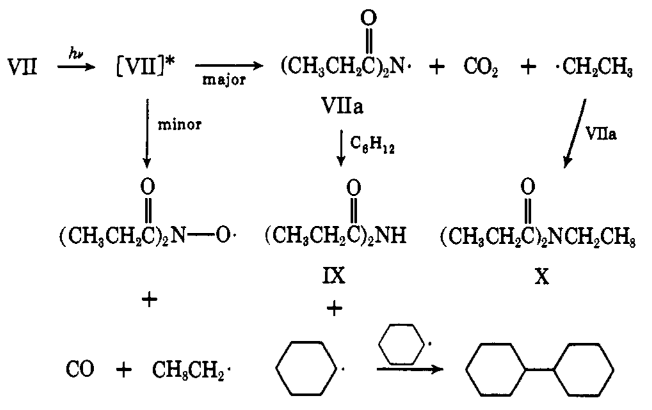
(9) C. Lagercrantz and S. Forshult, *Acta Chim. Scand.*, 23, 708 (1969).

(10) We are grateful to E. Hedaya for pointing out this possibility.

(11) A. Calder, A. R. Forrester, and R. H. Thompson, *J. Chem. Soc. C*, 512 (1969); G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc., Chim. Fr.*, 3283 (1965); J. W. Hartgerik, J. B. F. N. Enberts, and Th. J. de Boer, *Tetrahedron Lett.*, 2709 (1971); A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, 24, 1623 (1968).

(12) K. T. Wang, D. N. Brattesani, and B. Weinstein, *J. Heterocycl. Chem.*, 3, 98 (1966).

Scheme I



The finding of ethylene as a product suggests that a radical disproportionation reaction between ethyl radical and VIIa to form IX and ethylene occurs when benzene is used as a solvent. Thus, the diacylamino radical VIIa undergoes the "normal" radical reactions of hydrogen abstraction, coupling, and disproportionation. Although we studied photolysis of VI less thoroughly, it appears to follow a nearly identical pathway. In addition, in this case the diacylamino radical VIa was trapped with nitroso-*tert*-butane, thus providing further evidence for Scheme I as a general mechanism. The results parallel in many respects the results[2,3] of Danieli with acylamino radicals produced in a similar manner and at this level of investigation there appear to be no major differences in the chemistry of acylamino and diacylamino radicals.

Benzene is known to be a singlet sensitizer and, since the photolyses of VI and VII were not affected by oxygen, one can hypothesize decomposition at the stage of the excited singlet. Neither of these pieces of evidence are fool-proof, however, and further work needs to be done on the photophysical processes involved. It is interesting to note that *N*-acetoxysuccinimide (VIII) failed to photolyze in benzene solution and thus is apparently not susceptible to the sensitized reaction. However, the direct photolysis of VIII (as far as we studied it) appeared to correspond closely to that of VI and VII and hence the properties of cyclic diacylamino radicals do not appear to differ greatly from those of the acyclic radicals. The only difference which bears further investigation was the imide to *N*-alkylimide ratio which was 1:1 in the case of VI photolysis in diethyl ether and 2:1 in the case of VIII photolysis in the same solvent. This could be a measure of the relatively greater ability of the succinimidyl radical (because of its compact size) to move out of its cage and away from the ethyl radical. A detailed examination of cage *vs.* noncage processes will provide additional information on diacylamino radical chemistry.

If our interpretation (Scheme I) of the present results is correct, then none of the data provides evidence regarding the relative merits of the σ or π structures for diacylamino radicals. Prior to observation of the epr spectra from the $Pb(OAc)_4$ oxidations, the 1:1:1 triplet ($a_N = 6$ G) epr spectrum generated during photolysis of VI and VII could have been assigned to the diacylamino radicals themselves. Such a_N values would be characteristic of π (delocalized) radicals. Because of the plethora of literature data assigning epr spectra incorrectly, it is perhaps pertinent to justify our assignments more closely. In order for the observed signals in VI and VII photolysis to be due to the diacylamino radicals VIa and VIIa rather than the nitroxides XIV and XV, one would have to assume either that (1) the spectra of the diacylamino radicals are coincidentally identical with those of the nitroxides or (2) that treatment of *N*-hydroxyimides with $Pb(OAc)_4$ produces diacylamino rather than nitroxide radicals. The literature evidence (which includes studies of products arising from the nitroxides produced by $Pb(OAc)_4$) is completely against the latter possibility. Although the possibility that the two types of radicals have coincidentally identical epr spectra seems at first glance remote, it cannot be absolutely ruled out until spectra unequivocally assignable to diacylamino radicals are obtained. It is interesting in this regard to once again look at the quoted[4,5] data for the acylamino radicals IV ($a_N = 7$ G) and V ($a_N = 10.5$ G, g value 2.006). These values are very close to those we have observed and have assigned to nitroxide rather than diacylamino radicals.[13] If diacyl nitroxide radicals are very much more stable than diacylamino radicals, then traces of the former must always be scrupulously avoided if the latter are to be observed. One pathway for diacyl nitroxide formation whenever diacylamino radicals are formed could involve reaction with oxygen. We have thus conducted our epr investigations of photolysis-produced radicals in samples which have been degassed through several freeze–thaw cycles. Thus, we feel that, in our case, the production of the nitroxide radicals by the minor Scheme I pathway is more likely than by eq 3.

$$2(RC{=}O)_2N\cdot + 2O_2 \longrightarrow 2(RC{=}O)_2N{-}O{-}O\cdot \longrightarrow 2(RC{=}O)_2N{-}O\cdot + O_2 \quad (3)$$

In summary, the total results obtained have shown that triacylhydroxylamine photolysis will represent a clean, viable method for the production and chemical study of both cyclic and acyclic diacylamino radicals. The minor cleavage pathway which produces diacyl nitroxide radicals will, however, apparently not allow triacylhydroxylamine photolysis to be useful for epr investigation of diacylamino radicals.

Experimental Section

Spectra were obtained as follows: nmr, Varian A60A; mass spectra, AEI Model MS-12; ir, PE Model 457 or Beckman Model IR-5; uv, PE 402 or Cary 17; epr, Varian V-4502 with optical transmission cavity E-4534 and variable-temperature accessory. Solvents used were redistilled reagent grade. The *N*,*N*,*O*-triacetylhydroxylamine (VI) was synthesized as described earlier.[8] *N*-Hydroxysuccinimide was prepared according to a literature[12] procedure and this was converted to *N*-acetoxysuccinimide (VIII)[14] by acetylation with acetyl chloride in pyridine. Nitroso-*tert*-butane was prepared by the method of Emmons.[15] *N*,*N*-Diacetylhydroxylamine (XVI) was prepared by a modification of the method of Ames and Gray.[16] The last step of this procedure involved hydrogenolysis of *N*,*N*-diacetyl-*O*-benzylhydroxylamine to yield XVI. If the hydrogenolysis was conducted at 5° or if XVI was purified by recrystallization, it was found that a major portion of XVI rearranged to *N*,*O*-diacetylhydroxylamine. To avoid this, the hydrogenolysis was run at 0° and the crude XVI was isolated directly from the acetone hydrogenolysis solvent. Pure XVI could

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[13] After this manuscript was submitted, a paper appeared [W. C. Danen and R. W. Gellert, *J. Amer. Chem. Soc.*, **94**, 6853 (1972)] which conclusively showed that the reported[4] epr spectrum for IV was in reality that of the corresponding nitroxide and, in addition, presented the first epr data for an authentic acylamino radical.

(14) A. Hantzsch and J. Urbahn, *Chem. Ber.*, **28**, 753 (1895).

(15) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739, 6522 (1957).

(16) D. E. Ames and T. F. Gray, *J. Chem. Soc.*, 631 (1955).

then be obtained from the crude by rapid vacuum sublimation at 35°.

***N,N,O*-Tripropionylhydroxylamine (VII).** Propionic anhydride (195 g), 1-nitropropane (27 g), and NaOAc (15 g) were heated together on a steam bath at 80–85°. The product mixture was cooled and poured into 200 ml of H_2O. The aqueous mixture was extracted three times with 100-ml portions of $CHCl_3$ and the $CHCl_3$ extracts were combined, dried over $MgSO_4$, and evaporated. The residue was fractionally distilled to yield 30 g (55%, bp 92–94° at 2 mm) of the colorless liquid *N,N,O*-tripropionylhydroxylamine: nmr τ 8.88 (t, 6 H, $\mathrm{NCOCH_2C}H_3$), 8.70 (t, 3 H, $\mathrm{OCOCH_2C}H_3$), and 7.5 (m, 6 H, $\mathrm{NCOC}H_2\mathrm{CH_3}$ and $\mathrm{OCOC}H_2\mathrm{CH_3}$); ir (neat) 1795 and 1720 cm^{-1}; mass spectrum *m/e* 201 (M^+) and 57 (base peak).

Anal. Calcd for $C_9H_{15}O_4N$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.78; H, 7.68; N, 7.15.

Photochemistry. In a typical product analysis photolysis, three 10-ml quartz tubes were filled with 0.1 *M* *N,N,O*-tripropionylhydroxylamine (VII) in cyclohexane and the solution was freeze–thaw degassed three times, sealed, and irradiated for 3 hr at 254 nm in a Rayonet reactor. The tubes were removed, opened, and the solvent was stripped *in vacuo*. The crude residue was fractionally distilled to yield a colorless liquid (bp 30–35°, 0.2 mm), followed by a white solid as a sublimate on the walls of the flask and in the condenser. The white solid was collected and resublimed to yield pure propionimide (dipropionamide in *Chemical Abstracts*) (IX), mp 152–153° (lit.[17] 154°). The colorless liquid was redistilled to yield pure *N*-ethylpropionimide (*N*-ethyldipropionamide in *Chemical Abstracts*) (X), bp 110–112° (20 mm) (lit.[18] 114° (26 mm)). The nmr, ir, and mass spectra of IX and X confirmed their identities. In a similar manner, acetimide (diacetamide) (XI) and *N*-methylacetimide (*N*-methyldiacetamide) (XII) were isolated from the photolysis of *N,N,O*-triacetoxyhydroxylamine and identified by comparison with standard samples (purchased from Aldrich Chemical Co.). In a similar manner, succinimide and *N*-methylsuccinimide were isolated from the photolysis of *N*-acetoxysuccinimide and identified again by comparison with authentic purchased samples from Aldrich Chemical Co. For the quantitative analysis of these products gas chromatography was used (Hewlett Packard F&M 5700 and a 6 ft × 0.25 in. aluminum column packed with 10% DC-200 on Chromosorb Q 80–100 mesh, column at 145°, flow at 35 ml/min, injection block at 250°). During gas chromatography of residues from VI and VII photolyses in cyclohexane, one peak was noted which proved to be identical in retention volume with bicyclohexyl, purchased from Aldrich Chemical Co. That peak was also isolated preparatively and the identity proved spectroscopically.

The triacylhydroxylamines were found to be stable to room temperature and room light. To investigate thermal stability more closely, a 10% solution of *N,N,O*-tripropionylhydroxylamine (VII) in *m*-xylene was heated at reflux (134°) for 12 hr, and the residue after evaporation was analyzed for decomposition by nmr and gc. No change had occurred.

The evolution of CO_2 from the photolysis of VII was determined by trapping the photolysis gases (swept out by nitrogen bubbling through the solution being irradiated in an immersion reactor with a 450-W Hanovia lamp) in a standardized barium hydroxide solution followed by restandardization after photolysis.[19] The amount of starting material photolyzed was analyzed by gc using biphenyl as an internal standard and employing a 6 ft × $^1/_8$ in. 5% SE-52A on Chromosorb W column. In addition, the ratio of CO_2 to CO evolved during the photolysis of VI and of VII was determined from the above data and using special gc columns standardized for these two gases. The CO_2 analysis was carried out using a 6 ft × $^1/_8$ in. Porapak Q column at ambient temperature with a gas flow of 19 ml/min and the CO was analyzed with a 10 ft × $^1/_8$ in. 13X molecular sieve column at room temperature with a flow of 22 ml/min. The photolysis reactions for these latter studies were carried out in 10-ml quartz tubes fitted with gas-tight septums. A gas syringe was used to withdraw samples and inject into the gc for analysis. During the CO analysis for VI photolysis in cyclohexane, a peak was noted which proved identical with CH_4.

During an immersion reactor irradiation of VII in benzene, the nitrogen purge gas was directed through two gas scrubbers consisting of 35% Br_2 in CCl_4. After 10-hr irradiation, the traps were removed and the solvent was evaporated *in vacuo*. The oily residue was distilled and shown to be identical by nmr and gc with a standard sample of 1,2-dibromoethane. No dibromoethane was recovered from a control experiment where no irradiation took place.

For the quantum yield determinations, the intensity of radiation from the 254-nm Rayonet lamps was determined by ferrioxalate actinometry.[20] Quantum yields for disappearance of *N,N,O*-tripropionylhydroxylamine (VII) during irradiations in cyclohexane and ethanol were then determined by gc analysis for VII using a 10 ft × $^1/_8$ in. 2% DC-200 column at 155° and hexadecane and dodecanol as standards for the cyclohexane and ethanol experiments, respectively. Quartz tubes, freeze–thaw degassed three times at reduced pressure and then sealed, were irradiated in a Rayonet reactor equipped with a "merry-go-round" apparatus and measurements were made at low conversion (about 10%) of VII.

Epr Studies. Photolytic experiments were carried out directly in the epr instrument using an optical transmission cavity and variable-temperature accessory. The irradiation source was a water-jacketed Hanovia 450-W, Type L, mercury vapor lamp and the radiation was directed to the epr cavity by means of an aluminum reflector and a series of quartz lenses. Samples were irradiated in 3 or 4 mm OD quartz tubes fitted with vacuum stopcocks for degassing.

For the oxidative experiments, a benzene or CH_2Cl_2 solution of the triacylhydroxylamine was placed in the epr cavity and the instrument was carefully tuned to this sample. Then a solution of recrystallized $Pb(OAc)_4$ was added with a pipet and, as the solution mixed by diffusion, the magnetic field was continually swept in the vicinity of the nitroxide radical absorption. Spectra which are described in this paper are published elsewhere.[21]

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