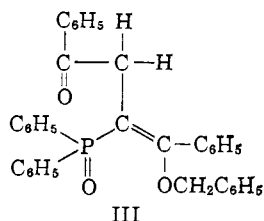


Figure 1.

quintet at 5.37, $J = 7$ c.p.s. (POCH_2CH_3); 2H^1 doublet at 6.33, $J_{\text{HP}} = 21$ c.p.s. (equivalent phenacyl protons); 3H^1 triplet at 8.52, $J = 7$ c.p.s. (CH_3CH_2-) (Fig. 1). The reaction was nearly complete in 10 min. in methylene chloride solution (*ca.* 1.7 M). II was isolated in 32% yield when this solution was evaporated after 5 days. II is very susceptible to moisture.

Structure I should give a positive P^{31} shift,^{8,9} while structure II would be expected to give a negative P^{31} shift.^{6,9}

The phosphitemethylene II reacted with benzyl bromide at 20° and gave the phosphine oxide enol ether III in quantitative yield. III had m.p. $179-180^\circ$ (benzene). *Anal.* Calcd. for $\text{C}_{35}\text{H}_{29}\text{O}_3\text{P}$: C, 79.5; H, 5.5; P, 5.9. Found: C, 79.8; H, 5.6; P, 5.9. Spectral properties are infrared bands (CH_2Cl_2 , μ): 5.95 ($\text{C}=\text{O}$), 6.15 ($\text{C}=\text{C}$), and 8.48 (PO); $\delta_{\text{P}^{31}} = -28.6$ p.p.m. (CDCl_3); H^1 n.m.r. (CDCl_3 , τ): 25H^1 multiplet at 2.70 (aromatics); 2H^1 singlet at 6.00 ($\text{C}_6\text{H}_5\text{CH}_2\text{O}$); 2H^1 doublet at 6.10, $J_{\text{HP}} = 16$ c.p.s. (two equivalent phenacyl protons).



To our knowledge, II is the first isolated, crystalline member of this family. Some phosphitemethylenes have been reported.¹⁰⁻¹²

(8) The crystalline 2,2,2-trimethoxy-3-phenyl-4-acetyl-5-methyl- Δ^4 -oxaphospholene, made from trimethyl phosphite and 3-benzylidene-2,4-pentanedione, has $\delta_{\text{P}^{31}} = +27.9$ p.p.m.; cf. F. Ramirez, A. V. Patwardhan, and S. R. Heller, *J. Am. Chem. Soc.*, **86**, 514 (1964), compound VI, Table I.

(9) $\delta_{\text{P}^{31}}$ in p.p.m.: $(\text{CH}_3\text{O})_3\text{P}$, -140.0 ; $\text{C}_2\text{H}_5\text{OP}(\text{C}_6\text{H}_5)_2$, -109.8 ; $\text{P}(\text{C}_6\text{H}_5)_3$, $+6$.

(10) W. J. Middleton, U. S. Patent 3,067,233 (Dec. 4, 1962).

(11) F. Ramirez and O. P. Madan, Abstracts, Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug., 1964, p. 13S.

(12) G. H. Birum, U. S. Patent 3,058,876 (Oct. 16, 1962).

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FAUSTO RAMIREZ

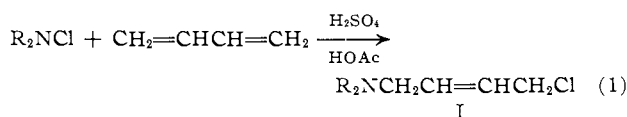
O. P. MADAN
C. P. SMITH

RECEIVED AUGUST 18, 1964

The Chemistry of Ion Radicals. The Free-Radical Addition of N-Chloramines to Olefinic and Acetylenic Hydrocarbons

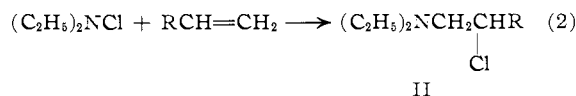
Sir:

We recently reported¹ the free-radical addition in acidic media of N-chloramines to butadiene, which afforded 1-chloro-4-dialkylamino-2-butenes (I) (eq. 1). Minisci and Galli² have subsequently suggested that

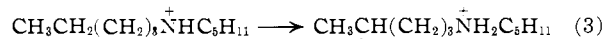


the addition of an aminium radical $\text{R}_2\text{N}^+\text{H}$ to an unsaturated hydrocarbon is limited to conjugated dienes. We therefore wish to report that chloramines undergo free-radical addition to terminal olefins and allenes and to terminal and internal acetylenes in sulfuric acid-acetic acid in yields of 30-60%, thereby demonstrating the applicability of the chloramine addition reaction to these classes of unsaturated hydrocarbons.

We reported previously^{1,3} that 1,1-diphenylethylene and norbornadiene reacted with chloramines *via* ionic rather than radical pathways; our further results now demonstrate that aliphatic terminal monoolefins undergo the desired radical addition (eq. 2) to afford β -chloramines (II) (Table I, entries 1, 2), although internal



olefins apparently undergo only ionic reactions (entry 4). However, intramolecular hydrogen abstraction by an aminium radical (eq. 3), which leads ultimately to a pyrrolidine (the Hofmann-Loeffler reaction⁴), precludes addition of the aminium radical to terminal olefinic bonds when the chloramine contains an appropriately placed methylene group (entry 3).



(1) R. S. Neale and R. L. Hinman, *J. Am. Chem. Soc.*, **85**, 2666 (1963).

(2) F. Minisci and R. Galli, *Tetrahedron Letters*, 167 (1964).

(3) R. S. Neale and E. B. Whipple, *J. Am. Chem. Soc.*, **86**, 3130 (1964).

(4) M. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

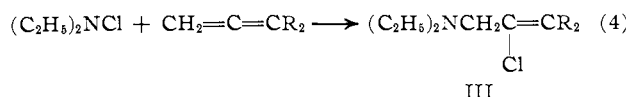
TABLE I

REACTIONS OF N-CHLORODIALKYLAMINES WITH UNSATURATED HYDROCARBONS IN 4 M SULFURIC ACID-ACETIC ACID

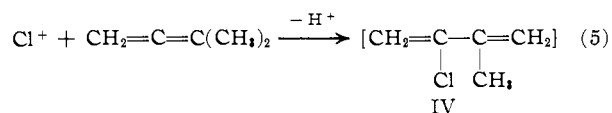
Entry	Chloramine	Hydrocarbon ^a	Temp., °C.	Products ^b	% yield ^c
1	(C ₂ H ₅) ₂ NCl	CH ₃ CH=CH ₂	32 ^d	(C ₂ H ₅) ₂ NCH ₂ CH(Cl)CH ₃	42
2	(C ₂ H ₅) ₂ NCl	CH ₃ CH ₂ CH=CH ₂	30 ^d	(C ₂ H ₅) ₂ NCH ₂ CH(Cl)CH ₂ CH ₃ ^e	33
3	(C ₅ H ₁₁) ₂ NCl	CH ₃ CH=CH ₂	45-30 ^d	N-Amyl-2-methylpyrrolidine diamylamine	(80) (15)
4	(C ₂ H ₅) ₂ NCl	<i>cis</i> -CH ₃ CH=CHCH ₃	35 ^d	CH ₃ CH(Cl)CH(OAc)CH ₃ No adduct	21
5	(C ₂ H ₅) ₂ NCl	CH ₂ =C=CH ₂	40 ^d	(C ₂ H ₅) ₂ NCH ₂ C(Cl)=CH ₂ ^f	35 (58)
6	(C ₂ H ₅) ₂ NCl	CH ₂ =C=C(CH ₃) ₂	30	AcOCH ₂ C(Cl)=C(CH ₃) ₂ ^g (C ₂ H ₅) ₂ NCH ₂ C(Cl)=C(CH ₃) ₂ ^h (C ₂ H ₅) ₂ NCH ₂ C(CH ₃)=C(Cl)CH ₂ Cl ⁱ (C ₂ H ₅) ₂ NCH ₂ C(Cl)=C(CH ₃)CH ₂ Cl ⁱ	(16) 11 34 17
7	(C ₂ H ₅) ₂ NCl	C ₄ H ₉ C≡CH	28	C ₄ H ₉ CH(Cl)CHO	45
8	(<i>n</i> -C ₄ H ₉) ₂ NCl	C ₄ H ₉ C≡CH	30	C ₄ H ₉ CH(Cl)CHO N-Butylpyrrolidine dibutylamine	37 (4) (89)
9	(<i>n</i> -C ₅ H ₁₁) ₂ NCl	C ₄ H ₉ C≡CH	30 ^j	N-Amyl-2-methylpyrrolidine diamylamine	(52) (25)
10	(C ₂ H ₅) ₂ NCl	C ₂ H ₅ C≡CC ₂ H ₅	30	CH ₃ CH ₂ COCH(Cl)CH ₂ CH ₃ CH ₃ CH ₂ C≡CCH(Cl)CH ₃ ^b CH ₃ CH ₂ COCH ₂ CH ₂ CH ₃	59 4 3

^a One equivalent added except entry 6 (0.7 equiv.). ^b Physical constants are given only for new compounds; elemental analyses were satisfactory in each case. ^c Yields based on chloramine; parentheses denote crude yields. ^d Reaction catalyzed by iron(II); temperature maintained by external cooling in all experiments. ^e B.p. 79° (20 mm.), *n*_D²⁰ 1.4375; picrate m.p. 76-78°. ^f B.p. 60-62° (24 mm.), *n*_D²⁴ 1.4424; hydrochloride m.p. 122-126°. ^g G.l.c. isolated sample had *n*_D²⁰ 1.4585 and correct C, H, Cl, and n.m.r. analyses. ^h B.p. 43° (3 mm.), *n*_D²⁰ 1.4620; trace of isomer also isolated CH₂=C(Cl)C(CH₃)₂N(C₂H₅)₂. ⁱ Mixture b.p. 75-77.5° (2.5 mm.), *n*_D²⁰ 1.4832. ^j No reaction in presence of air. ^k G.l.c. isolated, *n*_D²⁰ 1.4504; structure by n.m.r., no elemental analysis.

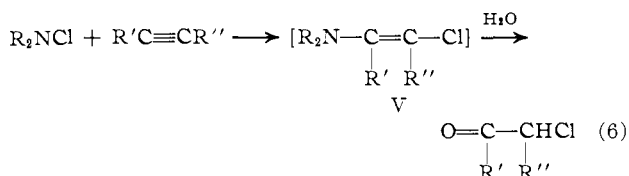
Allene reacted in a manner analogous to that of terminal olefins (entry 5) to afford the 1,2-addition product III (eq. 4). 3-Methyl-1,2-butadiene reacted



similarly in part, but afforded the majority of products from an initially ionic reaction (eq. 5). The product of this reaction, 2-chloro-3-methyl-1,3-butadiene (IV), immediately reacted with another molecule of the chloramine to give two 1,4-chloramination products as a result of addition in both possible directions (entry 6); this is a further example of the free-radical addition of a chloramine to a conjugated diene.¹ The preference of the aminium radical for rearrangement (eq. 3) or addition to an allenic bond is presently being determined.



Acetylenes also reacted with chloramines to yield adducts (entries 7, 8, and 10). These reactions, which occurred spontaneously, presumably gave enamines (V) as initial products; these were hydrolyzed on work-up to α -chlorocarbonyl compounds (eq. 6). Aminium radicals were shown in these reactions to be



very selective; only when a secondary C-H was available for intramolecular abstraction (entry 9) did this process predominate over addition to the triple bond (entries 7, 8). The direction of addition of the aminium radical to an unsymmetrical acetylene was selective only with a terminal acetylene (entry 7); use of 2-hexyne gave very nearly equal amounts of both α -chloroketones (62% yield).

The new reactions hereby described should find synthetic utility because none of the products (β -chloramines, 2-chloroallylamines, and α -chloroaldehydes or ketones) are readily available in any other one-step reactions directly involving unsaturated hydrocarbons. The reactions as presently carried out are subject to three limitations, however: the availability of the starting hydrocarbon, the preferred intramolecular rearrangement of aminium radicals of sufficient alkyl chain length (which did not occur in reactions of chloramines with butadiene¹), and the tendency of some olefinic hydrocarbons to undergo preferential ionic reactions.

All the reactions were carried out by stirring rapidly 190 ml. of an acetic acid solution 4 M in sulfuric acid and 0.5-0.7 M in chloramine under nitrogen for 20 min. at 20° and then adding the gaseous or liquid hydrocarbon (up to 1 equiv.) over ~10 min. When iron(II) catalysis was required⁵ 0.2-0.5 ml. of a suspension of Fe(NH₄)₂(SO₄)₂·6H₂O in acetic acid (~0.1-0.2 mole %) was added when the olefinic hydrocarbon was introduced. The progress of the reaction was followed by iodometric titration of the remaining chloramine and by the changes in solution temperature (total time: 10-60 min.). The work-up consisted in pouring the reaction mixture into 200 g. of ice and 500 ml. of water and extracting the neutral products with ether-pentane; 12 N sodium hydroxide solution was then added and the solution was heated with stirring

(5) Ultraviolet light was found to initiate these reactions equally well.

at pH 5 to completely liberate the products of the acetylene reactions or was fully basified at $<25^\circ$ to liberate basic products.

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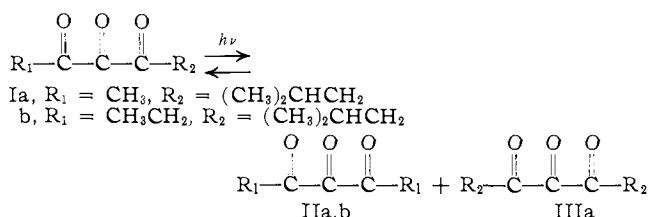
ROBERT S. NEALE

RECEIVED SEPTEMBER 26, 1964

Acyl Exchange Reactions of Vicinal Triones

Sir:

The irradiation of these triones induces the acyl exchange reaction



6-Methyl-2,3,4-heptanetrione (Ia)^{1,2} (18.33 g., 0.117

mole, bis-2,4-dinitrophenylhydrazone,² m.p. 233°) in ether (500 ml.) was swept with helium in a vacuum-line photochemical apparatus attached through condensers (water and Dry Ice) and a manostat (715 mm. maintained) to an automatic pump. The solution was irradiated at reflux with a G.E. sunlamp. Successive analyses (Table II) show that IIa and IIIa are formed, and photoequilibrium is attained. Carbon monoxide (0.005 mole) is evolved. This reaction is photochemical rather than thermal (Ia unchanged after 3 days at 105° in a sealed tube).

Distillation gave IIa² (3.21 g., 0.028 mole), Ia² (6.53 g., 0.042 mole), IIIa² (4.57 g., 0.023 mole), and a residue (2.57 g., two-peak chromatogram). 2,3-Butanedione (0.11 g., 0.0013 mole, H¹ n.m.r. in DCCl₃: methyl singlet at δ 2.08; *p*-nitrophenylhydrazone, m.p. 230°) and acetic acid (0.04 g.) were isolated from the trap condensate. With periodic acid, Ia gave carbon dioxide, acetic acid (*p*-toluidide m.p. 147°), and 3-methylbutanoic acid (*p*-phenylphenacyl ester m.p. 78°); and IIIa gave carbon dioxide and 3-methylbutanoic acid (*p*-toluidide m.p. 107°).

TABLE I
PHYSICAL PROPERTIES^a

Trione	B.p., °C. (mm.)	n_D^{20}	Spectra		H ¹ n.m.r. spectra ^b	
			Infrared, cm. ⁻¹	λ_{max} m μ (ϵ)	R ₁ -CO-CO-CO-R ₂	
Ia	54 (5)	1.4292	1724	220 (447) 464 (27.5)	3 H, δ 2.35 (a).	6 H, δ 0.98 (d), $J = 7.2$; 1 H, δ 2.00 (m); 2 H, δ 2.56 (d), $J = 6.6$
IIa	44-46 (12)		1722	464		δ 2.38 (s); hydrate, δ 2.20 (s)
IIIa	61-62 (2)	1.4366	1720	220 (1207) 468 (28.6)	12 H, δ 0.98 (d), $J = 7.2$; 2 H, δ 2.00 (m); 4 H, δ 2.57 (d), $J = 6.0$	
Ib	40-42 (2)		1720	464	3 H, δ 1.15 (t); 2 H, δ 2.76 (q), $J = 6.6$.	6 H, δ 0.99 (d), $J = 6.0$; 1 H, δ 2.25 (m); 2 H, δ 2.57 (d), $J = 6.0$
IIb	34-35 (2)	1.4301	1720	462	6 H, δ 1.15 (t); 4 H, δ 2.76 (q), $J = 6.6$	

^a Those of products and authentic triones identical. ^b In CCl₄ with TMS.

TABLE II
PHOTOCHEMICAL REACTIONS OF Ia AND OF AN EQUIMOLAR
MIXTURE OF IIb AND IIIa^a

Reaction time, hr.	Ia ^b	IIa ^b	IIIa ^b
0	100		
18	81	10	9
30	79	10	10
50	70	14	16
74	58	23	19
116	60	19	20
141	58	19	23
	Ib ^b	IIb ^b	IIIa
0		50	50
1	2	49	49
2.5	8	46	46
4	16	42	42
9	22	39	39
22	32	35	33
45	34	33	33

^a Mole % (± 2) of each trione. Analyses with Aerograph A-700 5 ft. \times $\frac{1}{4}$ in. column with 30% SE 30 on 45/60 Chromosorb B, isothermal 164° , He flow rate 1.04 ml./min. ^b Retention times: Ia, 2.38 min.; IIa, 1.00 min.; IIIa, 6.50 min.; Ib, 3.63 min.; and IIb, 2.00 min.

(1) All triones (Table I) were prepared according to F. Sachs and A. Rohmer [*Ber.*, **35**, 3310 (1910)] except that their solutions were protected from light, and dioxane and dichloromethane were the solvents used. Ia prepared in room light with ethanol and ether contained 5% IIa, 5% IIIa, and trione ethanulates. Its purification was difficult.

(2) Acceptable analyses obtained.

Similar results are obtained when IIb² (2.25 g., 0.0158 mole, bis-2,4-dinitrophenylhydrazone² m.p. 294°) and IIIa (3.11 g., 0.0157 mole) in ether (100 ml., nitrogen swept) are irradiated as before. Sequential analysis (Table II) shows the rapid formation of 2-methyl-4,5,6-octanetrione Ib, and equimolar amounts of Ib, IIb, and IIIa are present at photoequilibrium. Distillation gave IIb (1.41 g., 0.099 mole), Ib² (1.62 g., 0.095 mole), IIIa (2.12 g., 0.110 mole), and a residue (0.82 g.).

Acyl exchange occurs as solutions of triones in aldehydes stand in air, or are heated in the presence of peroxides. Ia (25 mole %) in 3-methylbutanal in a foil-covered container with air in the vapor space (10 ml.) gives IIIa (molar ratio of Ia:IIIa after 2 hr. 9:2, and after 48 hr. 7:2). Other products (v.p.c.) are 3-methylbutanoic acid, 2,7-dimethyl-4,5-octanedione, 2,3,4-pentanetrione, and acetic acid. A solution containing Ia (3.9 g., 0.025 mole), 3-methylbutanal (6.6 g., 0.077 mole), and 2,2-bis-(*t*-butylperoxy)butane (0.3 g.) at 100° under nitrogen in the dark gives IIIa (IIIa:Ia: 1 hr. 0.35; 5 hr. 0.55; 18 hr. 0.90; and 29 hr. 1.4), 2,3,4-pentanetrione, 2,7-dimethyl-4,5-octanedione, and peroxide-derived products (v.p.c.).

This evidence suggests a free-radical chain reaction.

Initiation involves formation of acyl radicals by