Tetrahedron Letters No.7, pp. 238-242, 1961. Pergamon Press, Inc. Printed in the United States of America.

# AMIDATION AND AMINOALKYLATION OF OLEFINS: BLOCKING TECHNIQUES IN RADICAL CHAIN REACTIONS

Lester Friedman

Department of Chemistry, New York University,

University Heights, New York

Harold Shechter

Department of Chemistry, The Ohio State University,

Columbus, Ohio

(Received 23 March 1961)

METHYL formate reacts with olefins in the presence of t-butyl peroxide to give 1:1 adducts and large proportions of higher telomeric methyl esters.[1] Olefins also add to amines by homolytic processes to form telomers derived by substitution of alkyl groups for hydrogen alpha to the amine group.[2] It is now reported that dimethylformamide and olefins react (equation 1) in the presence of initiators to give mixtures of isomeric adducts: N,N-dimethyl

$$RCH{=}CH_2 \quad + \quad H\text{-}CO\text{-}N(CH_3)_2 \;\begin{cases} \nearrow\; RCH_2CH_2CON(CH_3)_2 \quad \text{I} \\ \searrow\; R(CH_2)_3N(CH_3)CHO \quad \text{II} \end{cases} \qquad (1)$$

amides (I, amidation) and N-alkyl-N-methylformamides (II, aminoalkylation) along with the corresponding higher telomers. The radical chain processes thus involve competitive transfer from dimethylformamide of hydrogen which

[1] W.H. Urry and E.S. Huyser, J.Amer.Chem.Soc. 75, 4876 (1953). Similar reactions of ethyl formate and ethylene yield mixtures of ethyl esters of telomeric acids, $H\text{-}(CH_2CH_2)_x\text{-}CO_2C_2H_5$, and formate esters of telomeric secondary alcohols.

[2] W.H. Urry and O.O. Juveland, J.Amer.Chem.Soc. 80, 3322 (1958).

is adjacent to carbonyl or on a carbon attached to nitrogen. The adducts are hydrolyzed readily to carboxylic acids and N-alkyl-N-methylamines. The overall sequence of addition and hydrolysis thus serves as an effective joint method for carboxylating and aminoalkylating olefins.

A selective method of amidation results from reaction of t-butylformamide and olefins in the presence of initiators. Addition occurs efficiently (equation 2) to give N-t-butyl amides (III) and corresponding higher telomers.

$$(RCH{=}CH_2 + H\text{-}CO\text{-}NH\text{-}C(CH_3)_3 \longrightarrow \underset{\text{III}}{RCH_2CH_2CONH\text{-}C(CH_3)_3} \qquad (2)$$

By the blocking inherent in the t-butyl group in t-butylformamide, transfer of hydrogen is restricted to that adjacent to the carbonyl group. t-Butylformamide is also of advantage over dimethylformamide in that the yields of higher telomers are considerably smaller. Since N-t-butyl amides (III) may be hydrolyzed under appropriate conditions, a general method is available for converting olefins to higher carboxylic acids.

Selective homolytic aminoalkylation of olefins is obtained in reactions with N,N-dimethylacetamide (equation 3) and with N-methylacetamide (equation 4). The products are N-alkyl-N-methylacetamides (IV)

$$RCH{=}CH_2 + (CH_3)_2NCOCH_3 \longrightarrow RCH_2CH_2CH_2N(CH_3)COCH_3 \qquad (3)$$

$$RCH{=}CH_2 + CH_3NHCOCH_3 \longrightarrow RCH_2CH_2CH_2NHCOCH_3 \qquad (4)$$

and N-alkylacetamides (V), respectively, and their corresponding higher telomers. N,N-Dimethylacetamide and N-methylacetamide display blocking specificities in that hydrogen on carbon attached to nitrogen is transferred rather than that on carbon adjacent to carbonyl. Since the amides, (IV) and (V), are convertible to N-alkylmethylamines and alkylamines, the combination of selective addition and hydrolysis serves as a simple method for aminoalkylating olefins.

General experimental methods and additional theoretical features are illustrated in the following examples. Dropwise addition (16 hr) of 1-octene

(1.0 mole) and t-butyl peroxide (0.05 mole) to dimethylformamide (30 moles) at 132° and subsequent reaction (18 hr) results in 87% conversion of 1-octene to a 60:40 mixture[3] of the 1:1 telomers [b.p. 91° (0.5 mm), $n_D^{20}$ 1.4519, 56% yield] : N,N-dimethylnonanamide (VI) and N-methyl-N-nonylformamide (VII).[4,5] Reaction of 1-octene (1.0 mole), dimethylformamide (30 miles) and t-butyl peroxide (0.02 mole; atm press, 130-133°, 43 hr) during which additional initiator was added after 8 hr (0.02 mole), 20 hr (0.02 mole) and 36 hr (0.005 mole) gave VI and VII (47%), 2:1 telomers (21%) and crude 3:1 telomers (12%).[6] The composition and yield of the mixture of VI and VII were not significantly altered by initiating the additions with t-butyl peroxide or cumyl peroxide over the range, 115-150°. The preparative results thus indicate that the energies involved in formation of the $(CH_3)_2\dot{N}\text{-}C{=}O$ and $\cdot CH_2N(CH_3)CHO$ radicals are similar. In the absence of olefins, dimethylformamide (8.2 moles) is converted by t-butyl peroxide (0.55 mole) at 132° (65% yield) to N,N,N',N'-tetramethyloxamide (6.0%), N,N'-diformyl-N,N'-dimethylethylenediamine (72%) and N-formyl-N-methylaminoacetic acid dimethyl amide (22 %); these results are comparable to those recently reported.[7]

---

[3] All new products gave satisfactory analyses.

[4] Other products are (1) 2:1 telomers (23%): N,N-dimethyl 3-n-hexyl-undecanamide and N-methyl-N-1-(3-n-hexylundecyl) for mamide [b.p. 153° (0.2 mm)], and (2) 3:1 adducts [12%, b.p. 197-200°(0.3 mm)].

[5] Hydrolysis of the mixture of VI and VII was effected quantitatively to nonanoic acid and N-methylnonylamine in refluxing hydrochloric acid.

[6] Addition of dimethylformamide to 1-decene and methyl 10-undecylenate also occurred satisfactorily.

[7] K. Schwetlick, Angew. Chem. 72, 208 (1960)

t-Butylformamide[8] was added to methyl 10-undecylenate and 1-octene. Reaction of methyl 10-undecylenate (0.57 mole), t-butylformamide (17.8 moles), and t-butyl peroxide (0.041 mole; 24 hr, 130°) gave methyl 11- (t-butylcarbamoyl) undecanoate[3] [VIII, 61% yield, m.p. 41-43°, b.p. 177-180°(0.8 mm.)] and higher-boiling products (41 g). Similarly 1-octene (0.67 mole), t-butylformamide (19.2 moles) and t-butyl peroxide (0.044 mole) yielded N-t-butylnonanamide[3] (IX, 77% yield, b.p. 115° (1 mm), $n_D^{20}$ 1.4492) and higher telomers. Radical-dimerization of t-butylformamide (9.15 moles) by t-butyl peroxide (0.82 mole; 20 hr, 140°) also occurred to give N,N'-di-t-butyloxamide (73% yield, m.p. 181-182°).

Saponification of VIII to N-t-butyldodecanedioic acid amide[3] (X, m.p. 81.5-82.5°) was effected (97%) by minimal refluxing in aqueous-methanolic potassium hydroxide and acidification; hydrolysis of X in hot aqueous potassium hydroxide gave, after acidification, dodecanedioic acid (~100%). Dodecanedioic acid was obtained preparatively from VIII (0.088 mole) upon refluxing (6 hr) with stirred potassium hydroxide (0.55 mole), water (5 ml), diethylene glycol (15 ml) and butyl Cellosolve[9] (100 ml), dilution with water, separation, and acidification. A similar procedure resulted in effective hydrolysis of IX to nonanoic acid and t-butylamine.

Selective amidation of 1-octene was obtained with N,N-dimethylacetamide and N-methylacetamide, respectively. Reaction of N,N-dimethylacetamide (21.8 moles), 1-octene (0.67 mole), and t-butyl peroxide (0.027 mole; 72 hr, 125°) yielded N-methyl-N-nonylacetamide[3] (XII, 39% yield, 81% conversion

[8] Prepared by adding t-butylamine (25 moles) to cooled 90% formic acid (47 moles), distillation until the mixture reaches 175°, storing the residue over potassium carbonate, filtering, and distilling: 90% yield, b.p. 82° (10 mm), $n_D^{20}$ 1.4340.

[9] Acidic hydrolyses were unsatisfactory.

of 1-octene, b.p. 120-122° (1 mm), $n_D^{20}$ 1.4535) along with higher telomers. Similarly N-methylacetamide (7.2 moles), 1-octene (0.24 mole) and t-butyl peroxide (0.0165 mole; 128°, 42 hr) gave N-nonylacetamide [XIII, 33% yield, 90% conversion of 1-octene, b.p. 143-145° (1.5 mm), m.p. 34-35°] and higher telomers.[10] Radical-dimerizations of N,N-dimethylacetamide (12 moles) and N-methylacetamide (12 moles), respectively, by t-butyl peroxide (1 mole; 22 hr, 140°) occurred to yield N,N'-diacetyl-N,N'-dimethylethylenediamine [85%, b.p. 155-160°(2 mm), m.p. 90-92°] and N,N'-diacetylethylenediamine (71%, m.p. 174-176°).

Hydrolysis of XII and XIII in refluxing hydrochloric acid occurs efficiently to give N-methylnonylamine and nonylamine, respectively.[11]

[10] Formamide and 1-alkenes are quite insoluble at 135°; however, addition occurs in the presence of t-butyl peroxide to give telomers of relatively high molecular weight.

[11] This research was initially sponsored by The Ohio State University Development Fund.