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DIMERIZATION OF ACRYLAMIDES BY RHODIUM TRICHLORIDE

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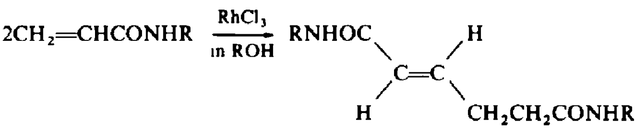
Abstract—Acrylamide and its N-monosubstituted derivatives in an alcoholic solution are dimerized by rhodium trichloride into the corresponding *trans*-α-hydromuconamides, but in the N,N-disubstituted derivatives, the cleavage of the amide group takes place. This difference is attributable to the alternation of coordinating positions (amide or olefin). The *trans*-α-hydromuconamides obtained were used to study the conjugating effect of amide bands.

IT HAS been reported that α,β-conjugated vinyl compounds such as acrylic esters and butadiene can be linearly dimerized by rhodium and ruthenium trichlorides,[1] but acrylonitrile forms a stable σ-complex with $RhCl_3$[2] and can undergo dimerization only when $RuCl_3$[3] or the complex prepared from acrylonitrile and $RuCl_3$[4] is used as a catalyst in the presence of hydrogen. From the mechanistic view point, these differences in reactivity may be attributed to the influence of conjugating functional groups (—C═C, —COOR, —CN) on both the coordinating ability of a C═C bond and Pearson's softness of acids[5] in coordinated transition metals (Ru is a soft acid and Rh is an intermediate between hard and soft ones). As an extension of this hypothesis, we have investigated the reaction of acrylamides with transition metal compounds and have found that acrylamide and its N-monosubstituted derivatives are transformed into the corresponding *trans*-α-hydromuconamides by $RhCl_3$, but this is not the case with N,N-disubstituted derivatives.



Olefinic compounds, such as ethylene, propylene and butadiene, can be linearly dimerized by rhodium or ruthenium compounds[1] and intermediate complexes in oligomerization of olefins by transition metals[6] have been isolated. In the case of acrylamide or its N-monosubstituted derivatives, the amide group is not hindered in coordination with the metal by the C═C bond and 1,2-addition is analogous to simple olefins, forming linearly dimerized *trans*-α-hydromuconamides.

Table 1 shows the results of the dimerization of acrylamide and its N-monosubstituted derivatives by $RhCl_3$. This reaction proceeds in heterogeneous systems, e.g. anhydrous rhodium trichloride, insoluble in common organic solvents, was used as a catalyst. In the reaction, the rhodium ion is reduced to form a mirror or to a black colloidal state and the yield of dimer is usually 2·5–5·5 mole per rhodium gram atom.

TABLE 1. *trans*-α-HYDROMUCONAMIDES

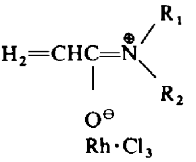
No.	N-substituent of $CH_2{=}CHCONR$	Crystal form	M.p. (°C)	Calc C%	Calc H%	Calc N%	Found C%	Found H%	Found N%	UV λ_{max}^{MeOH} (mμ) (ε)	Yield amide base	Yield Rh base (mole/g atm)
1	H[a]	granule	216–218·5[d]	50·69	7·09	19·17	50·73	7·10	19·72	210 (1·16 × 10^4)	24·8	5·5
2	Me[b]	needle	191–191·5	56·45	8·29	16·45	56·81	8·40	16·22	210 (1·76 × 10^4)	15·8	2·45
3	Et[c]	needle	199–200	60·58	9·15	14·13	60·94	9·12	14·12	210 (1·77 × 10^4)	20	2·67
4	 [a]	needle	250–250·5	70·55	9·87	9·14	70·41	9·81	9·06	213 (1·60 × 10^4) 240[e] (8·90 × 10^3)	63·2	5·35
5	 [a]	granule	256–257	73·45	6·16	9·52	73·63	6·22	9·42	205 (3·69 × 10^4) 220 (2·85 × 10^4) 240 (2·78 × 10^4)	38	3·5

[a] Recrystallization from MeOH.
[b] Recrystallization from THF.
[c] Recrystallization from dioxan.
[d] Sublimation.
[e] Shoulder.

The addition of redox reagents, such as *p*-benzoquinone, improves the yield. The identification of the products as *trans*-α-hydromuconamides was as follows: (a) the hydrogenation of the products with Raney Ni(W-7) in ethanolic solution at atmospheric pressure and room temperature gave the corresponding adipamides; (b) the UV spectra indicate typical α,β-unsaturated amides, showing maxima at about 210 mμ with ε_{max} 1·2–3·7 × 10^4; (c) the IR spectra show a strong δ_{C-} of olefin at 960 cm^{-1}, which indicates *trans*-form; (d) the NMR shows that the products have olefinical protons so disposed as to constitute an ABX_2 system, absorption of which is τ 3·14–3·48 (quartet) (H:1) and τ 3·88–4·20 (doublet) (H:1). This means that the products are not symmetrical molecular structures with a double bond at the β-position. The coupling constants J_{AB} for ABX_2 are 15·0 c/s which indicates a *trans* coupling at the double bond, and J_{BX} 6·0 c/s shows the coupling of a $=CH \cdot CH_2$ structure.

When N,N-disubstituted acrylamides react with $RhCl_3$, α-hydromuconamides are not obtained and cleavage of the amide group produces the corresponding secondary amines, the olefinical parts being polymerized.

There are two possibilities of coordination of acrylamides with transition metals, i.e. the C═C bond and the amide group. In the dimerization of acrylamide or its N-monosubstituted derivatives, the mechanism may be similar to that of dimerization of ethylene reported by Cramer[7] and the rhodium metal coordinates with the C═C bond. However, it appears that N,N-disubstituted acrylamides are coordinated with rhodium metal at the amide group as reported by Paul *et al*:[8]



$$CH_2{=}CH\underset{\substack{|\\ O^{\ominus}\\ Rh\cdot Cl_3}}{C}{=}\overset{\oplus}{N}\begin{smallmatrix}\diagup R_1\\ \diagdown R_2\end{smallmatrix}$$

($R_1 = R_2$; Et, ϕ)

The coordination of the amide group with the rhodium metal will account for the formation of a secondary amine instead of dimerization.

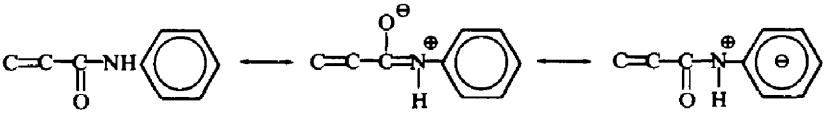
The IR spectra of the complexes of acrylamides with $RhCl_3$ may clarify the difference in coordination. The supposed reaction intermediates were prepared by addition of $RhCl_3 \cdot 3H_2O$ to a large excess of acrylamide, N-phenylacrylamide or N,N-diphenylacrylamide. The compounds formed decomposed gradually above about 100° and when heated under reflux in n-BuOH gave the corresponding dimers or the secondary amine hydrochlorides according to the N-mono- or N,N-disubstituted derivatives. In the IR spectra of the complexes of acrylamide and N-phenylacrylamide, the amide I band appears at 1660 cm^{-1}, which indicates no shift in the comparison with free acrylamides, but the vinyl group at 990 cm^{-1} in the free form is shifted to 970 cm^{-1} with weaker intensity. This supports the coordination position as the vinyl group. But, in the complex with N,N-diphenylacrylamide, the amide I band at 1660 cm^{-1} becomes smaller and new absorption of $\nu_{C=N^+}$ appears at 1720 cm^{-1}, but no shift in vinyl group at 1000 cm^{-1} was observed.

This indicates that the dimerization is limited to acrylamides carrying at least one active hydrogen at the amide group. The remnant of active hydrogen increases the possibilities for tautomerism of amide-iminoenol forms to distribute the electron density on the whole amide group, thus making coordinating metals at the amide group impossible.

The reactions with $RuCl_3$ as a catalyst gave only black tarry materials and with $PdCl_2$, the starting materials were recovered.

The α,β-substituted acrylamides, such as methacrylamide, N-cyclohexyl methacrylamide, crotonamide, were not subjected to dimerization by $RhCl_3$ because of steric hindrance in coordination with the metal.

Conjugating effects of amide I *band.* The dimerized products have two-fold splitting amide I bands because of the presence of an α,β-unsaturated amide group and an isolated amide group in a same molecule. This means that α-hydromuconamides are suitable compounds for the investigation of the conjugate effects of the amide I bands. Table 2 shows the amide I bands of *trans*-α-hydromuconamides in the comparison with the corresponding adipamides. In the N-alkyl derivatives, the introduction of an α,β-unsaturated group causes a shift to a higher wave number by 10–20 cm^{-1}. The degree of shift decreases in the following order: H > Me > Et > cyclohexyl, which is elucidated by the −I effect of alkyl groups. However, in a N-phenyl derivative, the phenyl group participates in resonance by the lone pair electrons in nitrogen at amide group,[9] thus the amide I band of N,N′-diphenyladipamide is shifted to a higher wave number by 18 cm^{-1} in the comparison with that of adipamide.



But, an unsaturated group at the α,β-position forms a conjugating system with amide group, and the −E effect predominates over the +I effect, shifting to a lower wave number by 16 cm^{-1}.

TABLE 2. AMIDE I BANDS OF *trans*-α-HYDROMUCONAMIDE AND ITS N,N′-SUBSTITUTED DERIVATIVES (KBr DISK)

R	α-Hydromuconamides (cm^{-1}) $-CH{=}CHCONHR$	 $-CH_2CH_2CONHR$	Δ_ν	Adipamides (cm^{-1})
H	1663	1643	20	1642
Me	1645	1630	15	1633
Et	1642	1630	12	1632
	1645	1635	10	1630
	1645	1661	−16	1660

EXPERIMENTAL

Apparatus. M.ps are uncorrected and were measured by a Yanagimoto micro m.p. apparatus with heating block and a Shibata precise m.p. apparatus with silicon bath when samples were sublimable.

IR spectra were measured in KBr disks using a Shimazu Infrared Spectrophotometer IR-27A and for the fine structural measurements were used a Hitachi Infrared Spectrophotometer EPI-2. UV spectra were run on a Hitachi–Perkinelmer UV-VIS Spectrophotometer. NMR spectra were run on a Varian A-60 instrument in DMSO-d_6 with TMS as an internal standard. Microanalyses by Nagoya Research Laboratory, Toyo Rayon Co. Ltd., Nagoya, Japan.

Materials. Acrylamide was purified from benzene. N-substituted acrylamides were prepared by reacting acryl chloride with the corresponding primary or secondary amines in benzene:[10] N-methyl- (b.p. 124–126°/30 mm), N-ethyl- (b.p. 104–106°/10 mm), N,N-diethyl- (b.p. 93·5–95°/19 mm), N-cyclohexyl- (m.p. 113°, recrystallization from n-hexane), N-phenyl- (m.p. 105–107°, recrystallization from cyclohexane). Methacrylamide and crotonamide were prepared from the corresponding acid chloride with ammonia in benzene.

Dimerization of acrylamide. Acrylamide (5·01 g), $RhCl_3 \cdot 3H_2O$ (0·42 g), hydroquinone (0·51 g) and *p*-benzoquinone (1·00 g) were dissolved in n-BuOH (100 ml). The soln was refluxed for 24 hr. The colour of the soln changed from red-brown to dark brown with formation of a rhodium mirror. The rhodium metal was precipitated and filtered off from the hot soln. The filtrate was evaporated to dryness *in vacuo*. About 20 ml of EtOH was added to the residue and the insoluble *trans*-α-hydromuconamide was obtained by reduced filtration, yield 1·24 g (24·8% based on acrylamide), m.p. 216–218·5°, recrystallized from MeOH as white sublimable crystals, mol. wt. 145 (measured by vapor pressure osmometry, Calc. 144); IR spectrum: (KBr disk) 3450, 3230 (s) (ν_{NH}), 1663 (sh), 1643 (vs) (amide I), 1420 (s) (δ_{CH} of —CH—CH=CH—), 963 cm^{-1} (m) (δ_{CH} of *trans* olefin); UV spectrum, λ_{max}^{MeOH} 210 mμ (ε: 1·16 × 10^4). (Found: C, 50·73; H, 7·10; N, 19·72. $C_6H_{10}N_2O_2$ requires: C, 50·69; H, 7·09; N, 19·71%). The hydrogenation of the compound in water with Raney Ni(W-7) under normal press at room temp gave adipamide (m.p. 223–224°, recrystallization from water, Lit.[11] 223–224°).

Dimerization of N-*methylacrylamide.* A n-BuOH soln (100 ml) containing 5 g N-methylacrylamide, 0·5 g $RhCl_3 \cdot 3H_2O$ and 0·3 g hydroquinone was heated under reflux for 40 hr. The soln turned from reddish brown to dark brown during heating and reduced Rh was deposited on the inner surface of the flask. After filtering off the Rh metal, the filtrate was evaporated *in vacuo* to a dark brown tarry residue. By the addition of about 20 ml $CHCl_3$, 0·12 g of white crystals were precipitated and filtered off. The filtrate was again evaporated to dryness *in vacuo*. Addition of acetone (20 ml) to the residue yielded an additional 0·67 g of white crystals. The total yield of product 15·8%. When recrystallized from THF gave 0·41 g of N,N′-dimethyl-*trans*-α-hydromuconamide as white needles, m.p. 191–191·5°, IR spectrum 2900 (m) (ν as CH of N—CH_3), 1645 (sh), 1670 (s) (amide I), 1555 (amide II), 1270 (amide III), 960 cm^{-1} (δ_{CH} of *trans* olefin); UV spectrum λ_{max}^{MeOH} 210 mμ (ε: 1·76 × 10^4); NMR spectrum: τ 7·75 (N—CH_3), τ 4·15 (doublet J_{AB} 15·0 c/s), τ 3·4 (quartet, J_{AB} 15·0 c/s; J_{BX} 5·0 c/s). (Found: C, 56·81; H, 8·40; N, 16·22. $C_8H_{14}N_2O_2$ requires: C, 56·45; H, 8·29; N, 16·45%). The hydrogenation of the product with Raney Ni in EtOH gave N,N′-dimethyl adipamide, m.p. 151–153°, undepressed by admixture with an authentic sample.

The dimerization of N-cyclohexyl-, or N-phenylacrylamide was similar.

Dimerization of N-*ethylacrylamide* (*in heterogeneous system*). N-Ethylacrylamide (5·12 g), $RhCl_3$ (0·31 g) and hydroquinone (0·35 g) were added to 100 ml n-BuOH. The $RhCl_3$ remained undissolved and after heating under reflux for 30 hr, the Rh metal was filtered off and the filtrate was evaporated to dryness *in vacuo*. Acetone (50 ml) was added to the residue and the insoluble material (0·43 g) filtered off and the filtrate again evaporated to dryness. The addition of ligroin (50 ml) precipitated 0·60 g the material. The total product was recrystallized from dioxan as white needles of N,N′-diethyl-*trans*-α-hydromuconamide, yield 20%, m.p. 199–200°; IR spectrum (KBr disk): 3300 (s) (ν_{NH}), 2950 (m) (ν as CH), 1642 (sh), 1642 (sh), 1630 (vs) (amide I), 1550 (amide II), 1440 (δ_{CH} of —CH_2—CH=CH—), 1270 (amide III), 960 cm^{-1} (δ_{CH} of *trans* olefin); UV spectrum: λ_{max}^{MeOH} 210 mμ (ε: 1·77 × 10^4); NMR spectrum: τ 4·20 (doublet, J_{AB} 15·0 c/s), τ 3·45 (quartet, J_{AB} 15·0 c/s, J_{BX} 5·0 c/s). (Found: C, 60·94; H, 9·12; N, 14·12. $C_{10}H_{18}N_2O_2$ requires: C, 60·58; H, 9·15; N, 14·13%). The hydrogenated product, N,N′-diethyladipamide, m.p. 165·5–167° from acetone), was identical with an authentic sample prepared from adipyl chloride and ethylamine.

The cleavage of the amide group in N,N-*diethyl acrylamide.* N,N-diethylacrylamide (5·0 g), $RhCl_3 \cdot 3H_2O$ (0·5 g) and hydroquinone (0·3 g) were dissolved in 100 ml n-BuOH and the mixture was heated under reflux for 30·5 hr. After the filtration, the filtrate was evaporated to dryness and 15 ml acetone was added to the residue to precipitate crystalline diethylamine hydrochloride (0·12 g). m.p 214–216°. from THF, yield 4·9%; IR spectrum: 3400 (ν_{NH}), 2960 (ν as CH), 2870 (ν s CH), 2450 (s) ($\nu_{NH^{+}}$), 1470 (m) (δ as CH_3), 1395 (δ_{CH} of —CH_2N), 1150, 1040 cm^{-1} (s) (ν_{CN}). (Found: C, 44·09; H, 11·06; N, 12·58. Calc. for $C_4H_{12}NCl$: C, 43·82; H, 11·08; N, 12·78%).

The cleavage of the amide group in N,N-*diphenylacrylamide.* A n-BuOH soln containing 4·2 g N,N-diphenylacrylamide, 0·44 g hydroquinone and 0·5 g $RhCl_3 \cdot 3H_2O$ was heated under reflux for 26·3 hr. After cooling, the reduced Rh metal was removed by filtration *in vacuo*, the filtrate was evaporated by reduced distillation. The residue was dissolved in about 300 ml acetone and dry HCl gas was passed through to form 0·47 g diphenylamine hydrochloride, m.p. 113–118°, yield 12·5%. The IR spectrum of the product was identical with that of an authentic sample. The product neutralised by KOH was recrystallized from ligroin to give diphenylamine, m.p. 50–52° (Lit. 52·8°).

The preparation of the complexes of acrylamides with $RhCl_3$. A large excess of acrylamide, N-phenylacrylamide or N,N-diphenylacrylamide were added to $RhCl_3 \cdot 3H_2O$ in MeOH and the soln was heated under reflux for about 1 hr. The solvent was removed and the excess acrylamides were extracted with $CHCl_3$. The complexes were gradually decomposed above ca. 100°. The IR spectra of the complexes were measured in KBr disk. The *acrylamide complex*: 3300, 3200, 1660, 1600, 1400, 970 cm^{-1}; The N-*phenylacrylamide complex*: 3030, 1670, 1610, 1560, 1500, 1440, 1400, 1320, 1250, 1080, 970, 760, 690 cm^{-1}; The N,N-*diphenylacrylamide complex*: 3500, 3030, 1720, 1600, 1530, 1500, 1450, 1320, 1280, 1090, 1000, 760, 700 cm^{-1}.

Attempted dimerization of acrylamide in AcOH *by* $PdCl_2$. Acetic acid (100 ml), acrylamide (5 g), $PdCl_2$ (1·0 g) and hydroquinone (0·5 g) was heated under reflux for 24·5 hr. The Pd metal was filtered off and the filtrate on evaporation yielded the starting material.

Attempted dimerization of methacrylamide by $RhCl_3$. n-BuOH (100 ml), methacrylamide (5·0 g), $RhCl_3$ (0·69 g) and hydroquinone (0·50 g) were heated under reflux for 24 hr. After removal of the reduced metal, the starting material were recovered from the filtrate.

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