

Proposed values for "O" and "H" interactions (Table III) were attained by optimisation of essay values. Complementary variation of w and z factors (see Table III) only changes diastereomer percentage in less than ± 2 . This is in keeping with the geometrical limits portulated in Fig. 3, and in favour of the internal consistency of the method.

In a forthcoming paper we shall show that the same procedure may be applied to the elucidation of transition states in the reactions of Grignard reagents with aldehydes yielding the same diastereomeric carbinols obtained in the processes summarized in Table I.

REFERENCES

1. A. García-Martínez y R. Pérez-Ossorio.- *Anales de Química*, **65**, 791 (1969).
2. F. Fernández González y R. Pérez-Ossorio.- *Anales de Química*, **68**, 1411 (1972). *Ibid.*, **69**, 101 (1973).
3. D.J. Cram and F.A. Abd el Hafez.- *J. Am. Chem. Soc.*, **74**, 5828 (1952).
4. G.J. Karabatsos.- *J. Am. Chem. Soc.*, **89**, 1367 (1967).
5. M. Cherest, H. Felkin and N. Prudent.- *Tetrahedron Letters*, 2199 (1968).
6. R. Pérez-Ossorio y J. Plumet.- To be published.
7. C. Cubillo y J. Plumet.- To be published.
8. R. Pérez-Ossorio y M.L. Quiroga.- To be published.
9. (1,3)parallel interactions of Ar in which o-tolyl group is involved were estimated by adding 0,3 Kcal/mol to those corresponding to phenyl group.
10. J.M. Cense.- *Tetrahedron Letters*, **21**, 2153 (1972).
11. A. Calvet et J. Levisalles.- *Ibid.*, **21**, 2157 (1972).
12. Treatment of asymmetric induction here exposed is independent of any particular conception of the transition state nature. Values of interactions here admitted are in keeping with ours.
13. J.A. Hirsch.- Table of Conformational Energies - 1967, in "Topics in Stereochemistry", vol I, N.L. Allinger and E.L. Eliel, Ed. Interscience Publ., New York, 1967.
14. G.J. Karabatsos and N. Hsi.- *J. Am. Chem. Soc.*, **87**, 2864 (1965).
15. T.L. Hill.- *J. Chem. Phys.*, **16**, 399 (1948).

METATHESIS CATALYSTS - II COMPETITIVE CHARACTER OF METATHESIS AND ALKYLATION REACTIONS CATALYSED BY $WCl_6 - C_2H_5AlCl_2$

Léonard Hocks⁽⁺⁾, A.J. Hubert and Ph. Teyssié - Laboratoire de Chimie Macromoléculaire et de Catalyse Organique - Institut de Chimie - Université de Liège - SART TILMAN par 4000 Liège - Belgium.

(Received in UK 23 May 1973; accepted for publication 7 June 1973)

The olefins metathesis catalyst $WCl_6 - C_2H_5AlCl_2$ is a strong Lewis acid which promotes consequently secondary cationic reactions such as prototropic isomerization, alkylation of the aromatic solvent, and oligomerization. All these reactions have an influence on the metathesis thermodynamic equilibrium and, in some cases, can even mask completely the metathesis reaction.

It is therefore interesting to study the factors which influence the relative occurrence of these reactions. In this communication, we report the crucial importance of the molar ratio olefin : catalytic complex in a given solvent. In addition, in an aromatic solvent (benzene), there is a competition between olefin metathesis and aromatic alkylation; in this latter case, the benzene is a reactant : Consequently, the benzene:olefin ratio is also a determining factor which influences the course of these two reactions.

Experimentally, in benzene solution, we observe indeed competitive olefin metathesis and alkylation reactions for molar ratio olefin : catalyst of 70 to 400. For molar ratios greater than 400, olefin metathesis is the main reaction, alkylation being negligible. **Alternatively**, for a molar ratio less than 70, alkylation is the only effective reaction (Fig. 1); moreover, in this latter case, the $WCl_6 - C_2H_5AlCl_2$ catalyst promotes the formation of monoalkylated products only after a few minutes¹⁾.

(+) The author is indebted to I.R.S.I.A. for a fellowship.

Similar results are obtained with variable concentrations of the catalyst system in a solution of olefin in benzene, or variable concentrations of the olefin in a given solution of catalyst in benzene, at a benzene:olefin molar ratio lower than 10; consequently, the molar ratio olefin:catalyst is an important variable which influences the course of the two competitive metathesis and alkylation reactions.

However, in the presence of increasing amounts of benzene (for an olefin:catalyst ratio of 400) we observe again a competition between metathesis and alkylation and, for very large benzene:olefin molar ratio, alkylation prevails completely over the metathesis reaction (Fig. 2).

These results indicate clearly the essential importance of the relative concentrations of the reactants on the course of the two metathesis and alkylation reactions; they allow also a better understanding and a rationalization of a number of data scattered in the recent literature^{1,2,3,4}). This behaviour can be explained in two complementary ways :

1°) Alkylation and metathesis are two parallel reactions. Absolute concentrations of catalyst, olefin and benzene influence the velocity of these two reactions, as indicated in the following kinetic equations :

$$v_A = k_A (\text{catalyst})^u (\text{olefin})^v (\text{benzene})^w$$

$$v_M = k_M (\text{catalyst})^x (\text{olefin})^y$$

where v_A , k_A and v_M , k_M are the rates and the rate constants for alkylation and metathesis reactions, respectively. But these kinetic equations alone cannot explain all the results of the figure 2; the variations of absolute concentrations and consequently the expected variations of rates, are indeed too small to explain such an increase of the alkylation reaction.

2°) On the other hand, we can postulate a competitive coordination of benzene and olefin on the active catalyst center. This coordination of benzene would favour the alkylation reaction, maybe by hindering further coordination of the second olefin necessary for metathesis reaction. Moreover, the formation of such a benzene complex from the olefin complex is strongly supported by the very high transalkylation rate¹) of the alkylated products by the tungsten catalyst, which has to be formed by observing a given order of reagents addition;

it would fit very well the $WCl_4(\text{olefin})_2$ active center proposed recently by Pampus⁵) for the metathesis reactions.

More kinetic and structural studies are necessary to afford detailed mechanistic conclusions : the problem is indeed a very complex one because yields of alkylation reaction from metathesis products increase with time in the range of olefin : catalyst ratio 70 to 400. Further kinetic investigations are in progress in our laboratory.

Figure 1: Yields of metathesis or alkylation reaction versus molar ratio olefin : catalytic system a, c, d, e (molar ratio benzene : olefin = 6)

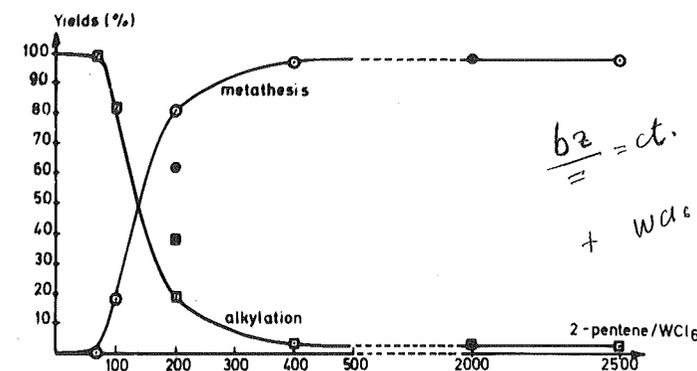
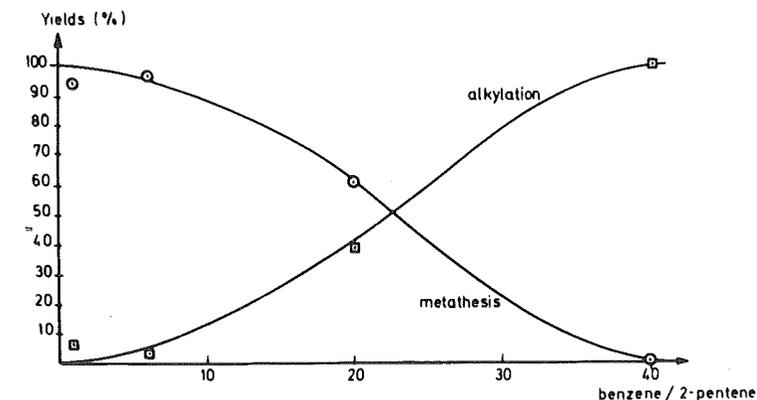


Figure 2: Yields of metathesis or alkylation reaction versus molar ratio benzene : olefin b, c, d (molar ratio olefin : catalyst = 400)



Caption for the figures 1 and 2.

- a) Experimental conditions : 2-pentene = 10^{-2} mole; catalytic system = $2,5 \cdot 10^{-5}$ mole; Al/W = 4; variable amounts of benzene; temperature = 25° C; reaction time = 1 minute.
- b) Experimental conditions : benzene = $6 \cdot 10^{-2}$ mole; 2-pentene = 10^{-2} mole; variable amounts of catalytic system; Al/W = 4; temperature = 25° C; reaction time = 1 minute.
- c) Yields are calculated using an internal g.l.c. standard (cyclooctane). Conversion of 2-pentene is complete after 1 minute.
- d) Yields of the metathesis reaction are defined, in this article, as the sum of the olefinic fraction in the mixture of olefin and alkylated products. It would be more correct to consider the real ratio of 2-butene or 3-hexene versus 2-pentene as the yields of the metathesis reaction, but the thermodynamic metathesis equilibrium is not always completely established after a minute of reaction time; further kinetic studies are in progress on this point.
- e) The \bigcirc and \square points indicate respectively the yields of metathesis and alkylation reactions versus variable concentrations of the catalyst system (olefin and benzene concentrations being constant). On the other hand, the \blacksquare points give the same results for variable concentrations in olefin with a constant concentration in benzene and catalytic system.

References.

- 1) L. Hocks, A.J. Hubert and Ph. Teyssié, *Tetrahedron Letters*, **35**, 3687 (1972).
- 2) N. Calderon, E.A. Ofstead, J.P. Ward, W.A. Judy and K.W. Scott, *J.A.C.S.*, **90**, 4133 (1968).
- 3) K.W. Scott, N. Calderon, E.A. Ofstead, W.A. Judy, J.P. Ward, *Adv. in Chem. Ser.*, **91**, 399 (1969).
- 4) V.M. Kothari, J.J. Tazuma, *J. Org. Chem.*, **36**, 2951 (1971).
- 5) G. Pampus, G. Lehnert and D. Maertens, *Polymer Preprints (American Chemical Society)*, **13(2)**, 880 (1972).

THE OXIDATION OF AROMATIC ANILS WITH LEAD TETRAACETATE - II -

A. Catto, F. Corbani, B. Rindone and C. Scolastico

(Istituto di Chimica Organica dell'Università, Via Saldini 50, Milano, Italy)

(Received in UK 30 May 1973; accepted for publication 7 June 1973)

In a previous paper⁽¹⁾ we reported the oxidation of some aromatic anils with lead tetraacetate (LTA) in benzene. The results of four substrates indicated a reaction mechanism occurring via the formation of a nitrene. Here we report the oxidation with LTA of aromatic anils substituted at the amine-derived nucleus.

The oxidation of (I) with LTA⁽²⁾ yielded benzaldehyde, 43%, and a mixture of (VII) and (VIII), 32%, which could be converted into the diacetyl derivative (IX) by acetylation. Compound (IX) was prepared from (X)⁽³⁾ via a PtO₂-catalysed reduction followed by acetylation and had m.p. 114-7°. Compound (VII), isolated by silica-gel chromatography, had m.p. 156-60°, ν_{\max} (nujol) 1658 cm⁻¹. The isomer (VIII), present in minor amount, could never be obtained pure.

The oxidation of (II) with LTA yielded benzaldehyde, 18%; (XI), 7%; (XV), 19%; (XVIII), 3%; (XIX), 12% and starting material, 2%. Compound (XI) was prepared from (XIII)⁽⁴⁾ by acetylation to yield (XIV), m.p. 82-4°, subsequently reduced to the unstable (XII). Acetylation of this yielded (XI), m.p. 173-6°. The reaction of benzaldehyde and (XII) gave (XIX), b.p. 130° at 10⁻⁵ mm/Hg. Compound (XV) was obtained by acetylation of (XVI)⁽⁵⁾ to oily (XVII) and this hydrogenated using PtO₂ as catalyst. The amide (XV) had m.p. 89-90°, ν_{\max} (nujol) 1635 cm⁻¹.

The oxidation of (III) with LTA gave benzaldehyde, 16%; (XX), 4%; (XXI), 14% and starting material, 62%.

The oxidation of (IV) with LTA gave benzaldehyde, 26%; (XXII), 23%, starting material, 20% and traces of (XXIII).

Compounds (V) and (VI) did not react under the reaction conditions used.