A Novel Dimerization of αβ-Unsaturated Carbonyl Compounds[1]

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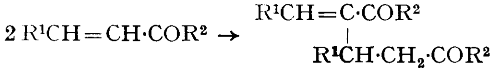
IN the oligomerizations of olefins and diolefins, the starting materials are mostly olefinic hydrocarbons having no polar group and the catalysts are the complex compounds of Group VIII metals.

Here is described a novel dimerization reaction of αβ-unsaturated carbonyl compound (I) to produce 1,3-di-carbonyl of 1-alkylidene-2-alkylpropane (II). The catalyst is a binary system of cuprous oxide and isocyanide, which is quite different from the catalysts for dimerization of olefinic hydrocarbons.

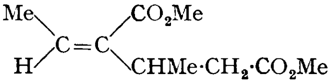


$$2\,R^1CH{=}CH{\cdot}COR^2 \rightarrow \begin{array}{c} R^1CH{=}C{\cdot}COR^2 \\ | \\ R^1CH{\cdot}CH_2{\cdot}COR^2 \end{array} \qquad (1)$$

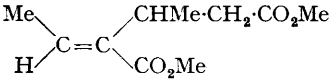
(I) (II)

a, $R^1{=}Me$, $R^2{=}OMe$; b, $R^1{=}R^2{=}Me$

For example, methyl crotonate (Ia) is dimerized to dimethyl 2-methylpent-3-ene-1,3-dicarboxylate (IIa) in a high yield. A mixture of 1·09 g. (10 mmoles) of cyclohexyl isocyanide, 30 mg. (0·2 mmole) of cuprous oxide, and 3·00 g. (30 mmoles) of methyl *trans*-crotonate was heated at 90° for 3 hr. Then, cuprous oxide was removed by filtration and the filtrate was distilled *in vacuo*. A fraction boiling at 70—80°/7 mm was collected, which was shown by g.l.c. analysis to consist almost exclusively of a mixture of *cis*- and *trans*-isomers of (IIa) (70%). The *cis–trans* mixture was not separated by g.l.c. The structure of (IIa) was convincingly confirmed by elemental analysis, n.m.r. and i.r. spectra, and molecular weight determination. N.m.r. spectrum analysis also revealed that the product dimer (IIa) consisted of 80% *cis*- and 20% *trans*-isomers.



Dimethyl 2-methylpent-*trans*-3-ene-1,3-dicarboxylate



Dimethyl 2-methylpent-*cis*-3-ene-1,3-dicarboxylate

N.m.r. of (IIa) (in CCl_4): d, (3H) τ 8·84 (*cis*) and 8·92 (*trans*); d, (3H) τ 8·16 (*cis*) and 8·14 (*trans*); m, (2H) τ 7·30—7·70; m, (1H) τ 6·50—7·10; s, (3H) τ 6·42 (*cis*) and 6·38 (*trans*); s, (3H) τ 6·33 (*cis*) and 6·29 (*trans*); q, (1H) τ 3·27 (*cis*) and 4·07 (*trans*). Principal i.r. bands (in Nujol) at 1710 vs, 1630 w, 1300—1100 s cm.$^{-1}$.

Dimerization was observed also in pent-3-en-2-one (Ib). From *trans*-pent-3-en-2-one, the *cis*-isomer of 4-methyl-5-acetyl-hept-5-en-2-one (IIb) (50%) was exclusively formed. N.m.r. of (IIb) (in CCl_4): d, (3H) τ 8·93; d, (3H) τ 8·05; s, (3H) τ 8·00; s, (3H) τ 7·83; m, (2H) τ 7·10—7·40; m, (1H) τ 6·60—7·10; q, (1H) τ 3·42. Principal i.r. bands (in Nujol) at 1700 s, 1660 s, 1630 s cm.$^{-1}$.

The catalytic activity of the cuprous oxide–isocyanide system is quite specific. Combination of a catalytic amount of cuprous oxide and a large amount of isocyanide is essential for the catalyst activity. The systems cupric oxide, copper(II) acetylacetonate, cuprous and cupric halides in combination with isocyanide were less effective under the same conditions. Furthermore, oxides of iron, nickel, zinc, and silver, with or without isocyanide, were inactive.

The isocyanide is needed in large quantities in comparison with the catalytic amounts of cuprous oxide, which alone does not catalyze the dimerization. For example, dimerization of (Ia) in the presence of only 1 mmole of cyclohexyl isocyanide produced the dimer (IIa) in only 5% yield after 7 hr. No compound derived from isocyanide was detected.

The dimerization of crotonitrile has been achieved with the copper–isocyanide system. Acrylates, methacrylates, and cinnamates, however, are not dimerized by this catalyst system. Alderson, Jenner, and Lindsey[2] reported the dimerization of acrylate to hex-2-enedioate by rhodium chloride catalyst.

$$CH_2{=}CH{\cdot}CO_2Me \rightarrow MeO_2C{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Me \qquad (2)$$

The behaviour of acrylate is used to distinguish the copper–isocyanide system from rhodium chloride, a typical transition-metal catalyst. The dimerization by the copper–isocyanide system is applicable only to the β-alkyl substituted αβ-unsaturated carbonyl compounds and nitriles.

In the dimerization of methyl *trans*-crotonate, the recovered crotonate at about 50% of conversion was shown by n.m.r. spectrum analysis to be a mixture of 90% *trans*- and 10% *cis*-isomers. The *cis–trans* isomerization was not caused by either single component of the catalyst system, cuprous oxide or isocyanide, which suggests the formation of a complex consisting of crotonate, cuprous oxide, and isocyanide, which is common to the dimerization as well as the *cis–trans* isomerization of monomer.

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[1] Part of the series on 'Synthetic Reaction by Complex Catalysts'.

[2] T. Alderson, E. L. Jenner, and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 5638.