Tetrahedron Letters, Vol.22, No.39, pp 3891 - 3894, 1981
Printed in Great Britain

0040-4039/81/393891-04$02.00/0

TRANSFORMATIONS OF CYCLOALKANES UNDER THE ACTION OF ACYL HALIDES IN THE PRESENCE OF $AIBr_3$.

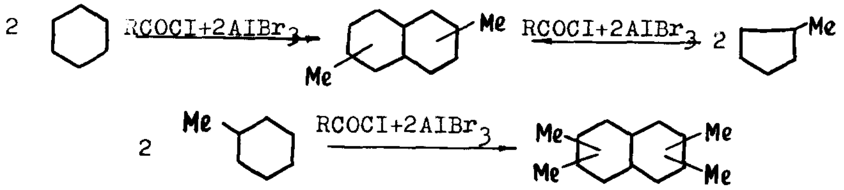
I.S.Akhrem*, A.V.Orlinkov, E.I.Mysov, M.E.Vol'pin
Nesmeyanov Institute of Organo-Element Compounds of the USSR Academy of Sciences, 28 Vavilova St., Moscow B-334, U.S.S.R.

Cycloalkanes have been found to react with acyl halides in the presence of $AIBr_3$ (mole ratio RCOX:$AIBr_3$=1:2) under very mild conditions affording products of hydrocarbon oxidative coupling or/and hydrocarbon acylation.

Despite success in activation of saturated hydrocarbons under the action of Lewis acids and transition metal complexes the problem of finding of active systems effecting transformation of hydrocarbons in mild conditions still arouses a great interest.

In the present work we have found that acylchlorides in the presence of $AIBr_3$ (mole ratio RCOCI:$AIBr_3$=1:2) react with cycloalkanes (cyclopentane, cyclohexane, methylcyclopentane and methylcyclohexane) under very mild conditions. These reactions proceed rather fast at room temperature and in some cases even at -10°C. Depending on the reagents ratio and hydrocarbon structure the reaction proceed predominantly or exclusively in one of three main directions.

1) Oxidative coupling of an unitial cycloalkane or its isomer affording bicyclic hydrocarbons, viz. decaline derivatives:



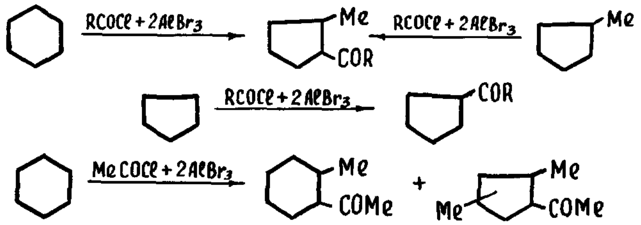
In the absence of solvent or with the excess of cycloalkane this process is observed for all hydrocarbons studied with the exception of cyclopentane. As indicated in Table 1, in the presence of the excess of cyclohexane (20°C) dimethyldecalines are formed in an hour quantitatively with respect to acetyl chloride and the degree of the cyclohexane conversion being 19% after 15 min. The mixture of dimethyldecalines contains six isomers and the main components are thermodynamically most favourable 2,6- and 2,7-dimethyldecalines.

According to Nenitzescu[1] the action of MeCOCI and $AICI_3$ on cyclohexane (20°C, 2 days) produces a small quantity of a hydrocarbon $C_{12}H_{22}$ to which the structure of 2,2-dimethylbicyclopentyl was assigned[2]. According to Gavrilov[3], cyclohexane under the action of activated $AICI_3$ (1:1) affords 10% of a mixture of dimethyldecalines after 20 hours at 40-60°C. However, by special test experiments we have shown that under conditions employed by us (20°C, 1 h) $AICI_3$, $AIBr_3$, MeCOCI+$AICI_3$ and equimolecular mixture of MeCOCI+$AIBr_3$ were practically inactive.

Besides dimethyldecalines the reaction of cyclohexane produces a small quantity of the $C_{18}H_{32}$ hydrocarbon being probably a tricyclic coupling product of dimethyldecalines with cyclohexane. Also 6% of a mixture of polymethylated cycloalkanes is formed, the latter being probably products of the further tranformations of dimethyldecalines. Really, we have found that the same mixture of polymethylcycloalkanes was formed under the action of MeCOCI+$AIBr_3$ (1:2) on dimethyldecalines.

Transformations of methylcyclopentane are similar to those of cyclohexane. On the contrary, oxidative coupling of methylcyclohexane proceeds with difficulty and that of cyclopentane is not observed at all.

2) Acylation of cycloalkanes with formation of alkylcycloalkylketones:



This reaction route is favoured by decreasing the cycloalkane/acyl halide ratio and also by performing the reaction in the CH_2CI_2. Transformations of cycloalkanes into saturated ketones are observed with all hydrocarbons studied and ketones of the cyclopentane series are formed almost exclusively. With the equimolecular ratio of hydrocarbon and acyl chloride this reaction route is predominant and in the case of cyclopentane it represent the only way of transformation with any ratio of hydrocarbon and acyl chloride from 6:1 to 1:10, i.e. also under conditions favouring an oxidative coupling of other cycloalkanes. As indicated in Table 1, under these conditions cyclopentane is transformed into alkylcyclopentylketones in 55-60% yield while other cycloalkanes produce 12-16% of saturated ketones.

Formation of saturated ketones from cyclohexane and cyclopentane under the action of the equimolecular mixture of MeCOCI and $AICI_3$ was observed by Nenitzescu[1,4] and other authors[5]. These reactions, however, are very slow and under our conditions (20°C, 1h) cyclohexane reacts with the MeCOCI and $AICI_3$ mixture affording only negligitably amount of the acylation product and cyclopentane is not acylated at all.

3) Acylation of cycloalkanes leading to α,β-unsaturated ketones:

A five-fold excess of acyl chloride relative to cycloalkane allows to effect the sufficiently selective transformation of cyclohexane and methylcyclopentane in this pathern. Contrary, the formation of unsaturated ketones was not observed under the same conditions with such species as cyclopentane and methylcyclohexane.

Cyclohexane is transformed (-10°C, 1h) into 2-methylacetylcyclopent-1-en in 40% yield. According to Tabushi[6] preparation of this alkene from cyclohexane under the action of the equimolecular mixture of MeCOCI and $AICI_3$ demands prolonged time and elevated temperatures.

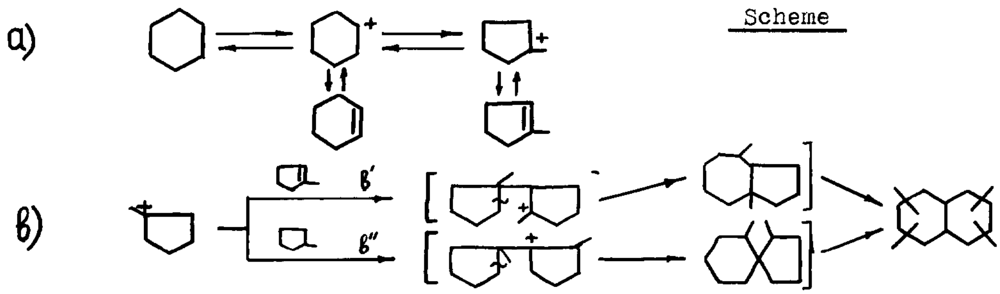
A proposed reaction scheme involves a hydride ion abstraction from hydrocarbon by $RCOCI+AIBr_3$ (1:2) to form corresponding or isomeric carbenium ions, which are in equilibrium with olefins (a). With an excess of cycloalkane a tertiary carbenium ion can either add cycloolefine (route b′) or effect the electrofilic attack on another cycloalkane molecule (route b″). The carbenium ions thus formed give rise to dimethyldecalines (only some of the possible intermediates are shown in the scheme). The lack of products of cyclopentane oxidative coupling is possible due to a low stability of the secondary cyclopentyl cation.

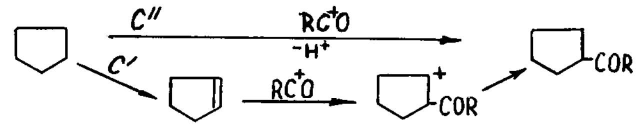
With decrease in the cycloalkane concentration in the mixture the process (b) is hindered and acylation reactions become predominant leading to saturated ketones (route c). Formation of a saturated ketone can be effected either by cycloolefine acylation (route c′) or by direct electrofilic proton substitution in a cycloalkane molecule (route c″).

With an excess of the acylating reagent a hydride ion abstraction from the tertiary carbon atom of saturated ketone becomes possible with transformation of the latter into α,β-unsaturated ketone (route d). The failure of cyclopentane to form unsaturated ketone is possibly due to disadvantage of formation of the secondary cyclopentyl carbenium from corresponding saturated ketone.

Structures of compounds prepared have been established by GLC-MS and NMR-^{13}C and ^{1}H spectra. 2,6- and 2,7-dimethyldecalines were dehydrogenated with Se at 400°C to produce 2,6- and 2,7-dimethylnaphtalenes. NMR-^{13}C spectra of all four hydrocarbons are identical with those of authentic samples[7,8].

Reactions of other hydrocarbons with acyl halides in the presence of $AIBr_3$ and the structure of acyl halides-$AIBr_3$ reaction products are under investigation.



c)


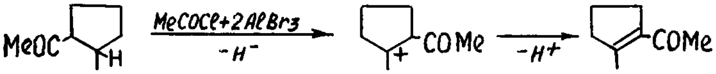
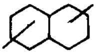
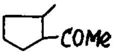
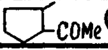
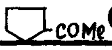
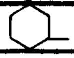
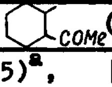
d)


Table 1. Products of interaction of cycloalkanes with RCOCI in the presence of AIBr$_3$ (mole ratio RCOCI:AIBr$_3$=1:2, 20°C, 1h).

RH	RCOCI	Mole ratio RH:RCOCI	Products (yield, %)[a,b]
	MeCOCI	12:1	 (17)[a,c],  (15)[b], C$_{18}$H$_{32}$(trace)
	MeCOCI	3:1	 (22)[a], (4)[a], Polymethyl-cycloalkanes[d]
	MeCOCI	1:1	(12)
	MeCOCI	1:5[e]	(40)[a]
	PrCOCI	10:1	(6)[a],  (15)[b]
	MeCOCI	6:1	(60)[b]
	PrCOCI	6:1	(55)[b]
	MeCOCI	6:1	 (4)[a], (7)[b], (8)[b]
	MeCOCI	6:1	(25)[a],  (16)[b]
	MeCOCI	1:5	 (28)[a]

[a] Calculated on the RH; [b] Calculated on the RCOCI; [c] The total yield of products towards MeCOCI excess 100% as a consequance of the ability of acetaldehyde formed to react with cyclohexane in AIBr$_3$ presence giving rise to dimethyldecalines. This reaction has been specially shown; [d] C$_8$H$_{16}$(5)[a], C$_9$H$_{18}$(0,5)[a], C$_{10}$H$_{20}$ (0,8)[a], mass spectra of C$_8$H$_{16}$ and C$_9$H$_{18}$ correspond to the mixture of 1,3- and 1,4-dimethylcyclohexane and to 1,3,5-trimethylcyclohexane respectively; [e] At-10°C.

References and Notes

1 C.D.Nenitzescu, C.N.Ionescu, Ann., 491, 189 (1931)
2. These result seem to be erroneous as we have found this is in fact a mixture of dimethyldecalines.
3. B.G.Gavrilov, V.G.Luksha et al., Zh.Org.Khim., 11, 597 (1975)
4. C.D.Nenitzescu, I.P.Cantuniary, Ber., 65, 807, 1449 (1932)
5. F.Unger, Ber., 65, 467 (1932)
6. I.Tabushi, K.Fujita, R.Oda, Tetrahedron Lett., 4247 (1968)
7. T.I.Pehk, A.H.Laht, I.A.Musaev et al., Nephtechimiya, 15, 329 (1975)
8. D.K.Dalling, K.H.Ladner, D.M.Grant et al., J.Amer.Chem.Soc., 99, 7142 (1977)

(Received in UK 17 July 1981)