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REACTIONS CATALYSED BY ALUMINIUM CHLORIDE—XXVIII*

THE REACTION OF CYCLOALKANES WITH CARBON MONOXIDE

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Abstract—The condensation of some cycloalkanes with carbon monoxide under pressure, in the presence of $AlCl_3$ at normal or slightly higher temperature has been investigated. Cyclopentane leads to cyclopentanecarboxylic acid. Methylcyclopentane yields the same products as cyclohexane, namely cyclohexanecarboxylic acid and 2-methylcyclohexanone. From methylcyclohexane, cyclohexyl methyl ketone is obtained together with a mixture of *trans*-2-methyl-cyclohexanecarboxylic acid with the 3- and/or 4-methyl isomers. From decalin, *trans*-*trans*-1-decalin-carboxylic acid and *trans*-hexahydro-α-benzosuberone are produced. The mechanism of these reactions is discussed.

IT was established during 1931-1936[1-3] that saturated hydrocarbons C_xH_y react with carbon monoxide under pressure in the presence of aluminium chloride at normal or slightly elevated temperature, yielding three kinds of products: (i) acid $C_xH_{y-1}COOH$; (ii) lower ketone $C_{x+1}H_yO$; (iii) higher ketone $(C_xH_{y-1})_2CO$.

The reaction has been applied to the following hydrocarbons: (Table 1). *Alkanes.* Propane,[4-6] n-butane,[3] isobutane,[3] n-pentane,[1,7] isopentane,[1,7] n-hexane[1] and isohexanes.[8]

Cycloalkanes. Cyclohexane.[1,2,7,9]

In order to explain this reaction, a mechanism was suggested[3,4,9] involving the intermediate formation of the formyl cation as in the Gattermann-Koch reaction. This explanation was adopted in most reviews and monographs describing the reaction between alkanes and carbon monoxide.[10]

But, as shown recently,[6] a different mechanism involving the reaction between carbon monoxide and a carbonium ion generated by the hydrocarbon under the influence of the catalyst, is much more probable.

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* Part XXVII: A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann.* **625**, 74 (1959).

[1] H. Hopff, *Ber. Dtsch. Chem. Ges.* **64**, 2739 (1931).

[2] H. Hopff, *Ber. Dtsch. Chem. Ges.* **65**, 482 (1932).

[3] H. Hopff, C. D. Nenitzescu, D. A. Isăcescu and I. P. Cantuniari, *Ber. Dtsch. Chem. Ges.* **69**, 2244 (1936).

[4] H. Pines and V. N. Ipatieff, *J. Amer. Chem. Soc.* **69**, 1337 (1947). H. Pines and V. N. Ipatieff, U.S. Pat. 2,346,701 (1944); *Chem. Abstr.* **38**, 6302 (1944).

[5] H. Hopff, *Angew. Chem.* **60**, 218, 245 (1948).

[6] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann.* **625**, 66 (1959).

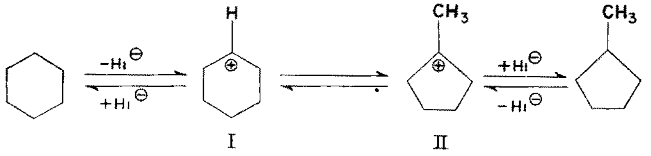
[7] H. Hopff, Ger. Pat. 512,718 (1927); *Chem. Zentr.* **I**, 1007 (1931); 520,154 (1927); *Ibid.* **I**, 3060 (1931); 535,254 (1928); *Ibid.* **I**, 1155 (1932).

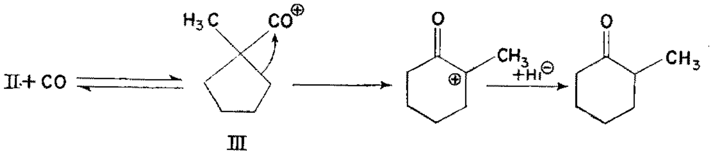
[8] K. Scharpenberg, *Brennstoffchemie* **36**, 346 (1955).

[9] C. D. Nenitzescu and D. V. Curcăneanu, *Ber. Dtsch. Chem. Ges.* **71**, 2063 (1938).

[10] C. A. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry* p. 765. Reinhold, New York (1941);
J. Schmidt, *Das Kohlenoxyd* (2nd Ed.) p. 251. Leipzig 1950;
R. C. Fuson, *Advanced Organic Chemistry* p. 188. John Wiley, New York (1950);
B. T. Brooks, *The Chemistry of Nonbenzenoid Hydrocarbons* Reinhold, New York (1950);
F. Asinger, *Chemie und Technologie der Paraffin-Kohlenwasserstoffe* p. 561. Akademie Verlag, Berlin (1956);
M. Orchin and I. Wender, *Catalysis* (Edited by P. H. Emmett) Vol. 5, p. 1. Reinhold, New York (1957).

This new mechanism when applied to cyclohexane leads to the following scheme:





In fact, the lower ketone obtained in this reaction from cyclohexane[1,2] is indeed 2-methylcyclohexanone, but the acid simultaneously formed is not 1-methylcyclopentanecarboxylic acid corresponding to the ions II and III, but instead cyclohexanecarboxylic acid, corresponding to the ion I.

In order to gather more experimental data, the reaction was applied to the following cycloalkanes:

1. The condensation of carbon monoxide with *cyclohexane* confirmed the results[1] that the acid produced is mostly cyclohexanecarboxylic acid.
2. The reaction of *methylcyclopentane* yields the same products in nearly the same amounts as in the previous case.
3. The reaction of *cyclopentane* requires heating at 70° and affords cyclopentanecarboxylic acid and dicyclopentylketone (as the higher ketone). The·lower ketone is present only in traces.
4. *Methylcyclohexane* readily reacts at room temperature, yielding in appreciable amount cyclohexyl methyl ketone. The acid formed is a mixture of isomeric acids $C_8H_{14}O_2$, which by partial esterification and hydrolysis may be separated into two nearly equal fractions. The fraction difficulty esterified and hydrolysed is *trans*-2-methyl-cyclohexanecarboxylic acid; the other fraction, with higher melting amide, probaby is a mixture of 3- and 4-methyl-cyclohexanecarboxylic acids.
5. Particularly interesting is the reaction of *decalin* with carbon monoxide which proceeds smoothly at room temperature, giving *trans–trans*-1-decalin-carboxylic acid and *trans*-hexahydro-α-benzosuberone.

DISCUSSION OF THE RESULTS

Alkanes and cycloalkanes possessing tertiary carbon atoms react at room temperature and yield all three types of products i–iii. The hydrocarbons which have only primary and secondary carbon atoms and which cannot acquire tertiary carbon atoms by isomerization, such as propane and cyclopentane, react at temperatures above 60° and do not yield lower ketones (ii) because these are probably destroyed under existing conditions.

The reactions have an induction period, easily observed in the case of methylcyclohexane or decalin which react at room temperature. The effect of water addition to the reaction mixture (as the crystalohydrate $AlCl_3{\cdot}6H_2O$) results in a reduction of the induction period, an increase in acid yield and the formation of unsaturated products and gums.

The non-acid higher fractions are a complex mixture of higher ketones (iii), condensation products of the ketones (ii) and (iii), condensation products of aldehydes eventually formed by hydride-ion reduction of acyl cations, and dimeric hydrocarbons resulting from dehydrogenation. This renders difficult the isolation of pure substances, therefore the higher ketones (iii) have been isolated only when the lower ketone is formed in minute amounts (propane[6] and cyclopentane).

Table 1 groups the structures and approximate yields (mole %) of the reaction products obtained from paraffinic hydrocarbons and carbon monoxide under pressure in the presence of aluminium chloride.

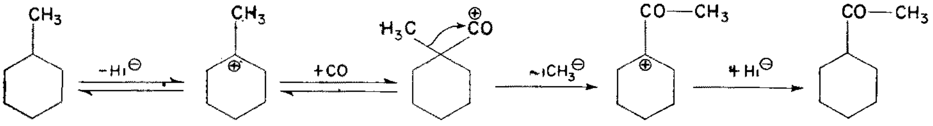
MECHANISM OF THE REACTION

The identity of products obtained from cyclohexane and methylcyclopentane (No. 8), proves that in this case isomerization is more rapid than condensation with carbon monoxide. On the other hand, reactions No. 2 and 3 yield different acids and higher ketones, indicating that the isomerization

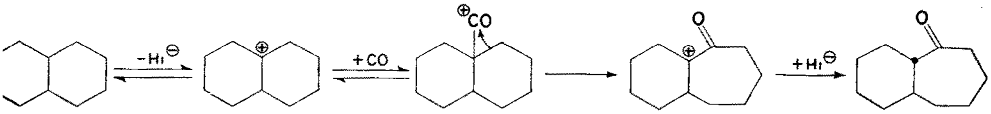
$$CH_3\cdot\overset{\oplus}{C}H\cdot CH_2\cdot CH_3 \underset{?}{\rightleftharpoons} (CH_3)_3C^{\oplus}$$

is slower then the reaction with carbon monoxide.

The mechanism previously proposed[6] is in good agreement with the formation of the lower ketone obtained in all these cases:



IV



V VI

The rearrangement of tertiary acyl cations to lower ketones always yields the least tensioned possible ring. From III a six-membered ring is formed by expansion; IV already has a six-membered ring and conserves it by methyl migration; while V can by no means yield a 5- or 6-membered ring and therefore expands its cycle to a 7-membered ring.*

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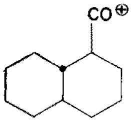
* It is supposed that hexahydro-α-benzosuberone is formed through V and not through VII (although the latter is common both to the acid and the lower ketone formed from decalin) since VII ought to yield in



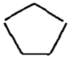
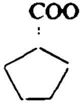
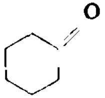
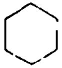
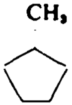
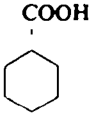
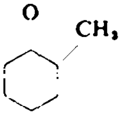
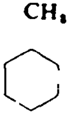
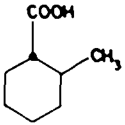
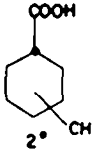
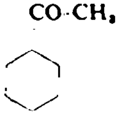
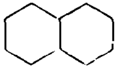
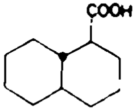
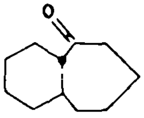
VII

comparable amounts hexahydro-α-benzosuberone as well as -β-, and since no β-derivative is formed.

TABLE 1. STRUCTURE AND YIELDS OF PRODUCTS OBTAINED IN THE REACTION BETWEEN SATURATED HYDROCARBONS, CO AND $AlCl_3$

No.	Hydrocarbon	(i) Acid	(ii) Lower ketone	(iii) Higher ketone
1	$CH_3{\cdot}CH_2{\cdot}CH_3$	$(H_3C)_2CH{\cdot}COOH$ 4[5]; 2[6]	$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3$?[5]; 0[6]	$(H_3C)_2CH{\cdot}CO{\cdot}CH_2{\cdot}CH(CH_3)_2$?[5]; 18[6]
2	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	$CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH$?[3] and $(H_3C)_3C{\cdot}COOH$ Traces[3]	$(H_3C)_2CH{\cdot}CO{\cdot}CH_3$ 6[3]	$(H_3C)_2CH{\cdot}CH_2{\cdot}CO{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH_3$?[3]
3	$(H_3C)_3CH$	$(H_3C)_3C{\cdot}COOH$ 1[3]	$(H_3C)_2CH{\cdot}CO{\cdot}CH_3$ 31[3]	$(H_3C)_2CH{\cdot}CH_2{\cdot}CO{\cdot}C(CH_3)_3$ 4[3]
4	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH$ 5[1]	$(H_3C)_2CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ 17[1]	
5	$(H_3C)_2CH{\cdot}CH_2{\cdot}CH_3$		$(H_3C)_2CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ 7[1]	
6	$(H_3C)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ and $CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH_3$		$(H_3C)_2CH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$?[9]	

TABLE 1 (*continued*)

No.	Hydrocarbon	(i) Acid	(ii) Lower ketone	(iii) Higher ketone
7		 5*	 Traces*	 8*
8	 and 	 1[1]; 2*	 4[1],*	
9		 2* and  2*	 26*	
10		 3*	 4*	

* Present work

The mechanism, however, does not account for the structure of the acids obtained in cases No. 2, 4, 8, 9, 10, since these are predominantly secondary (arising therefore from secondary carbonium ions)[*] though all lower ketones are derived from tertiary carbonium ions. The only instances when both the acid and the lower ketone originate in the same carbonium ion are isobutane (No. 3) which can form a tertiary but no secondary carbonium ion, and propane and cyclopentane (Nos. 1 and 7) which can form only secondary carbonium ions.

The formation of secondary carboxylic acids is surprising for two reasons: Firstly, tertiary alkyl carbonium ions are more stable than secondary ions and ought therefore to be favoured. Secondly, as Koch[11] recently discovered, on treating alkenes or alcohols with anhydrous formic acid in the presence of concentrated sulphuric acid, tertiary carboxylic acids and no secondary acids or ketones are obtained. For this reaction a mechanism was proposed[11] essentially identical with the mechanism suggested[6] for the reaction of alkanes with CO in the presence of $AlCl_3$.[12] It is evident that the mechanism of these two reactions must be different in order to account for the formation of different reaction products.

It was suggested[13] that mixed anhydrides of tertiary carboxylic acids with sulphuric acid and not free tertiary acyl cations are involved in Koch's reaction. This idea seems logical, since the anion $HO-SO_2-O^{\ominus}$ is a stronger nucleophile than $AlCl_4^{\ominus}$. The greater stability of tertiary acids under these conditions may be thus explained, but unfortunately the existence of such mixed anhydrides has not yet been experimentally proved.

The mechanism of the reaction between alkanes or cycloalkanes and carbon monoxide can be interpreted starting from a theory developed by Baddeley[14] for the explanation of certain anomalous isomerizations of alkyl groups in the Friedel–Crafts reaction applied to higher alkyl halides.[†] According to this author, equilibria between all forms of alkyl carbonium ions (energetically possible) are established in the presence of $AlCl_3$, by $Alk^{\oplus}$ or $H^{\ominus}$ shifts. In these equilibrium mixtures, tertiary carbonium ions will be present in far larger concentrations than secondary carbonium ions, because the former are more stable, but secondary carbonium ions are postulated to react more rapidly than tertiary ones.

In addition, a new feature must be taken into account, namely, that tertiary acyl

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[*] The proportion of tertiary acids contained in the secondary acids may be qualitatively inferred: with No. 2 the tertiary acid is formed in amounts large enough to allow isolation; with No. 8 isolation is not possible but the tertiary acid depresses substantially the melting point of the crude amide; and with No. 10, the amount of tertiary acid is negligible, the crude amide being almost pure.

[†] An alternative theory which is better supported by experimental data explains these anomalous Friedel–Crafts reactions on the basis of a newly discovered rearrangement of phenyl-alkanes, independent of, and subsequent to, the Friedel–Crafts reaction.[15] As yet no evidence of a similar isomerization of carboxylic acids in the presence of aluminium chloride being available, Baddeley's theory is the best alternative for the explanation of the structure of acids formed in the reaction between alkanes or cycloalkanes and carbon monoxide.

[11] H. Koch, *Brennstoffchemie* **36**, 321 (1955); *Fette, Seif. Anstrichmittel* **59**, 493 (1957); *Riv. Combust.* **10**, 77 (1956);
H. Koch and W. Haaf, *Angew. Chem.* **70**, 311 (1958); *Liebigs Ann.* **618**, 254 (1958).

[12] J. R. Roland, J. D. C. Wilson and W. E. Hanford, *J. Amer. Chem. Soc.* **72**, 2122 (1950).
W. Hanford and D. E. Sargent, *Organic Chemistry. An Advanced Treatise* (Edited by H. Gilman) Vol. IV, pp. 1001–1019. John Wiley, New York (1955).

[13] I. T. Eidus and K. V. Pusytsky, *Proceedings of Communications presented at the 8th Mendeleev Congress of General and Applied Chemistry, Organic Chemistry and Technology Section* p. 113. Ed. Acad. Sci. U.S.S.R., Moscow (1958).

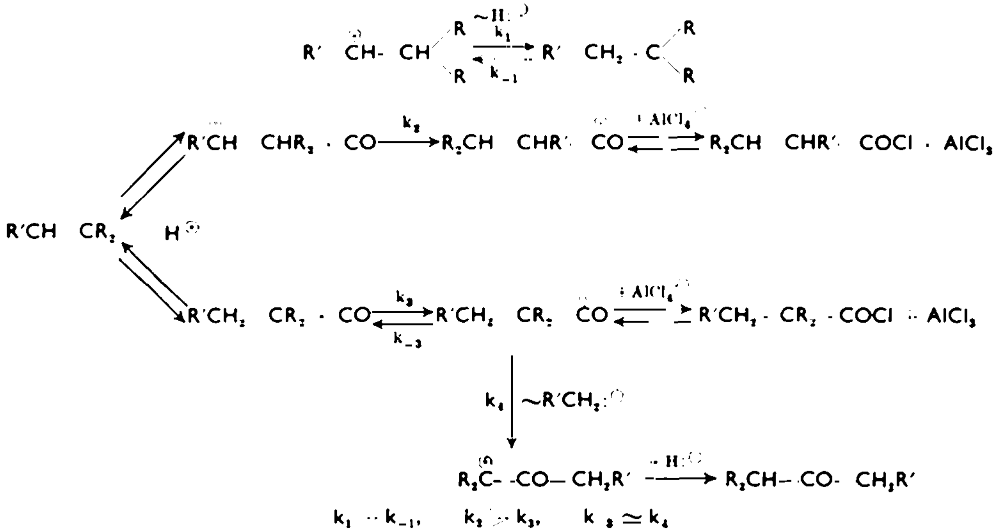
[14] G. Baddeley, *Quart. Rev.* **8**, 355, 366 (1954).

[15] C. D. Nenitzescu, I. Necsoiu, A. Glatz and M. Zalman, *Chem. Ber.* **92**, 10 (1959).

cations are formed reversibly from carbon monoxide and tertiary alkyl carbonium ions. At normal pressure decarbonylation is favoured; furthermore, these tertiary acyl cations may undergo rearrangement.[6]

The complex picture emerging from these considerations may be summarized as follows. Water-activated aluminium chloride abstracts hydride ions from methylene and methine groups yielding secondary and tertiary alkyl carbonium ions; these are subsequently undergoing hydride or alkyl shifts, hydrogen ion eliminations and reaction with carbon monoxide. The latter reaction yields acyl cations; when secondary, these are stable and irreversibly formed, but when tertiary, they decompose reversibly, or rearrange to lower ketones. Thus, the acids present in the final reaction mixture will be predominantly secondary, while the lower ketone will be exclusively derived from tertiary acyl cations. The higher ketones are formed by acylation (with secondary and tertiary acyl cations) of the olefins resulting by hydrogen-ion elimination, and will generally be complex mixtures. The relative concentrations and rates of isomerization and carbonylation of tertiary and secondary alkyl carbonium ions are too complex to be fully understood at present.

The following qualitative scheme accounts for the structure of the acid and lower ketone:



It must be mentioned that when a stationary concentration of carbonium ions is achieved, intermolecular hydride shifts may occur by an ionic chain mechanism, as indicated by the existence of an induction period.

EXPERIMENTAL

All analyses were performed by Miss E. Sliam and Miss V. Sǎndulescu.

1. *Cyclopentane*

A mixture of 540 g (7·7 moles) cyclopentane (b.p. 49–50°) and 758 g (5·7 moles) aluminium chloride were introduced into a steel autoclave with carbon monoxide compressed to 130 atm. At room temp no absorption takes place even after 72 hr. On heating to 70–80°, 120 l NTP (5·3 moles) CO are absorbed during 8 hr. The contents of the autoclave were hydrolysed with ice and HCl, and extracted with ether. The organic layer was treated with 10% NaOH solution, yielding after acidification 114 g acid, from which 40 g b.p. 210–215°, were identified as *cyclopentanecarboxylic acid* (4·6% yield). For better purification it was esterified with ethanol in the presence of benzenesulphonic acid, fractionated and hydrolysed with 30% NaOH. (Found, neutral equivalent, 116; $C_6H_{10}O_2$ requires: 114). The *amide* of the crude acid has m.p. 168–169° (from water) and after esterification and hydrolysis m.p. 172°. Lit. 178°,[16] 177–178°.[17] (Found: C, 63·68; H, 9·80; N, 12·38. Calc. for $C_6H_{11}NO$ (113·2): C, 63·91; H, 9·81; N, 12·29%). The mixed m.p. with an authentic sample[16] showed no depression. The *anilide*, m.p. 160°, crystallizes from dil. methanol. (Found: N, 7·40. $C_{12}H_{15}NO$ (189·25) requires: N, 7·49%). The p-*toluidide*, m.p. 134°, crystallizes from methanol. (Lit.[17] 135°).

The non-acid reaction product fractionated at normal, and also at reduced pressure, yields traces of lower ketone, b.p.$_{10}$ 45–55° (2,4-dinitrophenylhydrazone m.p. 143–145°, raised by recrystallizations from ethanol; mixed m.p. with authentic *cyclohexanone* 2,4-dinitrophenylhydrazone 162°), and a fraction b.p.$_3$ 85–90°, which contains *dicyclopentyl-ketone*, purified by regeneration from its semicarbazone, after which treatment it did not decolourize bromine water. B.p. 251°, n_D^{20} 1·479 d_4^{20} 0·9663. The *semicarbazone*, m.p. 167–168°, crystallizes from methanol. (Lit. 158–162°,[18] 165°,[19] 167°[20]). The 2,4-*dinitrophenylhydrazone*, m.p. 103°, crystallizes from methanol. (Lit. 103–104°[20]).

2. *Cyclohexane*

A mixture of 1000 g (12 moles) cyclohexane and 1850 g (14 moles) aluminium chloride absorb in 12 hr at 20° 10 moles CO (the absorption beginning after short heating at 60°). The mixture, similarly worked up, yields 52 g 2-*methylcyclohexanone* b.p. 160–167°. The *semicarbazone* has a m.p. 192°. (Lit. 197°[21-23] on rapid heating). The 2,4-*dinitrophenylhydrazone*, m.p. 132°, (Lit.[23] 135·5–137° cor.) gave no depression with an authentic specimen.

The acid product (90 g), isolated as above, distilled at 20 mm yielded after a 15 g forerun, a 32 g fraction b.p.$_{20}$ 130–140°, containing mostly *cyclohexanecarboxylic acid*. This crude acid gives an *amide* m.p. about 130°. Since fractionation does not allow further purification, use was again made of incomplete esterification and hydrolysis (the tertiary acids or the sterically hindered secondary acids may be thus eliminated from secondary acids, since the former are esterified and hydrolysed much more slowly than the latter). The *amide* prepared from the purified acid m.p. 169° (from water), showed no depression with an authentic sample of m.p. 183°. (Lit.[22] m.p. 184°). The *anilide*, m.p. 138°, was prepared from the chloride of the purified acid and crystallized from aqueous ethanol. A mixed m.p. with authentic cyclohexanecarboxanilide m.p. 143°. (Lit.[22] m.p. 143–144°) showed no depression. (Found: N, 6·89. Calc. for $C_{13}H_{17}NO$ (203·3): N, 6·89%).

3. *Methylcyclopentane*

A mixture of 113 g (1·4 moles) dry, olefin-free methylcyclopentane in a sealed glass tube (prepared by catalytic hydrogenation of 1-methylcyclopentene with 5% Pt on charcoal, and carefully refined and fractionated, b.p. 72–73°) and 180 g (1·35 moles) $AlCl_3$ was introduced into an autoclave. Then carbon monoxide at 50 atm and room temp, was introduced causing the glass tube to break and the hydrocarbon to react with $AlCl_3$. After 6 hr rocking at room temp, the autoclave was opened and the mixture worked up as before. About half of the initial hydrocarbon was recovered. The reaction product contained 1·2 g unitary acid (giving *amide* m.p. 179–181° and *anilide* m.p. 141–142° which did not depress a mixed m.p. of *cyclohexanecarboxylic acid* derivatives), and 32 g neutral product, of which 6 g had a b.p. 150–170°. This fraction readily yields a *semicarbazone* m.p. dec. 191–192° and a 2,4-*dinitrophenylhydrazone* m.p. 133°, identical with the corresponding derivatives of 2-*methylcyclohexanone*.

4. *Methylcyclohexane*

A mixture of 770 g (7·8 moles) methylcyclohexane and 810 g (6·1 moles) $AlCl_3$ were treated in an autoclave at room temp with CO at 150 atm. The pressure began to drop after an induction

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[16] C. D. Nenitzescu and I. P. Cantuniari, *Ber. Dtsch. Chem. Ges.* 65, 807 (1932).

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period of about 10 hr and ceased after the absorption of 7·2 moles CO. The reaction mixture was worked up as before.

Distillation of the neutral product gave two main fractions. The first fraction, b.p.$_2$ 60–80° 288 g, and a second fraction, b.p.$_2$ 120–138°, 175 g (no definite compound could be isolated from this second fraction; possibly it contained sterically hindered esters of methyl-cyclohexanecarboxylic acids, since on treatment with conc. H_2SO_4, an acid mixture was obtained similar to the acid reaction product). The first fraction on refractionation at normal pressure yielded 220 g of a colourless liquid, b.p. 176°, which did not decolourize bromine water, and proved to be *cyclohexyl methyl ketone*; *semicarbazone* m.p. and mixed m.p. 176° (Lit. 175°[19,24]); 2,4-*dinitrophenylhydrazone* m.p. 141° (Lit. m.p. 140°[24]). The reaction with NaOBr yields *cyclohexanecarboxylic acid*, b.p.$_8$ 100°, characterized through its *amide* (m.p. and mixed m.p. 184°) and *anilide* (m.p. and mixed m.p. 143–144°).

TABLE 2

Recrystallization	Crude	1	2	3
Solvent		20% Ethanol	Benzene	Water
Non-esterified acid	147°	159–161°	162°	167°
Acid from ester	151°	165–170°	170°	176°
Mixed m.p.	138°	142°	142°	145°

The acid reaction product (49 g fraction b.p.$_4$ 100–120°) was redissolved in 10% NaOH, extracted with ether to remove traces of non-acid products, acidified and refractionated yielding a colourless liquid, b.p.$_4$ 102°, b.p.$_{760}$ 238°. (Found: C, 67·57; H, 9·92. Neutral equivalent 143. Calc. for $C_8H_{14}O_2$ (142·2): C, 67·32; H, 9·71%. Neutral equivalent 142·2. This acid was first believed to be unitary since the m.p. of the amide (m.p. 145–146°) could not be raised by recrystallization from dil. ethanol but the m.p. of the amide (m.p. 145–146°) could not be raised by recrystallization from dil. ethanol or benzene. (Found: C, 67·71; H, 10·66; N, 9·82; $C_8H_{15}NO$ (141·2) requires: C, 68·04; H, 10·71; N, 9·92%); the *anilide* m.p. 112°. (Found: N, 6·72; $C_{14}H_{19}NO$ (217·3) requires: N, 6·45%).

The acid proved to be a mixture of isomeric $C_8H_{14}O_2$ acids and 35 g were esterified with ethanol-benzene–$C_6H_5SO_3H$, by refluxing 2 hr. This resulted in 20 g ester b.p.$_{45}$ 121°, b.p.$_{760}$ 202°, and 10 g *non-esterified acid*, b.p.$_{14}$ 160°. The ester was refluxed 8 hr with 10% aqueous NaOH, the unsaponified ester extracted with ether, and the solution acidified, resulting in 12 g *acid from ester*. These two acids were converted (through their chlorides, prepared with $SOCl_2$ at room temp) into amides which were consecutively recrystallized. Table 2 shows the m.p. of, and the mixed m.p. between, these amides.

Both amides depress the m.p. of cycloheptanecarboxamide (m.p. 192°), 2,3-dimethyl-cyclopentanecarboxamide (m.p. 170°) and cyclohexaneacetamide (m.p. 167°). But the amide of the *non-esterified acid* with m.p. 167° does not depress the m.p. of trans-2-*methyl-cyclohexanecarboxamide* with m.p. 182–183°.[25] The amide of the *acid from ester* with m.p. 176° is identical with the amide (with m.p. 176°) prepared by oxidation with NaOBr of the ketone obtained in the Nenitzescu reaction between cycloheptene, acetyl chloride, cyclohexane and $AlCl_3$.[27] Thus, the acid which is difficulty esterified is 2-*methyl-cyclohexanecarboxylic acid*, and the acid from ester probably is a mixture of trans-3- and trans-4-*methyl-cyclohexanecarboxylic acids*.[28]

If, before admitting CO, the autoclave is further charged with 0·2–0·5 moles finely ground $AlCl_3 \cdot 6H_2O$, the absorption begins earlier and the acid is formed in larger amounts and contains a white gum (polymer), little soluble in ether, which separates on acidification of the alkaline solution.

5. *Decalin*

Decalin, 1410 g (10·2 moles) distilled over sodium were introduced in a steel autoclave containing 1140 g (8·5 moles) $AlCl_3$ at -20°, then CO at 150 atm was introduced. The autoclave was rotated

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and allowed to warm to room temp. The absorption began after about 8 hr, and after 36 hr 242 l NTP CO (10·8 moles) had been absorbed. The mixture was worked up as before, and the neutral product carefully fractionated under reduced pressure. After a forerun of 300 g unreacted decalin, a 55 g fraction b.p.$_3$ 102 114° was collected (leaving 800 g higher-boiling products, which were not further investigated). The fraction yielded on redistillation *hexahydro-α-benzosuberone*, b.p.$_3$ 111°, b.p.$_{760}$ 258°. The *semicarbazone*, m.p. 220°, crystallized from ethanol or from benzene. Lit. 222–223° cor.;[29] 213–214°.[30] (Found: C, 64·63; H, 9·74; N, 18·88. Calc. for $C_{12}H_{21}N_3O$ (220·3): C, 64·54; H, 9·48; N, 18·82%). The 2,4-*dinitrophenylhydrazone*, brick-red, m.p. 168° crystallized from ethanol-benzene. Lit. m.p. 176·5–177 cor.;[29] 173 174°.[30] (Found: N, 16·25. Calc. for $C_{17}H_{12}N_4O_4$ (346·4): N, 16·18%). The mixed m.p. and I.R. spectra of the *semicarbazone* and *dinitrophenylhydrazone* show identity with authentic products.[29]

The acid product gave a 45 g fraction b.p.$_2$ 140-150° (leaving 42 g higher-boiling products), which redissolved in 10% NaOH solution, extracted with ether, acidified and refractionated on a short column yielded a unitary acid b.p.$_3$ 158°, b.p.$_{760}$ 275°, as a colourless very viscous liquid, which slowly crystallized, m.p. 94 98°. This acid proved to be trans trans-1-*decalincarboxylic acid*. Lit. m.p. 101·5–102·5°;[30] 102°;[31] 96·98°;[32] 87–88°.[33] (Found: C, 72·68; H, 9·78; neutral equivalent 183. Calc. for $C_{11}H_{18}O_2$ (182·2): C, 72·49; H, 9·95%, neutral equivalent 182·2). The *amide* was prepared by means of the acid chloride, at room temp, with the precautions recommended by Dauben and Hoerger,[34] and had m.p. 218-220°. (Lit. 223–224°;[30] 223°[31] 206–208°;[32] 222–223°.[33]). The p-*bromophenacyl ester*, m.p. 125°, crystallized from ethanol. (Found: C, 60·39; H, 6·27; Br, 20·43. $C_{19}H_{23}BrO_3$ requires: C, 60·16; H, 6·11; Br. 21·07%). The *anilide*, little soluble in ether, has m.p. 187° and crystallized from 80% ethanol. (Found: N, 5·54. $C_{17}H_{23}NO$ (257·4) requires: N, 5·44%). The p-*toluidide*, m.p. 200–201°, slightly soluble in ether, crystallized from ethanol. (Found: N, 5·23. $C_{18}H_{25}NO$ (271·4) requires: N, 5·16%).

The Schmidt degradation of the acid yielded trans–trans-1-*decalyl-amine*, whose N-*acetyl-derivative* melted at 184–185° and crystallized from 80% methanol. Lit. m.p. 184°;[35] 182°.[31,36] (Found: N, 7·21. Calc. for $C_{12}H_{21}NO$ (195·3): N, 7·17 %). The N-*benzoyl-derivative*, m.p. 195 196°, crystallized from 80% methanol. Lit. m.p. 195°;[31,35,36] 194–195°.[33] The N-*benzenesulphonyl-derivative*, m.p) 141 142°, crystallized from 60% methanol. (Found: C, 65·19; H, 7·65. $C_{16}H_{23}NO_2S$ (293·4. requires: C, 65·49; H, 7·90%). The *picrate*, m.p. 210°, crystallized from water. (Found: C, 50·44; H, 6·08. $C_{10}H_{19}N{\cdot}C_6H_3N_3O_7$ (382·4) requires: C, 50·25; H, 5·80%).

The identity with *trans trans*-1-decalin-carboxylic acid was proved by mixed m.p. of the amide, acetylamino- and benzoylamino-derivative, with authentic samples.[31]

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