radicals to give ethane, and the abstraction of hydrogen from adjacent organic molecules by methyl radicals to produce methane as shown in reaction III.

Experimental

Phenyliodoso acetate, m. p. 160°, was prepared from iodosobenzene and glacial acetic acid. It was crystallized from acetic acid and its purity was determined by the standard iodine–sodium thiosulfate titration.

A mixture of 1.0 g. of trinitrotoluene, 3.6 g. of phenyliodoso acetate and 10 cc. of acetic acid was heated under reflux for one hour. The solution was dark brown at the end of this period. The reaction mixture afforded 0.2 g. of trinitro-*m*-xylene, m. p. 173–177°. Crystallization from glacial acetic acid raised the m. p. to 180–181°. Mixed with an authentic sample of trinitro-*m*-xylene, the m. p. was 180–182°.

Attempts to bring about the methylation of trinitro-*m*-xylene resulted in the recovery of unchanged starting material. Fieser, *et al.*, have recorded the stability of trinitro-*m*-xylene to lead tetraacetate.

Phenyliodoso acetate was heated in a flask under reflux. Above the melting point a brisk evolution of gas took place. The gas was collected and was shown to be a mixture of carbon dioxide, ethane and methane.[6] The liquid reaction product was heated with aqueous sodium hydroxide under reflux and then steam distilled. Phenyl iodide, in considerable amount, was isolated from the distillate. The alkaline residue was acidified and steam distilled. The distillate afforded a small amount of material which was identified as phenol. It is suggested by the authors that the phenol is probably due to the decomposition of diphenyl iodonium acetate.

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[6] The authors are indebted to James G. Knudsen for the numerous gas analyses which were carried out.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA

RECEIVED SEPTEMBER 12, 1945

Reaction between Amines and Pentachloroethane

BY WALTER H. C. RUEGGEBERG[1] AND MELVIN M. FALKOF[1]

In connection with certain chemical warfare problems, we found that aliphatic amines will react smoothly with pentachloroethane at room temperature, or above, to produce amine hydrochlorides in excellent yields.

In general, we found that primary and secondary aliphatic amines react spontaneously with pentachloroethane, generating heat upon contact. Tertiary aliphatic amines, on the other hand, react decidedly more slowly and require heating to effect the formation of the amine hydrochloride. Aromatic amines, as, for example, aniline and pentachloroethane, react only with difficulty even at temperatures above 150°. These differences of reactivity and activation energies are probably related to the basicities of the different amines. After the reaction is complete, the hydrochlorides are filtered off with suction and kept *in vacuo* over concentrated sulfuric acid.

***n*-Butylamine Hydrochloride.**—*n*-Butylamine (3.7 g.) is added dropwise with agitation to a mixture of pentachloroethane (11.0 g.) and dry diethyl ether (14.0); yield 4.5 g.; m. p. 215°.

Anal. Calcd. for $C_4H_{12}NCl$: Cl, 32.35. Found: Cl, 32.34.

Dimethylamine Hydrochloride.—Dimethylamine (2.3 g.) is dissolved in dry benzene (8.8 g.) and this mixture is added dropwise with occasional shaking to pentachloroethane (20.2 g.); yield 3.5 g.; m. p. 170–171°.

Anal. Calcd. for C_2H_8NCl: Cl, 43.48. Found: Cl, 43.17.

Piperidine Hydrochloride.—Piperidine (4.3 g.) is added dropwise to pentachloroethane (11.3 g.) with occasional shaking. After all of the amine has been added, the reaction mixture is cooled to room temperature and dry diethyl ether (14 g.) is added to increase the fluidity of the reaction product, yield 4.4 g.; m. p. 247–248°.

Anal. $C_5H_{12}NCl$: Cl, calcd., 29.16; found, 28.90.

Triethylamine Hydrochloride.—A mixture of triethylamine (5.0 g.) and pentachloroethane (21.4 g.) is heated to 100° over a period of about fifteen minutes; yield 4–5 g.; m. p. 253–255°.

Anal. Calcd. for $C_6H_{16}NCl$: Cl, 25.75. Found: Cl, 25.57.

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[1] Captains, C. W. S., Army of the United States.

CHEMICAL DIVISION
C. W. S. TECHNICAL COMMAND
EDGEWOOD ARSENAL, MARYLAND

RECEIVED SEPTEMBER 4, 1945

The Catalytic Dehydrocyclization of Paraffins

BY H. STEINER

The catalytic dehydrocyclization of paraffins to aromatic hydrocarbons continues to attract considerable interest. This communication deals with experiments carried out lately by a number of authors on the poisoning of the catalysts used in this reaction and in particular the conclusions drawn from these experiments regarding the mechanism of the catalytic action are discussed.[1,2]

It was shown by Pitkethly and Steiner[3] in the typical case of the dehydrocyclization of *n*-heptane to toluene, over a catalyst containing 10% Cr_2O_3 on alumina, that heptene, which is found always in the products, is an intermediate in this reaction. Thus the over-all reaction consists of two consecutive steps, (1) a dehydrogenation of the paraffin (heptane) to the olefin (heptene), and (2) a subsequent cyclization of the olefin to the aromatic body (toluene). Perhaps the best proof of this mechanism can be found in experiments at small conversions, where, as the contact time approaches zero, the rate of heptene formation remains finite while the rate of toluene formation asymptotically approaches zero. This shows that cyclization starts only after some olefin has formed and suggests strongly that the latter is an intermediate product.[4] The recent experiments of Mattox also show this effect. At longer contact times the concentration of the olefin reaches a maximum and subsequently declines slowly. In this region the stationary state treatment can be applied to a first approximation. Thus, assuming that both dehydrogenation and cyclization

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[1] H. S. Taylor and H. Fehrer, THIS JOURNAL, **63**, 1387 (1941); D. T. Salley, H. Fehrer and H. S. Taylor, *ibid.*, **63**, 1131 (1941).

[2] W. J. Mattox, *ibid.*, **66**, 2059 (1944).

[3] Pitkethly and Steiner, *Trans. Farad. Soc.*, **35**, 979 (1939).

[4] Hoog, *ibid.*, **35**, 1009 (1939).

proceed according to the unimolecular law we have

$$\mathrm{d}p_0/\mathrm{d}t = k_dp_p - k_cp_0 = 0$$

which gives

$$p_0/p_p = k_d/k_c \qquad (1)$$

p_0 = partial pressure of olefin (heptene)
p_p = partial pressure of paraffin (heptane)
k_d = rate constant for dehydrogenation[5]
k_c = rate constant for cyclization[5]

This expression is useful because it allows one to calculate, from easily accessible experimental data, the ratio of the dehydrogenation to the cyclization rate. This can be compared with the rate of toluene production, which is a direct measure of the cyclization rate only. Relation (1) was shown to be independent of the partial pressure of either olefin or paraffin,[3] and not to be influenced by added hydrogen.

Taylor and Fehrer have extended the simple treatment of Pitkethly and Steiner by taking into account the strong adsorption on the catalyst of the intermediate olefin, but they showed that this does not affect relation (1). Thus this relation seems fairly well established and it is interesting to apply it to experiments carried out by Taylor and collaborators[1] and by Mattox[2] on the poisoning of the dehydrocyclization catalyst. In this way one can investigate the influence of the catalyst poison on the two individual rates, that of dehydrogenation and that of cyclization.

On carrying on the reaction in a flow system for several hours, it is observed generally that the formation of toluene declines steadily, whereas the simultaneous formation of heptene remains nearly constant. Typical experiments are those of Taylor and Fehrer, who studied the reaction with *n*-heptane as substrate over a Cr_2O_3 catalyst containing 10% ZrO_2 (see Table I).

TABLE I

PROGRESSIVE POISONING OF CYCLIZATION CATALYST (Cr_2O_3 10% ZrO_2)

Reaction period	Mole % of liquid product Heptane	Heptene	Toluene	Heptene/Heptane
1st half hour	48	12	40	0.25
2nd half hour	59	14	27	.24
3rd half hour	68.5	14.5	17	.21
4th half hour	74	15	11	.20

From these results they conclude that in their experiment the activity of the catalyst for cyclization declines, while that for dehydrogenation remains approximately constant. These conclusions do not take into account the kinetics of the reaction and in particular the fact that heptene is an intermediate product, the formation of which is determined by the difference in the rates of dehydrogenation and cyclization and not by the dehydrogenation rate only. Thus the fact that the amount of heptene in the product remains nearly constant, while at the same time the amount of toluene declines, must mean that both the cyclization and dehydrogenation activity of the catalyst fall off to about the same extent. If the former only were affected, the formation of heptene would increase. This is brought out quantitatively by the application of relation (1) to these experiments.[6] It is seen from col. 5 of Table I that the values for the ratio heptene/heptane at progressive stages of the poisoning of the catalyst decline by not more than 20%. Thus using relation (1) one can say that the ratio of the cyclization and dehydrogenation rates declines very slowly. At the same time the toluene formation, which is a measure of the cyclization rate only, declines to one-fourth of its original value (see Table I, col. 4). It is clear from this that in the course of the reaction the dehydrogenation rate must decrease by very nearly the same extent as that of the cyclization.

Salley, Fehrer and Taylor[1] first observed that water vapor is a poison for the cyclization catalyst. More extensive experiments were carried out by Mattox,[2] who used heptane as substrate over a catalyst containing 8% Cr_2O_3 on Al_2O_3. Simultaneously with the heptane he introduced water vapor, and also a mixture of water vapor and ethylene obtained by dehydrating ethyl alcohol over an alumina catalyst. These experiments are summarized in Table II.

TABLE II

CYCLIZATION EXPERIMENTS WITH ADDITION OF WATER VAPOR AND ETHYLENE

Experiment no.		1	2	3	4	5
Space vel., cc./cc./hour		1.98	1.96	2.00	2.02	2.00
Ratio, moles H_2O/mole C_7H_{16}		0	0.25	0.50	1.00	0.38
Toluene	Mole % of liquid product	47.2	18.3	8.9	3.3	3.3
Heptene		11.7	10.0	8.2	7.0	14.1
Heptane		40.9	71.8	83.0	89.6	82.7
Heptene/heptane		0.286	0.139	0.099	0.078	0.17

The first experiment is a standard test carried out with heptane only, in expts. 2–4 increasing amounts of alcohol were added giving on dehydration the quantities of water given in line 3 and an equivalent amount of ethylene. Finally, in expt. 5, water vapor only was added. It is seen from a comparison of expt. 1 with expts. 2 to 4 that the formation of toluene declines fifteen-fold as increasing amounts of water and ethylene are added. At the same time the ratio of heptene to heptane declines by a factor of 3.6. Comparison of the standard experiment with expt. 5 shows that in this case the amount of toluene formed and the heptene/heptane ratio decreases 13 and 1.6 fold, respectively. In these experiments the ratio of dehydrogenation to cyclization rate declines markedly, though in every case this ratio is very much less affected than the cycliza-

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[5] These rate constants include terms allowing for adsorption on, and desorption from, the catalyst.

[6] The application of this relation is justified because these experiments were carried out at contact times where the stationary concentration of heptene has been built up.

tion rate as revealed by the decline of the toluene yield. It appears therefore that here the dehydrogenation rate is even more affected by the poisoning action than the cyclization, but the decline still runs parallel to that of the cyclization.

The interpretation given to the results discussed leads to the conclusion that both reactions, dehydrogenation and cyclization, are affected by the poisoning of the catalyst. Where the poisoning action is due to accumulation of polymer, which is probably the reason for the decline of activity in the course of a run, the two reactions are affected to much the same extent. When water and particularly when ethylene is the poison the dehydrogenation rate is repressed even more than that of cyclization, but the decline is still parallel.

These conclusions are contrary to the views of Taylor and Fehrer mentioned previously. It follows that their further deductions concerning the relation of the two reactions and the seat of catalytic action need revision. In their view, because of the very different effect of catalyst poisons on the two reactions, the two reactions take place on different active centers of the catalyst. The present interpretation leads to the opposite conclusion—which also appears the simpler—that, because of the close relationship revealed by the parallel effect of poisons on both reaction rates, it seems likely that they proceed on identical centers of the catalyst surface.

MANCHESTER OIL REFINERY, LTD.
MANCHESTER, ENGLAND
RECEIVED JUNE 30, 1945

Methylation of Methyl 6-Hydroxydehydroabietate

BY HAROLD H. ZEISS

Methyl 6-hydroxydehydroabietate can be satisfactorily methylated with dimethyl sulfate in an ethereal solution of methylmagnesium chloride.[1] It has been reported that methylation with dimethyl sulfate in alcoholic alkali gives small or vanishing yields. This difficulty was attributed to the steric hindrance exerted by the adjacent isopropyl group, although this explanation appeared surprising in view of the reactivity of the 6-position of the dehydroabietic structure.

It has now been found that the use of dimethyl sulfate in aqueous alcoholic alkali gives a good yield with ease and rapidity.

Experimental

To a solution of 3 g. of methyl 6-hydroxydehydroabietate (m. p. 158–159°) in 60 ml. of ethanol and 42.5 ml. of 1% aqueous sodium hydroxide 1 g. of dimethyl sulfate is added at room temperature and the turbid mixture refluxed for two and one-half hours. Ten ml. of 12% sodium hydroxide is then added to destroy the excess dimethyl sulfate. After distilling off the alcohol and cooling, the residue is extracted with several portions of ether and the extract washed with water until neutral. Replacement of the ether with ethanol and the addition of water to turbidity gives broad white plates of methyl 6-methoxydehydroabietate in a pure state. The yield in three crops has been 2.1 g. (68%); m. p. 65–66°.

The method was repeated with another 3 g. of methyl 6-hydroxydehydroabietate (m. p. 158–159°). From this run methoxy ester of the same m. p. was obtained again in 68% yield.

RIDBO LABORATORIES, INC.
PATERSON 3, NEW JERSEY
RECEIVED JULY 10, 1945

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[1] (a) Campbell and Todd, THIS JOURNAL, **62**, 1287 (1940); (b) Campbell, U. S. Patent 2,359,826; (c) L. F. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 994.

NEW COMPOUNDS

Some Polysubstituted Benzene Derivatives

3-Benzoylmesitonitrile.—A mixture of 10.1 g. of 3-bromomesityl phenyl ketone,[1] 4.5 g. of cuprous cyanide and 6 ml. of pyridine was heated for twelve hours under reflux in a metal bath maintained at 220–225°. The hot reaction mixture was poured into a dilute ammonium hydroxide solution and, after several hours, a mixture of 100 ml. of ether and 70 ml. of benzene was added to the resulting tarry mass. The organic layer, after being washed with dilute ammonium hydroxide and with water, was filtered. Removal of the solvent left the nitrile as an oily residue which crystallized when allowed to stand with methanol. It was recrystallized from methanol; m. p. 107–108°; yield 83%.

Anal. Calcd. for $C_{17}H_{15}ON$: C, 81.90; H, 6.07. Found: C, 81.70; H, 6.18.

1,2-Di-(2,4,6-triisopropylbenzoyl)-ethylene.—A solution of 76.5 g. of fumaryl chloride in 100 ml. of dry carbon disulfide was added gradually over a period of one and one-half hours to a mixture of 245 ml. of 1,3,5-triisopropylbenzene, 300 ml. of carbon disulfide and 140 g. of anhydrous aluminum chloride. The reaction mixture was stirred continuously during the period of addition and for two hours afterward. It was poured on a mixture of 1 kg. of ice and 100 ml. of concentrated hydrochloric acid. Removal of the solvent left the 1,2-di-(2,4,6-triisopropylbenzoyl)-ethylene as a gummy, red solid. It separated from acetone in yellow needles; m. p. 190.5–192°; yield 47%.

Anal. Calcd. for $C_{34}H_{48}O_2$: C, 83.55; H, 9.90. Found: C, 83.40; H, 9.76.

1,2-Di-(2,4,6-triisopropylbenzoyl)-ethane.—A suspension of 9.7 g. of 1,2-di-(2,4,6-triisopropylbenzoyl)-ethylene in 150 ml. of ethanol was shaken with 0.05 g. of platinum oxide in an Adams hydrogenation machine. One mole of hydrogen was absorbed. Acetone was added to bring the product into solution and the catalyst was removed by filtration. The filtrate evidently contained the expected enediol, 1,4-di-(2,4,6-triisopropylphenyl)-1,3-butadiene-1,4-diol, for it rapidly turned yellow when exposed to the air. It continued to give a positive indophenol test for about twenty minutes. Dilution of the solution with water precipitated the 1,2-di-(2,4,6-triisopropylbenzoyl)-ethane in the form of white crystals. These gave a negative indophenol test. The diketone crystallized from methanol in colorless hexagonal plates; m. p. 140–141°.

Anal. Calcd. for $C_{34}H_{50}O_2$: C, 83.21; H, 10.27. Found: C, 83.37; H, 10.42.

N-Methylmesitamide.—A solution of 27.5 g. of mesitoyl chloride in 20 ml. of low-boiling petroleum ether was added dropwise, with stirring, to 100 ml. of a 35% methylamine solution. The reaction mixture was kept ice cold during the addition and was stirred at room temperature for one

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[1] Hyde and Adams, THIS JOURNAL, **50**, 2503 (1928).