27.5 g. of bromobenzene, in 50 ml. of ether. The mixture was refluxed 2 hours, cooled and ice and dilute sulfuric acid were added. The aqueous layer was extracted with ether, the combined organic solutions were washed with water, the ether was evaporated and volatile impurities were removed by steam distillation. The remaining yellow oil was taken up in ether, the solution was washed with water, dried, and the solvent was removed to give 4.5 g. of carbinol as a yellow glass. This had an infrared hydroxyl band at 2.78μ; no carbonyl peak was present, showing that the reaction had gone to completion. That extensive dehydration had not occurred was proved by the absence of a strong peak at 249 mμ.

Dehydration of the crude carbinol was then accomplished by refluxing, for 2 hours, its solution in 200 ml. of acetic acid and 100 ml. of redistilled acetic anhydride. Most of the solvent was removed, with mild heating, on the water-pump, the residue then being heated at 100° and 1 mm. until, as shown by infrared, all the acetic anhydride was gone. The 4.4 g. of remaining crude material was shown by infrared and ultraviolet spectra to be chiefly the diphenylethylene XLI. The ultraviolet peak at 249 mμ, ϵ 12,300, proved the presence of a conjugated system, while the absence of the hydroxyl band in the infrared proved that dehydration had occurred. A small peak at 5.88μ suggested that the acetate of the carbinol was present, as an impurity, in the reaction product. This material was used directly in the oxidation step.

Synthetic *dl*-Dehydroabietic Acid (I).—The best conditions found for the chromium trioxide oxidation are those described below; all other conditions gave lower yields. In all cases, the spectra of the resulting neutral fraction showed that organic material, other than benzophenone, was present. Reoxidation of this neutral material, however, never gave more than a minute amount of dehydroabietic acid.

The crude diphenylethylene above (2.053 g., 4.73 mmoles) was dissolved in 35 ml. of chloroform and 140 ml. of acetic acid was added. Addition of 5.0 g. (0.05 mole) of chromium trioxide in 20 ml. of water, over a 5-minute period, caused the solution to turn very dark. After 1 hour at room temperature, the solution was warmed for 2 hours at 60–70°, cooled, and water and ether were added. The aqueous layer was extracted with ether and the combined organic solutions were washed several times with water. The acidic material was then extracted with 5% aqueous sodium hydroxide, the ether solution then being washed with water until the washings, which were added to the basic extracts, were neutral. The neutral fraction, largely benzophenone, was then obtained from the ethereal solution. The basic extracts were acidified with hydrochloric acid and the resulting oily acid extracted into ether. This ethereal solution was washed with water, dried, and the solvent removed to yield a yellow gum which was dissolved in acetic acid and treated with hydrogen in the presence of 10% palladium-on-charcoal. The mixture was stirred, under hydrogen, for 20 hours, two additions of fresh catalyst being made in the process. The catalyst was then removed, ethereal washings of it being added to the solution which was next evaporated to dryness *in vacuo*. About 600 mg. of yellow gum resulted which was crystallized from methanol–water to give only 255 mg. (18%) of almost white *dl*-dehydroabietic acid, m.p. 172–175°. The analytical sample, m.p. 179.5–180.5°, was obtained by several recrystallizations from methanol–water. (Natural, optically active, dehydroabietic acid melts at 172–173°.) The infrared spectrum of this synthetic acid was taken on the same paper as that of the natural product. The two spectra were completely identical, peaks occurring at 5.98, 6.73, 6.89, 7.29, 7.38, 7.87, 12.12μ and elsewhere.

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 80.30; H, 9.41.

Synthetic Methyl *dl*-Dehydroabietate.—*dl*-Dehydroabietic acid (50 mg.) was treated with excess diazomethane, as described above for the methylation of the thioketal acid, except that the reaction mixture was allowed to stand for 2 hours prior to the work-up. The resulting yellow oil was crystallized from methanol–water to give 22 mg. of racemic ester. Additional recrystallizations from this solvent pair gave the analytical sample, m.p. 71.5–73°, as fine, white needles, similar in appearance to the natural ester, m.p. 62–63°. The infrared spectra in chloroform of the racemic compound and of authentic methyl dehydroabietate were superimposable, the carbonyl band appearing at 5.86 μ.

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.09; H, 9.44.

[Contribution from the Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Ill.]

Alumina: Catalyst and Support. XIV. Dehydrogenation, Dehydrocyclization and Isomerization of C_5- and C_6-Hydrocarbons over Chromia–Alumina Catalysts[1,2]

By Herman Pines and Sigmund M. Csicsery[3]

Received July 17, 1961

Alumina *per se* has intrinsic acidic properties which influences the reactions of hydrocarbons over chromia–alumina catalysts. Catalysts containing alumina made from aluminum isopropoxide have relatively strong acidic sites. Extensive cationic isomerization and polymerization of the dehydrogenation products of *n*-pentane, *n*-hexane, methylpentanes and methylcyclopentane were observed over this catalyst. Dehydrogenation and dehydrocyclization proceed without appreciable isomerization and polymerization over chromia–alumina where the alumina was obtained from potassium aluminate. The reaction product of *n*-hexane dehydrogenation over this non-acidic catalyst contained 52 mole % benzene *vs.* 13 mole % over the acidic chromia–alumina catalyst. In case of 2- and 3-methylpentane and methylcyclopentane the results were reversed: the yields of benzene obtained from the acidic catalyst were higher.

The dehydrogenation of paraffins over chromia–alumina catalysts had been a subject of extensive studies for almost three decades.[4] No attention has been paid however to the role of alumina in this reaction.

Recent investigations in our laboratory have revealed that the catalytic properties of aluminas depend upon their methods of preparation. Alumina obtained from aluminum isopropoxide by

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[1] Paper VII of the series "Aromatization of Hydrocarbons." For previous papers of these series see S. M. Csicsery and H. Pines, *Chemistry & Industry*, 1398 (1961).

[2] Presented in part at the Princeton University Conference on "Active Centers in Heterogeneous Catalysis," May 11–12, 1961, Princeton, N. J.

[3] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Fund.

[4] For review of the literature see: (a) A. H. Steiner, in "Catalysis," Vol. IV, edited by P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1956, pp. 529–560. (b) G. F. Ciapetta, R. M. Dobres and R. W. Baker, Vol. VI, pp. 492–692. (c) C. Hansch, *Chem. Revs.*, **53**, 353 (1953).

TABLE I

DEHYDROGENATION OF *n*-PENTANE

Experiment	1		2		3	
Cut number	1	2	1	4	1	3
Catalyst	A		A		B	
Reacn. temp., °C.	451		520		517	
Contact time, sec.	6.8		4.1		2.8	
n-Pentane reacted, mole %	9.8	9.9	43.3	39.9	26.7	35.9
Compn. of reacn. produc., mole %						
C_1–C_2-Hydrocarbons[a]	1.78	1.86	10.23	11.20	6.08	4.33
Propane, propylene	7.50	5.92	7.80	5.60	5.83	3.22
n-Butane	0.50	0.42	1.65	0.74	0.10	0.22
Isobutane	0.47	0.26	0.90	0.16	0.02	0.05
n-Butenes	3.65	3.34	2.47	2.18	2.15	1.38
Isobutylene	3.90	2.60	2.36	1.09	0.20	0.14
Isopentane	4.25	4.20	9.24	4.84	0.10	0.30
n-Pentenes	31.51	37.40	25.04	34.18	66.60	70.85
Methylbutenes	41.62	38.28	27.46	26.28	2.18	4.69
n-Pentadienes	1.01	1.87	2.80	4.17	10.59	10.01
Isoprene	0.27	0.44	0.92	1.05	0.11	0.22
C_5-Cyclics	.50	.56	.39	0.24	.17	.13
Benzene	.10	.09	.34	0.12	.05	.07
Toluene	.58	.56	1.87	1.00	.14	.16
Xylenes and ethylbenzene	.53	.43	0.19	0.29	.08	.07
Carbonaceous material	1.83	1.77	6.34	6.86	5.60	4.16
Total	100.00	100.00	100.00	100.00	100.00	100.00

[a] The composition of the combined C_1–C_2-hydrocarbons from the total experiment:

	C_1/C_2	C_2H_6/C_2H_4
Expt. 2	2.6	8
Expt. 3	1.6	6

hydrolysis had strong intrinsic acidic properties (alumina A), whereas alumina prepared from potassium aluminate indicated only very weak intrinsic acidity (alumina B).[5] Pines and co-workers reported recently that the steps involved in the aromatization of *n*-heptane[6,7] and *n*-octane[6,8] can be influenced by the type of aluminas used in the preparation of the chromia–alumina catalysts. It was also reported that the aromatization of 1,1-dimethylcyclohexane, 4,4-dimethylcyclohexane and methylcycloheptane is influenced by the nature of the alumina used in the preparation of the catalyst.[9]

The present study compares the reactions of pentanes, hexanes and of methylcyclopentane over chromia–alumina catalysts consisting of alumina prepared from aluminum isopropoxide (A) and from potassium aluminate (B).

Results and Discussion.—The hydrocarbons were passed over a fixed catalyst bed at atmospheric pressure around 520°. Contact times were between two and six seconds. The condensed products were removed every 12 minutes, and analyzed by vapor phase chromatography. Non-condensable gases were collected and analyzed by the same method. After several such "cuts" the experiment was discontinued and the carbonaceous material accumulated on the catalyst was burned off with an air–nitrogen mixture. The catalyst was reconditioned for at least two hours before each experiment with hydrogen at around 525°. Reaction conditions and product distributions of the first and third cuts of the experiments made with the different hydrocarbons are summarized in Tables I–V. Product compositions are given in mole percentages of the total conversion. Conversions to carbonaceous material are presented in mole percentages of the total converted feed hydrocarbon. Olefins and diolefins with the same carbon skeleton are not listed separately, since with the exception of the methylcyclopentene isomers they were present in nearly constant relative concentrations in all experiments. We believe that these constant ratios of olefins having the same carbon skeletons represent equilibrium concentrations around 525°. These experimental values differ to some extent from equilibrium concentrations calculated from free energy data at 527° reported by Rossini, *et al.*[10] (Table VI).

Results of the reactions of the different hydrocarbons are summarized in Table VII. Data from the first cuts only are included in this summary. The experiments were made at nearly identical conditions.

Surface areas of both catalysts were determined by the B.E.T. method. Catalyst A had a surface area of 87.3 m.^{2}/g. and catalyst B 89 m^2./g. The

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(5) H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **82**, 2471 (1960).

(6) C. T. Chen, W. O. Haag and H. Pines, *Chemistry & Industry*, 1379 (1959).

(7) H. Pines and C. T. Chen, *J. Org. Chem.*, **26**, 1057 (1961).

(8) H. Pines and C. T. Chen, Proceedings of 2nd International Congress on Catalysis, July 4–9, 1960, Paris, France.

(9) H. Pines and C. T. Chen, *J. Am. Chem. Soc.*, **82**, 3562 (1960).

(10) Frederick D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44," Carnegie Press, Pittsburgh, Penna., 1953.

TABLE II

DEHYDROGENATION OF *n*-HEXANE

Experiment	4		5	
Cut number	1	3	1	3
Catalyst	A		B	
Reacn. temp., °C.	523		518	
Contact time, sec.	3.1		3.2	
n-Hexane reacted, mole %	32.1	27.8	29.4	28.4
Compn. of reacn. prod., mole %				
C_1–C_2-Hydrocarbons[a]	8.08	8.10	4.46	4.30
Propane, propylene	2.75	2.80	2.12	2.00
n-Butane	2.19	2.06	1.06	0.96
Isobutane	1.40	1.20	0.08	0.08
n-Butenes	4.22	3.95	1.85	1.60
Isobutylene	5.40	3.20	0.05	0.05
n-Pentane	0.52	0.33	0.23	0.17
Isopentane	0.23	.13	..	..
n-Pentenes	1.41	.62	0.59	0.60
Methylbutenes	1.04	.53	..	..
Isomerized C_6-paraffins	4.12	4.03	..	..
n-Hexenes	23.40	29.20	29.40	27.30
2-Methylpentenes	7.30	6.80	..	..
3-Methylpentenes	9.40	9.40	0.23	0.30
2,3-Dimethylbutenes	2.25	2.20	..	..
Methylcyclopentenes	0.37	0.40	..	..
Hexadienes	3.23	3.60	4.05	4.18
Benzene	13.00	12.40	52.50	55.00
Toluene	0.95	0.55	0.16	0.14
Xylenes and ethylbenzene	1.84	.90	0.02	0.02
Higher aromatics	0.60	.40	..	..
Carbonaceous material	6.30	7.20	3.20	3.30
Total	100.00	100.00	100.00	100.00

[a] The composition of the combined C_1–C_2-hydrocarbons from the total experiment

	CH_4/C_2H_6	
Expt. 4	1.1	No C_2H_4 detected
Expt. 5	0.8	No C_2H_4 detected

TABLE III

DEHYDROGENATION OF 2-METHYLPENTANE

Experiment	6		7	
Cut number	1	3	1	3
Catalyst	A		B	
Reacn. temp., °C.	525		525	
Contact time, sec.	3.1		3.1	
2-Methylpentane reacted, mole %	28.1	27.0	28.6	34.0
Compn. of reacn. prod., mole %				
C_1–C_2-Hydrocarbons[a]	4.11	3.14	1.78	1.23
Propane, propylene	14.20	7.82	14.02	12.55
n-Butane	1.31	0.51	0	0.03
Isobutane	3.16	1.05	0.58	.94
n-Butenes	3.31	1.66	0	.06
Isobutylene	11.22	7.85	4.18	3.36
n-Pentane	0.53	0.64	0.41	0.50
Isopentane	0.47	0.49	.21	.23
n-Pentenes	1.09	1.33	.62	.58
Methylbutenes	2.06	2.42	1.11	.86
Isomerized C_6-paraffins	3.06	2.78		
2-Methylpentenes	15.90	25.89	51.88	54.64
3-Methylpentenes	11.90	17.17		
2,3-Dimethylbutenes	3.40	4.87	0.53	0.46
Methylcyclopentenes	0.53	0.95	2.67	2.46
Hexadienes	3.92	6.56	16.09	16.27
Benzene	7.10	5.33	1.00	1.42
Toluene	1.76	0.90	0.21	0.34
Xylenes and ethylbenzene	3.76	1.76	0.09	0.14
Higher aromatics	1.05	0.49		
Higher aliphatics	0.11	0.09	0.02	0.03
Carbonaceous material	6.05	6.30	4.60	3.90
Total	100.00	100.00	100.00	100.00

[a] The composition of the combined C_1–C_2-hydrocarbons from the total experiment

	C_1/C_2	C_2H_6/C_2H_4
Expt. 6	0.4	6
Expt. 7	0.3	5

TABLE IV

DEHYDROGENATION OF 3-METHYLPENTANE

Experiment	8		9	
Cut number	1	3	1	3
Catalyst	A		B	
Reacn. temp., °C.	525		528	
Contact time, seconds	3.1		3.1	
3-Methylpentane reaceted, mole %	25.9	25.5	28.8	35.6
Compn. of reacn. prod., mole %				
C_1–C_2-Hydrocarbons[a]	9.50	8.66	13.50	9.55
Propane, propylene	2.75	2.20	0.84	0.65
n-Butane	2.50	2.20	1.90	1.60
Isobutane	1.80	1.40	0.05	0.04
n-Butenes	4.90	4.70	5.60	3.80
Isobutylene	7.55	5.40	0.45	0.35
n-Pentane	0.61	0.44	.30	.24
Isopentane	.47	0.40	.10	.30
n-Pentenes	.90	1.17	.52	.30
Methylbutenes	1.63	1.60	.60	.27
Isomerized C_6-paraffins	4.70	3.75		
3-Methylpentenes	20.30	25.30	56.20	63.40
2-Methylpentenes	14.00	16.50	0.90	0.55
2,3-Dimethylbutenes	3.40	3.55	1.60	1.05
Methylcyclopentenes	1.22	1.32	1.76	1.80
Hexadienes	5.10	6.50	8.30	8.80
Benzene	6.19	4.50	1.60	2.54
Toluene	1.41	0.80	0.25	0.30
Xylenes and ethylbenzene	3.00	1.54	.11	0.10
Higher aromatics	0.72	0.62	.02	0.01
Carbonaceous material	7.35	7.45	5.40	4.35
Total	100.00	100.00	100.00	100.00

[a] The composition of the combined C_1–C_2-hydrocarbons from the total experiment

	C_1/C_2	C_2H_6/C_2H_4
Expt. 8	1.0	13
Expt. 9	1.1	11

TABLE V

DEHYDROGENATION OF METHYLCYCLOPENTANE

Experiment	10		11	
Cut number	1	3	1	3
Catalyst	A		B	
Reacn. temp., °C.	520		523	
Contact time, sec.	2.6		2.6	
Methylcyclopentane reacted, mole %	15.4	15.5	14.8	17.2
Compn. of reacn. prod., mole %				
C_1–C_2-Hydrocarbons[a]	3.16	2.79	3.10	2.55
Propane, propylene	2.07	1.34	1.12	0.97
n-Butane	0.15	0.07	0.12	.03
Isobutane	.08	.04	.08	.07
n-Butenes	.69	.32	.33	.40
Isobutylene	.65	.25	.36	.33
Cyclopentane	.77	.52	1.90	.32
Cyclopentene	1.10	1.03	2.50	.75
Cyclopentadiene	2.25	2.21	3.86	2.30
Methylcyclopentenes	22.30	30.50	31.40	32.15
Cyclohexene	1.14	0.44		
Methylcyclopentadienes	15.26	19.34	8.52	21.16
Benzene	12.00	5.80	1.36	0.64
Toluene	3.28	1.24	0.63	0.24
Xylenes and ethylbenzene	1.16	0.35		
Higher aromatics	0.50	0.32		
Higher aliphatics	0.94	1.24	1.92	1.19
Carbonaceous material	32.50	32.20	42.80	36.90
Total	100.00	100.00	100.00	100.00

[a] The composition of the combined C_1–C_2-hydrocarbons from the total experiment

	C_1/C_2	C_2H_6/C_2H_4
Expt. 10	1.9	3
Expt. 11	3.4	1.9

TABLE VI

COMPOSITIONS OF OLEFIN MIXTURES HAVING THE SAME CARBON SKELETON

	Experimental,[a] %	Calculated,[b] %
1-Butene	32	24.1
cis-2-Butene	28	30.4
trans-2-Butene	40	45.5
1-Pentene	19	20.5
cis-2-Pentene	28	31.4
trans-2-Pentene	53	48.1
2-Methyl-1-butene	32	42.0
3-Methyl-1-butene	6	6.5
2-Methyl-2-butene	62	51.5
1-*cis*-3-Pentadiene	45	55
1-*trans*-3-Pentadiene	55	45
1-Hexene	11	10.50
cis-2-Hexene	24	29.13
trans-2-Hexene	48	31.03
cis-3-Hexene		12.80
trans-3-Hexene	17	16.54
2-Methyl-1-pentene	31	35.6
4-Methyl-1-pentene	5	2.4
2-Methyl-2-pentene	44	39.8
4-Methyl-2-pentenes (*cis* and *trans*)	20	22.2
3-Methyl-1-pentene	9	12.7
3-Methyl-*cis*-2-pentene	51	29.6
3-Methyl-*trans*-2-pentene	28	44.4
2-Ethyl-1-butene	12	13.3
2,3-Dimethyl-1-butene	47	58.3
2,3-Dimethyl-2-butene	53	41.7

[a] The values from the various experiments varied ±2%. [b] The calculations of equilibria at 527° were based on the data described in ref. 10.

average pellet weights of both catalysts were 0.022 g. Both catalysts contained 13.8 wt. % Cr_2O_3.

The experimental results confirmed previous observations[9] that the intrinsic acidities of the aluminas used in the preparation of the chromia–alumina catalysts influence the character of the dehydrogenation reaction. Over catalyst A an extensive skeletal isomerization and dehydroisomerization occurred while over catalyst B the olefins and diolefins formed had the same skeletal arrangement as the starting paraffins. Over catalyst A *n*-pentane yielded methylbutenes and pentenes in a ratio of 1.1 and isoprene and pentadienes in a ratio of 0.33 while over catalyst B the respective ratios were 0.03 and 0.01. Over catalyst A 12% of the reacted methylcyclopentane was converted to benzene, while in the presence of catalyst B the yield of benzene was only 1.4%.

The ratios of isobutylene to *n*-butenes obtained from *n*-pentane and *n*-hexane over catalyst A are much higher than the 0.57 equilibrium ratio.[10] The high values of isobutylene concentrations could be interpreted either by the dehydroisomerization of the *n*-alkanes followed by cleavage, or by a combination reaction involving the polymerization of the olefins produced by the dehydrogenation and followed by a typical cationic β-scission reaction.

Aromatic hydrocarbons—benzene, toluene and xylenes from *n*-pentane, and toluene, ethylbenzene, xylenes and C_9-aromatics from the C_6-hydrocarbons—were produced over the acidic catalyst A. The xylenes were usually found in ratios corresponding to their equilibrium concentration, except in the reaction product of 2-methylpentane where the relative concentration of *m*-xylene was higher. Formation of the aromatic hydrocarbons having a greater number of carbon atoms than the original alkanes could be explained by acid-catalyzed polymerization of the olefins and diolefins which were formed by the dehydrogenation reaction. The polymers could then undergo β-scission to form propylene, isobutylene and fragments which may undergo an aromatization reaction. Only negligible amounts of xylenes and of higher aromatics were formed from hexanes over the non-acidic catalyst B.

The aromatization of *n*-hexane to benzene proceeds with much higher yield over the non-acidic catalyst B than over the acidic catalyst A, 52.5% *vs.* 13.0%. This is not too surprising since according to kinetic studies[11,12] the first step in the aroma-

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(11) R. C. Pitkethly and H. Steiner, *Trans. Faraday Soc.*, **35**, 979 (1939).

(12) H. Steiner, *J. Am. Chem. Soc.*, **67**, 2052 (1945).

TABLE VII

DEHYDROGENATION OF C_5- AND C_6-HYDROCARBONS OVER CHROMIA–ALUMINA CATALYSTS AT ABOUT 520° AND 3 SECONDS CONTACT TIME

	n-Pentane		*n*-Hexane		2-Methylpentane		3-Methylpentane		Methylcyclopentane	
Experiment	2	3	4	5	6	7	8	9	10	11
Catalyst	A	B	A	B	A	B	A	B	A	B
Hydrocarbon reacted, mole %	43.30	26.70	32.10	29.40	28.10	28.60	25.90	28.80	15.40	14.80
Dehydrogenation to monoolefins, mole %[a]	52.50	68.78	42.35	29.63	31.20	52.41	37.70	58.70	23.44	31.40
Dehydrogenation to diolefins, mole %[a]	3.72	10.70	3.23	4.05	3.92	16.09	5.10	8.30	15.26	8.52
Dehydrocyclization to 5-membered ring species, mole %[a]	0.39	0.17	0.37	0	0.53	2.67	1.22	1.76		
Dehydrocyclization to benzene, mole %[a]			13.00	52.50	7.10	1.00	6.19	1.60	12.00	1.36
Isomerized paraffins, mole %[a]	9.24	0.10	4.12	0	3.06	0	4.70	0	0	0
Isomerized monoölefins, mole %[a]	27.46	2.18	18.95	0.23	15.30	0.53	17.40	2.50	1.14	0
Conversion to higher aromatics, mole %[a]	2.40	0.27	3.39	0.18	6.57	0.30	5.13	0.38	4.94	0.63
Formation of C_3-hydrocarbons, mole %[a]	7.80	5.83	2.75	2.12	14.20	14.02	2.75	0.84	2.07	1.12
Formation of *n*-C_4-hydrocarbons, mole %[a]	4.12	2.25	6.41	2.91	4.62	0	7.40	7.50	0.84	0.45
Formation of *i*-C_4-hydrocarbons, mole %[a]	3.26	0.22	6.80	0.13	14.38	4.76	9.35	0.50	.73	.44
Isobutane/*n*-butane, mole ratio	0.55	.20	0.64	.08	2.41	∞	0.72	.03	.53	.67
Isobutylene/*n*-butenes, mole ratio	0.96	.11	1.28	.03	3.38	∞	1.54	.08	.94	1.09
Methylbutenes/*n*-pentenes, mole ratio	1.09	.03	0.74	0	1.89	1.80	1.81	1.15		
Isomerized hexenes/non-isomerized hexenes, mole ratio			0.81	0.01	0.96	0.01	0.86	0.04	0.05	0

[a] Mole % of the reaction product.

tization reaction is the dehydrogenation of alkanes to the corresponding alkenes. In the presence of catalyst A *n*-hexenes produced from *n*-hexane would undergo skeletal isomerization to methylpentenes, the latter could not then aromatize to benzene by a simple ring closure reaction. Methylpentanes, on the other hand, undergo aromatizations to benzene much easier over catalyst A than over catalyst B. These facts can also be explained by the interpretation given above.

The isomerizing activity of catalyst A decreases with time; in the case of the *n*-pentane experiment the ratio of methylbutenes to pentenes produced in four successive fractions were 1.09, 0.89, 0.85 and 0.78 (Table I, expt. 2). Similar changes were observed with other hydrocarbons. The deactivation of the acidic properties of catalyst A is probably due to a conjunct polymerization reaction which causes the deposition of carbonaceous material on the acidic sites of the catalyst. This type of the deactivation of acid sites of aluminas was reported previously.[13] In addition to conjunct polymerization the carbonaceous material could also be formed by Diels–Alder type condensation of the conjugated dienes formed during the reaction. It is not surprising therefore that the deposition of carbonaceous material is higher over catalyst A than B. The amount of carbonaceous material produced is extensive in the case of the dehydrogenation of methylcyclopentane.

The primary fragments of cracking accompanying dehydrogenation can be determined only on catalyst B, which does not catalyze secondary reactions associated with acid sites. These primary fragments are: $C_3 + C_2$ from *n*-pentane; *n*-$C_4 + C_2$ from *n*-hexane; $C_3 + C_3$ and *i*-$C_4 + C_2$ from 2-methylpentane, *n*-$C_4 + C_2$ from 3-methylpentane; $C_3 + C_3$ from 2,3-dimethylpentane[14]; and *i*-$C_4 + C_2$ from 2,2-dimethylpentane.[14] In all these reactions bond rupture occurred between the second and the third atom from a terminal carbon atom, and preferentially between the two most substituted carbon atoms.

The cleavage of a methyl group from acyclic hydrocarbons is moderate. However in the case of methylcyclopentane the only significant cracking reaction is demethanation. Cyclopentane, cyclopentene and cyclopentadiene were present in the reaction products in substantial quantities.

Small amounts of carbon monoxide and traces of carbon dioxide were formed in each of the dehydrogenation experiments.

Experimental Part.—The chromia–alumina catalysts were prepared by the method described previously.[9] The surface areas of the catalysts were determined by the B.E.T. method. Nitrogen was used as the adsorbate at the temperature of liquid nitrogen. Before each determination the samples were heated at 540° for 1 hour in air, 2 hours in hydrogen and evacuated at 10^{-5} mm. for 2 hours at 500°.

The dehydrogenation reactions were performed in a 20 mm. o.d. Pyrex tubular reactor which was placed in a vertical furnace. The catalyst bed was 210 mm. long.

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[13] H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, **83**, 2487 (1961).

[14] S. Csicsery, Doctoral Thesis, Northwestern University, 1962.

A thermowell held thermocouples inside the reactor. The catalyst pellets were diluted with glass pieces of similar sizes about 1:2 weight ratio to decrease temperature changes during the reaction. All the experiments were made at atmospheric pressure. The liquid feeds were pumped into the reaction tube by a syringe-type displacement pump. The liquid products were condensed successively in ice–water and acetone–Dry Ice traps.

The gases were trapped in a liquid nitrogen condenser and at the end of each experiment collected over saturated salt-water. Hydrogen was measured in a Precision wet test meter.

At the end of each experiment the carbonaceous materials were burned off at 540° with an air–nitrogen mixture; CO_2 was absorbed in 0.1 N NaOH solution, and back-titrated with 0.6 N HCl using phenolphthalein and methyl orange indicators. The difference between the two end-points is equal to the CO_2 absorbed. Equal rate of formation of carbonaceous materials was supposed during each cut within any single experiment in the preparation of Tables I-V. Catalysts were reconditioned under hydrogen flow at 525° before each experiment for at least 2 hours.

Liquid and gaseous reaction products were analyzed by gas chromatography using two Podbielniak Chromacon vapor phase chromatographic analytical apparatus (models No. 9475 3A and 9580) with the following columns: 1. silica gel "950," 60/200 mesh, 8 ft., for C_1–C_2-compounds; 2. 35% dimethylsulfolane–dipropyl sulfone (ratio 3:7) on 30/60 mesh firebrick, 35 ft., for C_2–C_4-aliphatics; 3. 33% dimethylsulfolane on 100/120 mesh firebrick, 10 ft., for C_2–C_6-aliphatics; 4. 7% di-*n*-propyl tetrachlorophthalate on 30/60 mesh Celite, 22 ft., for C_8-diolefins and aromatics; 5. 5% 7,8-benzoquinoline on 100/120 mesh firebrick, 26 ft., for xylenes.

The hydrocarbons used were pure grade commercial products.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Correlation of Solvent Effects on the Stereoselectivities of Diels–Alder Reactions by Means of Linear Free Energy Relationships. A New Empirical Measure of Solvent Polarity[1a]

BY JEROME A. BERSON,[1b] ZACHARIAS HAMLET AND WILLIAM A. MUELLER

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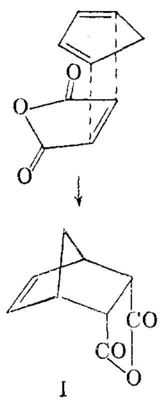
The logarithms of the ratios of stereoisomeric products in the kinetically controlled Diels–Alder additions of cyclopentadiene to methyl methacrylate and methyl *trans*-crotonate in various solvents are linearly related to a solvent parameter, Ω, defined as the logarithm of the *endo*/*exo* product ratio for the cyclopentadiene–methyl acrylate addition. The Alder Rule of "maximum accumulation of unsaturation" is of minor importance in determining the ratios of products; methyl acrylate obeys the rule in all solvents, methyl methacrylate violates it in all solvents, and methyl *trans*-crotonate shows borderline behavior, conforming to the rule in polar solvents but not in non-polar solvents. The solvent effects are correlated fairly well in quantitative terms by the Kirkwood–Onsager theory. The qualitative trend of the solvent effects is explicable in terms of an interaction between the permanent dipoles of the diene and dienophile. The parameter Ω is a new empirical measure of solvent polarity; it is linear in Z, in log k_{ion} for *p*-methoxyneophyl *p*-toluenesulfonate, and in log k_{rearr} for the Curtius rearrangement of benzoyl azide.

The first few experiences[2] in the study of the stereoselectivity of diene additions were deceptively simple. In the classic case,[3] cyclopentadiene and maleic anhydride reacted to give essentially exclusively the *endo* adduct I rather than the *exo* adduct II. On the basis of this (and several other examples in which the *endo* adduct was at least the heavily predominant if not exclusive product) was formulated[2] the Rule of "maximum accumulation of unsaturation." Since the Diels–Alder reaction is reversible, it was to be expected that, in those additions taking place under circumstances that permitted equilibrium to be established in favor of an *exo* adduct of greater stability, the Rule would be violated, and a number of such cases have come to light.[2,4] Nevertheless, the kinetically favored product has usually been assumed to be *endo*, in accord with the Rule, and most theories of the mechanism of the Diels–Alder reaction have postulated[4a,5,6] some kind of attractive interaction between the reacting partners that was much stronger in the *endo* transition state than in the *exo*. Recently, however, it has become increasingly clear that *exo* addition predominates in many cases in which the product-ratio is presumed[7,8] or demon-



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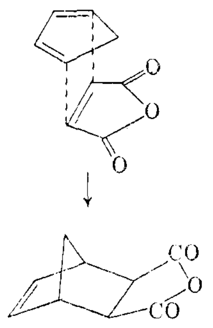

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[2] For a summary, see K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937).

[3] K. Alder and G. Stein, *Ann.*, **504**, 222 (1933); **514**, 1 (1934).

[4] *Cf. inter alia* (a) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944); (b) K. Alder, F. W. Chambers and W. Trimborn, *Ann.*, **566**, 27 (1950); (c) D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951); (d) J. A. Berson and R. Swidler, *ibid.*, **75**, 1721 (1953).

[5] A. Wasserman, *J. Chem. Soc.*, **828**, 1511 (1935); 432 (1936); 612 (1942); *Trans. Faraday Soc.*, **34**, 128 (1938); **35**, 841 (1939).

[6] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[7] (a) J. S. Meek and W. Trapp, *J. Am. Chem. Soc.*, **78**, 6049 (1956); (b) W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, *ibid.*, **80**, 5488 (1958); (c) M. Schwarz and M. Maienthal, *J. Org. Chem.*, **25**, 449 (1960).