the first there is no indication as to whether it is in the 1 or 3 position.

Summary

The preparation and properties of several nicotinyl acyl methanes have been described and their reactions with alcohol and hydrogen surveyed.
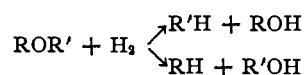
MADISON, WIS.   RECEIVED OCTOBER 22, 1934

Hydrogenation and Hydrogenolysis of Ethers

BY EDWARD M. VAN DUZEE AND HOMER ADKINS

Ethers react with hydrogen under suitable conditions of temperature, pressure and catalyst, i. e.

$$ROR' + H_2 \begin{cases} \nearrow R'H + ROH \\ \searrow RH + R'OH \end{cases}$$

If R or R' is unsaturated, hydrogenation may precede or follow hydrogenolysis. These reactions have been observed by Sabatier, Senderens, Mailhe, Murat and Ipatieff and others to occur over nickel and by Skita, Grave, Waser and others over platinum or palladium.[1] The rapidly increasing importance of Raney nickel made it seem advisable to survey the behavior of typical ethers toward hydrogen over this catalyst. Such a survey was desirable since the intelligent use of the catalyst in preparational and constitutional work may require a knowledge of the type of reaction (or lack of it) which may be expected to occur with a given type of ether at a given temperature.

There are summarized in Table I the data obtained in this survey. In addition, a considerable number of ethers were found to be stable toward hydrogen over Raney nickel[2] at 200°, i. e., monoethyl ether of ethylene glycol, p-methoxycyclohexanol, monomethyl ether of ethylene glycol, duodecyl phenyl ether, di-isopropyl ether, di-n-butyl ether, di-cyclohexyl ether, duodecyl n-butyl ether, duodecyl ethyl ether, diacetone glucose, cyclohexyl ethyl ether, cyclohexyl methyl ether, 1,3-dimethoxycyclohexane, 1,4-di-methoxycyclohexane, monocyclohexyl ether of trimethylene glycol, 4-cyclohexylbutyl cyclohexyl ether, cyclohexyl n-butyl ether, ethyl n-butyl ether of ethylene glycol, 3-cyclohexylpropyl cyclohexyl ether, methyl n-butyl ether of ethylene glycol, n-butyl ether of trimethylene glycol, 3-cyclohexylpropyl n-butyl ether, diethyl 2-cyclohexylethylmalonate, diethyl 3-cyclohexylpropylmalonate.

Discussion of Results

The answer to three questions will be considered with respect to the behavior of an ether toward hydrogen under the conditions of catalyst and pressure underlying the data in Table I.

(a) In what temperature range will the cleavage of the ether become reasonably rapid?[3]

(b) Which of the carbon to oxygen linkages in $R \cdots O \cdots R'$ will be ruptured by the reaction indicated in (a)?

(c) In what temperature range (in case R or R' is unsaturated) will the hydrogenation of R or R' become reasonably rapid?

The benzyl ethers undergo hydrogenolysis at a lower temperature than do other ethers. This is in accord with previous observations and with the well-known fact that a carbon to oxygen linkage β to a double bond $(C=C-C \cdots O)$ is very easily broken by a variety of reagents. The benzyl ethers undergo cleavage exclusively between the benzyl group and the oxygen at temperatures of 100 to 150°. Within this range a definite conclusion cannot be drawn as to the effect of variation in R upon the temperature of cleavage of benzyl ethers since traces of impurities in various ethers may account for apparent differences in the temperature required for hydro-

(1) Sabatier and Senderens, Bull. soc. chim., [3] 33, 616 (1905); Mailhe and Murat, ibid., [4] 11, 122 (1912); Ipatieff and Lugovoi, J. Russ. Phys.-Chem. Soc., 46, 470 (1914); Ipatieff and Philipow, Ber., 41, 1001 (1908); ibid., 46, 3589 (1913); Skita and Brunner, ibid., 49, 1600 (1916); Skita and Rolfes, ibid., 53, 1245, 1253 (1920); Skita, ibid., 54, 1560 (1921); Grave, THIS JOURNAL, 46, 1460 (1924); Waser and Brauchli, Helv. Chim. Acta, 7, 743, 746 (1924); Waser, Sommer, Landweer and Gaza, ibid., 12, 418 (1929); Marty, Compt. rend., 187, 47 (1928).

(2) Adkins and Covert, THIS JOURNAL, 54, 1651 (1932). The volume of the water should be maintained by addition during the reaction of aluminum with sodium hydroxide, and the temperature should be 110–115° during the period of heating.

(3) That the cleavage involved hydrogenolysis and not simply disproportionation (RCH₂OR' → RCHO + R'H) followed by hydrogenation (RCHO + H₂ → RCH₂OH) was shown by the fact that benzyl n-butyl ether, for example, was stable at 200° over Raney nickel under 100 atmospheres of nitrogen.

TABLE I

HYDROGENATION AND HYDROGENOLYSIS OF ETHERS OVER RANEY NICKEL

Reaction in a copper liner in a steel bomb under a pressure of 150–250 atm. over approximately 5 g. of Raney nickel per 100 g. of ether.

R	R'	Moles used and recovered		Hrs. at	temp.	% yield
PhCH₂	n-Bu[a]	0.28	0.02	1.5	175	92 n-BuOH, 92 Toluene
PhCH₂	s-Bu	.28	.05	0.5	125	100 s-BuOH, 80 Toluene
PhCH₂	Ph(CH₂)₃—	.18	.12	.5	100	71 Toluene, 57 3-Ph-propanol-1
PhCH₂	n-C₁₂H₂₅—	.11	.06	1.5	160	72 Toluene, 74 Duodecyl alcohol
PhCH₂	Me[b]	.44	.24	0.5	160	64 Toluene, 65 MeOH
PhCH₂	o-(C₆H₄CO₂Me)—[c]	.24	.03	.4	150	77 Toluene, 89 Me Salicylate
PhCH₂	HO(CH₂)₃—[d]	.38	.12	7	175	13 Toluene, 78 Trimethylene Glycol
PhCH₂	PhO(CH₂)₂—	.35	.16	1.3	150	37 Toluene, 19 Cyclohexanol, 55 2-Phenoxy-EtOH
PhCH₂	EtO(CH₂)₂—	.41	.14	4	175	30 Me-cyclohexane, 34 Toluene, 63 Cellosolve
PhCH₂	Ph[e,f]	.22	.07	0.4	100	100 Toluene, 87 Phenol, 6.3 Cyclohexanol
PhCH₂	Naphthyl[f]	.10		.5	125	60 Toluene, 100 x Hydronaphthols
PhCH₃	o-Tolyl[f]	.52	.07	1.0	125	85 Toluene, 87 p-Cresol
PhCH₂	m-Tolyl[f]	.26	.03	1.1	150	74 Toluene, 71 m-Cresol, 27 m-Me-cyclohexanol
PhCH₂	p-Tolyl[g,f]	.26	.01	1	150	86 Toluene, 58 o-Cresol, 30 o-Me-cyclohexanol
Ph	Me[b]	1.00	.11	4.4	200	66 Cyclohexyl Me ether,[m] 16 MeOH, 14 Cyclohexane
Ph	Et[b]	0.70	.03	7.5	175	85 Cyclohexyl Et ether,[m] 15 EtOH, 5 Cyclohexane
Ph	n-C₁₂H₂₅—	.14	.09	10	250	25 Undecane, 26 Duodecyl alcohol, x Cyclohexane
Ph	Ph(CH₂)₃[h]	.37	0	5	200	74 3-Cyclohexyl-Prⁿ cyclohexyl ether
Ph	Ph(CH₂)₄—	.22		2.5	200	55 4-Cyclohexyl-Bu cyclo-ⁿ hexyl ether
Ph	i-C₅H₁₁O(CH₂)₂—	.46		7.5	200	77 Isoamyl cyclohexyl ether of ethylene glycol
Ph	—(CH₂)₂CH(COOEt)₂[i]	.38	0.08	4	200	56 Di-Et-2-cyclohexyl-Et malonate, 19 Di-Et-Et-malonate, 6 Cyclohexanol
PH	—(CH₂)₃CH(COOEt)₂[j]	.27	.11	5	200	54 Di-Et 3-Cyclohexyl-Pr-malonate, 15 Cyclohexanol
Ph	Ph	.59	0	5	175	53 Cyclohexane, 75 Cyclohexanol, 14 Cyclohexyl Ph etherⁿ
Ph	m-Tolyl[k]	.16	0	5	190	89 Cyclohexane, 77 m-Me-cyclohexanol
Ph	p-Tolyl[k]	.16	0.11	0.5	150	56 p-Cresol, 30 Benzene
Ph	p-Tolyl	.16	.01	2.1	175	100 p-Me-cyclohexanol, 70 Cyclohexane
p-Anisyl	o-Tolyl	.38	.30	1.1	200	63 o-Me-cyclohexanol, 21 Cyclohexyl Me ether
Me	β-Naphthyl[f]	.45	0	5	160	73 Ac-tetrahydro-β-naphthyl Me ether, 13 Hydronaphthalenes
Me	p-(C₆H₄OH)—[l]	.40	0.04	5.5	200	88 p-Methoxycyclohexanol
Di Me	m-(C₆H₄)=[b]	.57	.15	8.5	200	24 1,3-Dimethoxycyclohexane, 52 Cyclohexyl Me ether, 23 MeOH, 6 Cyclohexane
Et	Ph₃C—[o]	.17	0	9	175	66 EtOH, 93 Dicyclohexyl-Ph-methane
n-Bu	Ph(CH₂)₃—	.35	0	5	200	77 3-Cyclohexylpropyl n-Bu ether
1,3,5-Tri-p-anisylbenzene		.30	0	8	200	90 1,3,5-Tri-p-methoxycyclohexylcyclohexane

[a] Senderens, *Compt. rend.*, **178**, 1412 (1924). [b] Perkin, *J. Chem. Soc.*, **69**, 1190 (1896). [c] M. p. 47–48°, b. p. 160–161° at 1 mm. Cf. Cohen, *ibid.*, **97**, 1745 (1910). [d] Bennett and Hock, *ibid.*, 474 (1927). [e] B. p. 124–125° at 4 mm. Cf. Sintenis, *Ann.*, **161**, 337 (1872). [f] Staedel, *ibid.*, **217**, 43 (1883). [g] B. p. 142–144° at 3 mm. [h] Grignard, *Compt. rend.*, **138**, 1049 (1904); v. Braun, *Ber.*, **43**, 2842 (1910). [i] Leuchs, *ibid.*, **44**, 1509 (1911). [j] Merchant, Wickert and Marvel, THIS JOURNAL, **49**, 1829 (1927). [k] Ullmann and Sponagel, *Ann.*, **350**, 87 (1906). [l] Helfer, *Helv. Chim. Acta*, **7**, 951 (1924). [m] Waser, Sommer, Landweer and Gaza, *Helv. Chim. Acta*, **12**, 437 (1929). [n] Kursanov, *J. Russ. Phys.-Chem. Soc.*, **48**, 1172 (1916). [o] Gomberg, *Ber.*, **35**, 1834 (1902).

genolysis. However, it is abundantly evident that the benzyl aryl ethers cleave at a lower temperature than do the benzyl alkyl ethers, especially if the latter bear a hydroxyl group. In no case did the benzyl ethers undergo hydrogenation, i. e., the temperature for hydrogenolysis over Raney nickel is lower than for hydrogenation. In some cases, where hydrogenolysis was carried out at 150° or above, products of that reaction underwent hydrogenation.

The diaryl ethers were somewhat more stable toward hydrogenolysis than were the benzyl alkyl ethers, cleavage occurring in the temperature range 150–200°. Hydrogenation of the ethers did not occur to any considerable extent, although the products of hydrogenolysis were hydrogenated. The cleavage occurred adjacent to the phenyl in the phenyl tolyl ethers, and adjacent to anisyl in p-anisyl o-tolyl ether.

The aryl alkyl ethers were distinctly more stable toward hydrogenolysis than were the ethers discussed above. In ten cases the corresponding cyclohexyl alkyl ether was obtained in good yield as the result of hydrogenation at 200° or lower. The presence of alkoxy groups or phenyl groups in the 3 or 4 position, or carbethoxy groups in the alkyl radical did not prevent hydrogenation, although the yield of hydrogenated ether was lowered due to a larger amount of hydrogenolysis in these cases. A striking exception was that duodecyl phenyl ether did not undergo hydrogenation even at 250°, at which temperature hydrogenolysis occurred.

The dialkyl ethers were quite stable toward hydrogen at 200°. It is apparent that at temperatures sufficiently high to cleave a dialkyl ether over Raney nickel, a carbon to carbon cleavage would also occur.[4]

It should be pointed out that while Raney nickel has numerous advantages over reduced nickel deposited on a support, the latter is a much better catalyst for the hydrogenation of an aryl ether to the corresponding cyclohexyl compound. For example, nickel on kieselguhr gave a 42% yield of dicyclohexyl ether from diphenyl ether[5] as contrasted with the negligible yield over Raney nickel. Even the readily cleaved benzyl ether of ethylene glycol was hydrogenated to the corresponding cyclohexyl ether in a 22% yield over the nickel on kieselguhr precipitated by ammonium carbonate.[5,6] Dr. Walter H. Zartman in hitherto unpublished results obtained an 80% yield of methoxycyclohexane from anisole at 180°, and a 70% yield of 1,4-dimethoxycyclohexane from 1,4-dimethoxybenzene at 200° using 3 to 4 g. of the nickel on kieselguhr catalyst with 0.25 to 0.4 mole of the aromatic ethers. These latter yields are to be contrasted with the 66% yield of methoxycyclohexane, and the negligible yield of 1,4-dimethoxycyclohexane obtained over

Raney nickel. The greater tendency of Raney nickel as contrasted with nickel on kieselguhr to bring about the rupture of oxygen to carbon linkages was also evidenced by the superiority of the latter for the hydrogenation of furfural acetal to tetrahydrofurfural acetal.[6]

Experimental Part

The benzyl ethers were prepared through the reaction of benzyl chloride and various sodium alkoxides according to the procedure illustrated below. Sodium (69 g., 3 moles) was added gradually to 600 ml. of butanol contained in a 2-liter 3-necked flask provided with a mechanical stirrer, mercury seal and reflux condenser. After all the sodium had dissolved, 380 g. of benzyl chloride (3 moles) was added gradually while the mixture was kept boiling gently. The refluxing was continued for an hour. After cooling the mixture, water and a little ether was added. The ethereal layer was washed well with water, dried over calcium chloride and fractionated through a Widmer column. The yield of ether was 363 g. (74% of the theoretical), b. p. 111–112° (23 mm.).

The above procedure was modified in that in some cases toluene instead of excess alcohol was used as a reaction medium. In the case of the aryl alkyl ethers prepared by this method the sodium was dissolved in methanol or ethanol and the phenol then added. The yields of benzyl ethers were in general from 70 to 80%. Lower yields were obtained in certain cases, e. g., for s-butyl 55%, for 3-hydroxypropyl 42%, for 2-phenoxyethyl 51%, and for β-naphthyl 31%.

Fifteen other ethers were also prepared by essentially the same procedure as given for the benzyl ethers. The yields obtained in each case are given below, the group bearing the halogen being in heavy type

$C_{12}H_{25}OC_6H_5$, 69%: $C_6H_5(CH_2)_3OC_6H_5$, 71%
$i\text{-}C_5H_{11}OC_6H_5$, 38%: $(C_6H_5)_2COC_2H_5$, 76%
$C_6H_5(CH_2)_3OC_4H_9$ (n), 78%: $n\text{-}C_{12}H_{25}OC_2H_5$, 86%
$C_{12}H_{25}OC_4H_9$ (n), 65%: $HO(CH_2)_3OC_4H_9$ (n), 30%
$n\text{-}C_4H_9O(CH_2)_2OCH_3$, 46%: $C_6H_5O(CH_2)_3C_2H_5$, 25%
$n\text{-}C_4H_9O(CH_2)_2OC_2H_5$, 47%; $n\text{-}C_4H_5OC_5H_{11}$, 41%
$HO(CH_2)_3OC_5H_{11}$, 10%: $HO(CH_2)_2OC_6H_5$, 75%
and $HO(CH_2)_3OC_6H_5$, 58%

Six ethers were prepared according to the Ullmann method,[7] the procedure being illustrated below. Potassium hydroxide (56 g., 1 mole) was dissolved in 140 g. of o-cresol (1.3 moles) and

(4) Cf. Wojcik and Adkins, THIS JOURNAL, **55**, 1293 (1933).
(5) Adkins and Cramer, ibid., **52**, 3244 (1930).
(6) Covert, Connor and Adkins, ibid., **54**, 1659 (1932).
(7) Cf. Weston and Adkins, ibid., **50**, 859 (1928).

heated at 200–220° for three hours under a pressure of 15 mm. The mixture was then cooled and 187 g. of p-bromoanisole (1 mole), 108 g. of o-cresol (1 mole) and 5 g of Naturkupfer C added. The mixture was refluxed at 200° for three hours and cooled. The product was treated with water and made strongly alkaline with a 10% solution of sodium hydroxide. The p-anisyl o-tolyl ether was extracted three times with ether, the solution filtered and the product fractionated

through a Widmer column. The product (109 g., 51%) distilled at 151–153° at 5 mm. The yields obtained in the other cases were as follows: phenyl o-tolyl 52%, phenyl m-tolyl 68%, phenyl p-tolyl 43%, p-anisyl m-tolyl 60% and p-anisyl p-tolyl 39%. The diethyl phenoxyethyl and phenoxypropyl malonic esters were made from the corresponding bromides and sodium malonic ester.

The properties and analyses of compounds not hitherto reported are given in Table II.

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR COMPOUNDS HITHERTO UNREPORTED

Compound	Empirical formula	B. p. °C.	Mm.	n_D^{25}	d_{25}^{25}	MRD Obs.	MRD Calcd.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Duodecyl ethyl ether	$C_{14}H_{30}O$	125–130	6–7	1.4278	0.8015	68.5	68.44	78.42	77.89	14.11	13.77
Duodecyl n-butyl ether	$C_{16}H_{34}O$	150–153	13	1.4305	.7988	78.5	77.68	79.25	79.29	14.14	14.12
Duodecyl phenyl ether	$C_{18}H_{30}O$	180–182 (M. p., 23)	7	1.4820	.8939	83.6	83.24	82.37	81.91	11.51	11.39
Duodecyl benzyl ether	$C_{19}H_{32}O$	186–188	7	1.4771	.8829	88.6	87.86	82.53	81.96	11.68	11.39
Phenyl isoamyl ether of ethylene glycol	$C_{13}H_{20}O_2$	118	2	1.4867	.9575	62.5	61.88	74.94	74.64	9.69	9.48
Benzyl ethyl ether of ethylene glycol	$C_{11}H_{15}O_2$	115–118	13	1.4872	.9761	53.5	52.69	73.28	73.50	8.95	8.78
Methyl n-butyl ether of ethylene glycol	$C_7H_{16}O_2$	144–146		1.3988	.8390	38.0	38.70	63.57	63.57	12.21	12.39
Ethyl n-butyl ether of ethylene glycol	$C_8H_{18}O_2$	161–162		1.4017	.8325	43.7	42.43	65.69	65.51	12.41	12.49
Benzyl s-butyl ether	$C_{11}H_{16}O$	108–109	29	1.4787	.9342	50.5	50.04	80.42	80.17	9.83	9.91
Mono-n-butyl ether of tri- methylene glycol	$C_7H_{16}O_2$	81–85	13	1.4238	.8936	37.6	37.69	63.57	63.40	12.21	12.13
Monocyclohexyl ether of trimethylene glycol	$C_9H_{18}O_2$	91–93	2	1.4600	.9792	45.3	44.72	68.29	67.80	11.47	11.63
Benzyl phenyl ether of ethylene glycol	$C_{15}H_{16}O_2$	176–181	2	1.5566	1.0787	68.0	67.54	78.90	79.06	7.07	7.00
3-Phenylpropyl benzyl ether	$C_{16}H_{18}O$	166	7	1.5347	0.9974	70.6	70.87	84.90	85.15	8.02	8.12
3-Phenylpropyl n-butyl ether	$C_{13}H_{20}O$	116–118	10	1.4714	.8896	60.4	60.35	81.18	80.68	10.49	10.39
o-Tolyl p-anisyl ether	$C_{14}H_{14}O_2$	151–153	5	1.5708	1.0976	64.3	63.34	78.46	78.63	6.59	6.71
m-Tolyl p-anisyl ether	$C_{14}H_{14}O_2$	141–143	2	1.6597	1.0951	64.1	63.34	78.46	78.06	6.59	6.44
p-Tolyl p-anisyl ether	$C_{14}H_{14}O_2$	162–164	5	(M. p., 45–46)				78.46	78.03	6.59	6.52
4-Phenylbutyl phenyl ether	$C_{16}H_{18}O$	144–146	1	1.5504	1.0170	71.0	70.53	84.90	85.15	8.02	8.17
4-Cyclohexylbutyl cyclo- hexyl ether	$C_{16}H_{30}O$	150–153	5	1.4730	0.9077	73.9	73.23	80.59	80.29	12.69	12.68
3-Cyclohexylpropyl cyclo- hexyl ether	$C_{15}H_{28}O$	138–140	5	1.4705	.9092	68.9	68.63	80.28	80.43	12.58	12.28
3-Cyclohexylpropyl n-bu- tyl ether	$C_{13}H_{26}O$	117–118	10	1.4445	.8526	61.9	61.52	78.70	78.70	13.22	13.28
3-Cyclohexyloxypropyldi- ethyl malonate	$C_{16}H_{28}O_5$	173–175	4	1.4534	1.0066	80.6	79.87	63.95	63.50	9.40	9.65
2-Cyclohexyloxyethyldi- ethyl malonate	$C_{15}H_{26}O_5$	162–164	4	1.4534	1.0220	75.6	74.46	62.89	62.58	9.16	9.27
Cyclohexyl isoamyl ether of ethylene glycol	$C_{13}H_{26}O_2$	113–115	7	1.4416	0.8919	63.5	63.21	72.83	72.38	12.24	12.15
Anilide of benzyl ether of salicylic acid	$C_{20}H_{17}O_2N$	M. p., 117–118						78.68	78.25	5.65	5.54
1,3,5-Tri-p-anisylbenzene	$C_{27}H_{24}O_3$	M. p., 142–142.5						81.78	81.25	6.11	6.10
1,3,5-Tri-p-methoxycyclo- hexylcyclohexane	$C_{27}H_{48}O_3$	230–240	1					77.07	77.60	11.51	11.48

Summary

The behavior of various types of ethers toward hydrogen over Raney nickel has been surveyed.

The results are summarized in Table I and in the section entitled discussion of results.

The Synthesis of Condensed Polynuclear Hydrocarbons by the Cyclodehydration of Aromatic Alcohols. III. The Cyclization of Some Phenylated Alcohols and Related Olefins[1]

BY RICHARD O. ROBLIN, JR., DAVID DAVIDSON AND MARSTON TAYLOR BOGERT

For several years there has been great activity in the synthesis and study of polynuclear aromatic hydrocarbons, particularly those of biological significance or related to products occurring in nature. The volume of this work appears to be steadily mounting and has already reached formidable proportions.

A convenient method for the synthesis of such hydrocarbons, and one which has been frequently employed and extensively developed, is the cyclodehydration of aromatic alcohols, followed by dehydrogenation of the resultant hydroaromatic products.

In the eagerness to synthesize new and interesting compounds, but little time has been given to the study of the reaction itself or of its mechanism. We have therefore felt that studies in this direction might contribute information of value to many investigators in this field, and the data so far accumulated have justified that belief.

Of the results already published from our laboratories, those on the synthesis of ionene,[2] of phenanthrene,[3] and of the indanes,[4] indicate that in most cases the main course of the reaction is first the dehydration of the alcohol to an olefin, and then the rearrangement of the latter by cyclization. In only one case (Table A, XVII) was there evidence that the cyclization was effected by a direct condensation of the alcoholic hydroxyl with the ortho hydrogen of the aromatic nucleus.

(1) Presented at the St. Petersburg, Fla., Meeting of the American Chemical Society, Mar. 27, 1934, before the Division of Organic Chemistry. Based upon the Dissertation submitted by Richard O. Roblin, Jr., 1934, in partial fulfilment of the requirements for the Ph.D. degree in the Faculty of Pure Science, Columbia University, to which the reader is referred for further experimental details and literature citations.—M. T. B.

(2) Bogert, Davidson and Apfelbaum, THIS JOURNAL, **56**, 959 (1934).

(3) Bogert, Science, [N. S.] **77**, 289 (Mar. 17, 1933).

(4) Bogert and Davidson, THIS JOURNAL, **56**, 185 (1934).

The present contribution describes a detailed investigation of the cyclization of some simple phenylated alcohols and related olefins, most of which are readily obtainable in good yield by the familiar Grignard reaction. The ease with which these alcohols and olefins can be converted into the corresponding tetralins and naphthalenes, makes the process a very satisfactory one for the synthesis of such hydrocarbons.

In addition to confining our experiments to a limited group of closely related initial compounds, it seemed wise also to adopt some one standard cyclizing agent, in order that the results might be more truly comparable and more clearly interpretable. Of the many reagents which have been employed for such a purpose, sulfuric acid was found most satisfactory for use at room temperature, except for primary alcohols. Because of the oxidizing and sulfonating action of this acid at the high temperatures required to dehydrate such alcohols, phosphoric acid was substituted in those cases.

In Table A we have incorporated also the alcohols and olefins investigated in our earlier papers,[2,4] so as to make this summary more comprehensive and to give a better survey of the results to date.

Classified according to final products, the initial compounds tabulated below can be arranged as follows: (1) those giving mainly polymers = I, IV, VII, IX, X and XXVI; (2) those giving mainly indanes = II, III, VIII, XI, XII, XIII and XXV; (3) those giving both indanes and tetralins = VI and XVI; (4) those giving mainly tetralins = V, XIV, XV, XVII, XVIII, XIX, XXI, XXII, XXIII, XXIV, XXVII, XXVIII and XXIX.

An examination of these results will disclose the following interesting facts among others: