5. A tentative explanation has been given to account for the rapid falling off of the oxygen absorption rates long before an appreciable amount of the substance in question had undergone oxidation.

6. It has been pointed out that an inhibitor of the auto-oxidations studied in this investigation does not necessarily have to be a "good reducing" agent or an "easily oxidizable" substance. For example anthraquinone, which *is not oxidized during* the oxidation of anethol, is a far better inhibitor of this oxidation than anthracene, which is inducedly oxidized to anthraquinone.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 53]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. X. THE MEASUREMENT OF THE RELATIVE LABILITY OF BONDS BY MEANS OF RATES OF REACTIONS AND OF TEMPERATURES OF DECOMPOSITION. I. THE HYDROGEN-OXYGEN BOND IN CERTAIN ALCOHOLS

BY JAMES F. NORRIS AND RALPH C. YOUNG[1]

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Previous communications from this Laboratory have described the results of the study of the influence of structure on the lability of certain bondings between atoms in organic molecules. The method employed was to measure the relative rates at which the several members of a series of similar compounds reacted with a fixed reagent. The investigation in this way of a large number of alcohols gave definite results in regard to the influence of structure on the rates at which the hydrogen-oxygen linkage was broken, with the resulting replacement of hydrogen by the *p*-nitrobenzoyl radical.[2]

The results showed that the structure of the radical had a marked effect on the oxygen bond, RC—, in these compounds. It seemed desirable to study this bond by an entirely different method, to determine whether or not the effects shown were observable in transformations involving this bond that could be measured without the use of reaction velocities. A satisfactory method was found which involved the study of the action of heat on the triphenylmethyl ethers derived from a series of alcohols. Previous work[3] had shown that triphenylmethyl ethyl ether decomposes almost quantitatively, when heated, into triphenylmethane and acetaldehyde.

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[1] From the thesis of Ralph C. Young, presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Norris and Ashdown, THIS JOURNAL, **47**, 837 (1925); Norris and Cortese, *ibid.*, **49**, 2640 (1927).

[3] Norris and Young, *ibid.*, **46**, 2580 (1924).

$C_2H_5O—C(C_6H_5)_3 = CH_3CHO + (C_6H_5)_3CH$.—In this transformation the oxygen bond indicated was severed by heat. As the earlier work showed that this bond in the alcohols was greatly affected by changing the structure of the alkyl radical, it seemed probable that the members of a series of triphenylmethyl ethers would decompose at different temperatures when heated and that of two ethers the one containing the more stable oxygen linkage would break at the higher temperature.

The triphenylmethyl ethers derived from the alcohols were, accordingly, made and studied. It was found that in all cases the decomposition was definite. The ethers prepared from primary alcohols yielded aldehydes and those from secondary alcohols, ketones.

The temperature at which each ether started to decompose was measured with an accuracy of ±2°. The results are given in Table I, in which are also given the second-order velocity constants of the reactions between *p*-nitrobenzoyl chloride and the alcohols containing the radicals listed.

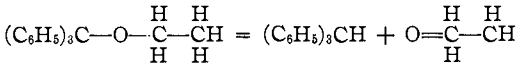
TABLE I

RESULTS OF EXPERIMENTS

Radical in ethers $(C_6H_5)_2C—OR$	Temp. (°C.) of decomposition	Velocity constant, *p*-$NO_2C_6H_5$-$COCl + H—OR =$ *p*-$NO_2C_6H_4$-$COOR + HCl$	Radical in ethers $(C_6H_5)_2C—OR$	Temp. (°C.) of decomposition	Velocity constant, *p*-$NO_2C_6H_5$-$COCl + H—OR =$ *p*-$NO_2C_6H_4$-$COOR + HCl$
Methyl	262	0.184	*Iso*-amyl	237	0.073
Ethyl	242	.085	*Sec.*-propyl	220	.010
n-Propyl	230	.066	*Sec.*-butyl	216	.0073
n-Butyl	239	.074	Benzyl	226	.017
*Iso*butyl	228	.031	β-Phenylethyl	236	.040

The results show that the two series of numbers follow in the same order, with but one exception. If we compare any two ethers, the one decomposing at the lower temperature is derived from the alcohol which reacts more slowly with the acyl chloride. This statement holds true in the case of 44 out of 45 of the possible comparison. The exception is in the case of the comparison of the β-phenylethyl and *n*-propyl radicals.

It is possible that in the decomposition of the ethers as indicated by the equation



$$(C_6H_5)_3C—O—\overset{H}{\underset{H}{C}}—\overset{H}{\underset{H}{C}}H = (C_6H_5)_3CH + O{=}\overset{H}{\underset{H}{C}}—\overset{H}{C}H$$

the lability of the carbon–hydrogen linkage shown is involved. The lability of the latter bond, necessarily, changes with the alteration of the structure of the alkyl radical, but it does not appear reasonable that the lability of this bond is the determining factor in the decomposition. It is a well-known fact that the carbon bond of the triphenylmethyl radical is very labile. Ethers which do not contain this radical undergo decomposition at relatively high temperatures. The most striking evidence, however, that the point of rupture of the molecule is at this bond is the fact that the temperatures at which decomposition takes place bear a definite relationship to the lability of the same oxygen linkage when measured by an independent method. When two series of data fall in the same or in the opposite order they must be related to the same cause.

It is a striking fact that the two sets of data change in the same direction with a change in the radical. This means that the oxygen linkage which reacts the more rapidly forms a compound which is more stable toward heat. Heat with a higher intensity factor (higher temperature) is required to break the bond. The results lead to the important conclusion, in the cases studied at least, that rates of reactions and temperatures of decomposition lead to the same conclusions in regard to the relative stability of the linkages between atoms.

The results indicated that the temperature at which a molecule begins to decompose when heated can be determined with a reasonable degree of definitiveness. As a result, work is now in progress in this Laboratory on the breaking of the C—H and C—C bonds by heat. Most work on the pyrolysis of organic compounds has been carried out at temperatures that produce the simultaneous splitting of several types of bonds, and, consequently, the results are not easily interpreted.

The fact that the triphenylmethyl alkyl ethers decomposed in such a simple way and at well-defined temperatures, and that in all probability the carbon-oxygen linkage was the one involved, offered an excellent opportunity of studying the effect of various types of substances on the temperature at which the bond breaks. In this way it was hoped to discover substances that possess the property of influencing the stability of this particular bond. The action of a number of elements and compounds is described later in this paper. It can be noted here that the temperature of decomposition of triphenylmethyl-ethyl ether was changed from 242 to 205° by ZnO, to 195° by $BaCl_2$, to 142° by $Al_2O_3 \cdot xH_2O$, to 132° by $KHSO_4$ and to room temperature by $AlCl_3$. The influence of the more active of these catalysts will be studied on other compounds containing the carbon-oxygen bond.

Work has been started on the determination of the temperatures at which esters derived from triphenylcarbinol decompose. In these compounds there are two types of C—O linkages: $(C_6H_5)_3C—O—COR$. It has been found that aluminum chloride breaks almost exclusively the oxygen bond to the triphenylmethyl radical, whereas anhydrous ferric chloride breaks largely the oxygen bond to the acyl radical. The results have led to a study of the selective action of catalysts on the more important bondings in organic compounds.

In the experimental part of this paper will be found an account of the investigation of the action of aluminum chloride on triphenylmethyl ethyl ether.

Experimental Part

Method of Obtaining Decomposition Temperatures of the Ethers.—A glass tube 1 cm. in diameter and 22 cm. long with side arm was connected with capillary tubing to a long horizontal capillary tube containing a column of mercury 1 cm. long. The tube together with a thermometer was supported in an oil-bath. A second oil-bath was also used and the whole was well protected from air drafts. As the temperature was raised the mercury was pushed along by the expanding air and its position was read off in millimeters from a scale at intervals of two degrees. By the plotting of

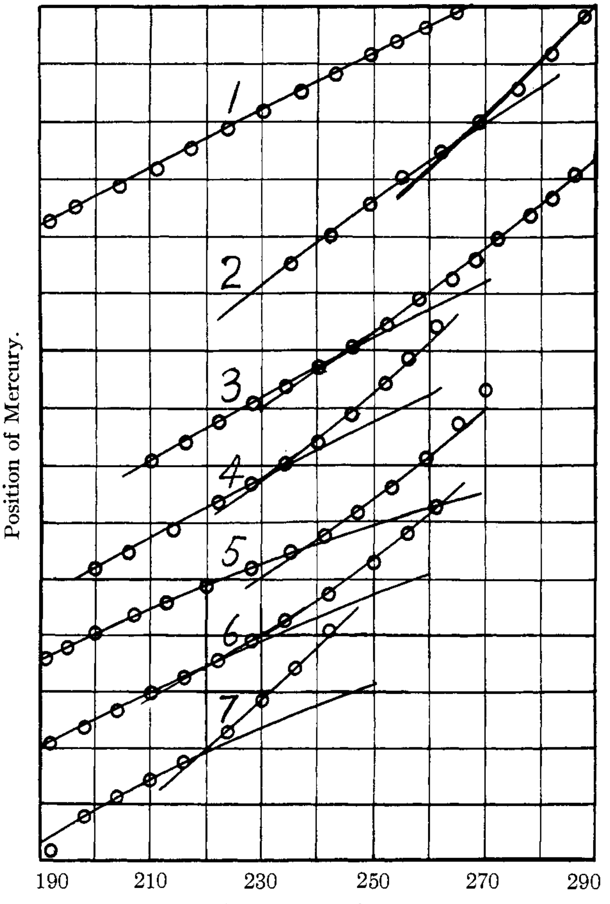


Fig. 1.—Position of mercury above an arbitrary zero for various values of the temperature. Each division = 2 cm. displacement. 1, Blank run; 2, triphenylmethyl methyl ether; 3, triphenylmethyl ethyl ether; 4, triphenylmethyl *n*-propyl ether; 5, triphenylmethyl *n*-butyl ether; 6, triphenylmethyl isopropyl ether; 7, triphenylmethyl *sec.*-butyl ether.

the positions of the mercury as ordinates against the temperatures as abscissas, a line connecting the points appeared as a smooth curve (Curve 1 in the chart). If, however, approximately 0.5 g. (0.0019 mole) of an ether were in the tube, when temperatures were reached at which decomposition occurred the gaseous product formed caused an increase in the rate at which the mercury moved, and the curves obtained had an inflection from which could be obtained the temperatures of decomposition. Since preliminary experiments showed that the ethers decomposed at about 200°, the heating was so regulated that 170° was reached in seventy-five minutes and from that temperature the rate was 1° per minute. About 60° below the temperature at which decomposition took place, the tube was closed by inserting a glass plug in a one-holed rubber stopper with which the tube was fitted. Readings were then taken. Approximate curves, plotted on a small scale, for six of the ethers are given in the accompanying chart. The decomposition temperatures given in Table II were obtained from large scale graphs and read to the nearest degree. Independent determinations are tabulated. Heating of the ethers in a silica tube seemed to cause no lowering of the decomposition temperature nor did a rate of heating one-half that given above.

Table II

Results of Experiments

Radicals in ethers $(C_6H_5)_3C—O—R$	Decomposition temperatures, °C.			
Methyl	262	262	262	262
Ethyl	241	242	242	242
n-Propyl	230	230	230	
n-Butyl	238	239	240	
*Iso*butyl	227	228	227	
Iso-amyl	234	237	237	
*Iso*propyl	219	220	220	224
Sec.-butyl	216	216	214	
Benzyl	226	226		
β-Phenylethyl	236	237	236	237

Preparation of the Ethers.—The method of preparation of the ethers was similar to that of triphenylmethyl ethyl ether, in which case triphenylchloromethane was allowed to react with sodium ethylate in excess alcohol as the solvent.[3] After four hours of refluxing, the solvent was removed and the residue poured into water, taken up in ethyl ether and dried over calcium chloride. The method of purification of the crude product obtained from the ethyl ether solution will be given for the various ethers and also the results of the thermal decomposition (in Table III). Amounts recoverable from the mother liquors are not included in the yields given for the pure ethers. The results obtained in decomposing triphenylmethyl *n*-propyl ether are typical of the other ethers. From 20.9 g. of this ether there were obtained 2.5 cc. of a colorless liquid from 45 to 110°, 0.7 g. from 110 to 300° and 13 g. from 300 to 359°, the greater part of which distilled between 355 and 359°. The residue amounted to 2.5 g. The colorless liquid after fractionation gave a product boiling between 47 and 50°. By its boiling point, odor, test with fuchsine reagent and phenylhydrazone, it was identified as *n*-propionic aldehyde. The higher-boiling fractions which had solidified on cooling were crystallized from alcohol and triphenylmethane obtained in a yield of about 80%.

The Effect of Catalysts in Lowering the Decomposition Temperatures of Triphenylmethyl Ethyl Ether and Triphenylmethyl Methyl Ether.—Experiments were performed to find the lowest temperature to which it

TABLE III

ETHERS PREPARED, MELTING POINTS, BOILING POINTS AND ANALYTICAL DATA

	R in $ROC(C_6H_5)_3$	Crystallized from	Yield, %		°C.
1	CH_3-[4]	MeOH	55	M. p.	82.6–82.9
2	C_2H_5-[5]	Pet. ether and $(Et)_2O$	50	M. p.	81.2–81.8
3	$CH_3CH_2CH_2$-[6]	Pet. ether and *n*-PrOH	10	M. p.	50.5–52.5
4	$CH_3CH_2CH_2CH_2$-	(Fract. dist. *in vacuo*)	60	B. p.	212.8–213.0 (5 mm.)
5	$(CH_3)_2CH$-[7]	Pet. ether and $(Et)_2O$	50	M. p.	112.9–113.8
6	$CH_3CH_2CH(CH_3)$-	(Fract. extr. with pet. ether and fract. dist. *in vacuo*)	40	B. p.	196–198 (5 mm.)
7	$CH_3CH(CH_3)CH_2$-	Pet. ether and *iso*-BuOH	10	M. p.	51–53
8	$CH_3CH(CH_3)CH_2CH_2$-	(Fract. dist. *in vacuo*)	60	B. p.	205–205.5 (5 mm.)
9	$C_6H_5CH_2$-	Pet. ether and $(Et)_2O$	30	M. p.	103–104
10	$C_6H_5CH_2CH_2$-	Pet. ether and $(Et)_2O$	40	M. p.	87.1–87.8
11	$(p\text{-}CH_3C_6H_4)_3COC_2H_5$[8]	Ethyl ether	60	M. p.	111–112

No.	Carbon, % Calcd.	Found		Hydrogen, % Calcd.	Found		Prods. of thermal dec., triphenylmethane and
1	...	...	...	..	..	..	HCHO
2	...	...	...	..	..	..	CH_3CHO
3	87.41	87.27	87.17	7.28	7.27	7.14	CH_3CH_2CHO
4	87.34	87.37	87.07	7.59	7.58	7.56	$CH_3CH_2CH_2CHO$
5	87.41	87.31	87.49	7.28	7.51	7.44	CH_3COCH_3
6	87.34	87.73	87.70	7.59	7.88	7.39	$C_2H_5COCH_3$
7	87.34	87.39	87.38	7.59	7.76	7.75	$(CH_3)_2CHCHO$
8	87.27	87.08	87.12	7.87	7.93	7.88	$(CH_3)_2CHCH_2CHO$
9	89.14	88.93	88.98	6.28	6.39	6.49	C_6H_5CHO
10	89.01	88.91	88.87	6.59	6.83	6.84	$C_6H_5CH_2CHO$
11	...	...	...	..	..	..	CH_3CHO, $(p\text{-}CH_3C_6H_4)_3CH$[a]

[a] No triphenylmethane formed. On account of the lack of agreement in the literature as to the boiling and melting points of tritolylmethane, it was impossible to identify the white solid hydrocarbon (m. p. 62°) as such.

was necessary to heat triphenylmethyl ethyl ether and triphenylmethyl methyl ether to obtain tests for aldehyde by means of fuchsine reagent and also by odor. One gram of the ether was heated in a tube supported in the vapors of a boiling liquid and a slow stream of carbon dioxide swept out any gaseous products of decomposition into a tube cooled in ice water to which could be added fuchsine solution at the end of one-half hour. It was customary also to have this tube connected with a second containing fuchsine solution through which the carbon dioxide was allowed to bubble. On account of the removal of the sulfur dioxide by the car-

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[4] Prepared by Friedel and Crafts, *Ann. chim. phys.*, [6] **1**, 502 (1884).

[5] Norris and Young, Ref. 3.

[6] Prepared by Mamontow from *n*-propyl alcohol, triphenylchloromethane and sulfuric acid [*J. Russ. Phys.-Chem. Soc.*, **29**, 233 (1887)].

[7] Prepared by Helferich, Speidel and Toeldte from *iso*propyl alcohol and triphenylchloromethane in pyridine [*Ber.*, **56B**, 766 (1923)].

[8] Prepared by Tousley and Gomberg, *Am. Chem. J.*, **26**, 1518 (1904).

bon dioxide, a pink color would develop but the rate was slow unless aldehyde was present. It was found that if a test for aldehyde was obtained by the fuchsine the odor could also be detected, and the reverse was also true. Half-gram portions of several inorganic compounds were added to 1 g. of the ether in separate experiments to determine what effect they would have on the temperature necessary for the production of aldehyde and triphenylmethane as the latter compound was also identified. In tabular form are given the catalysts and the temperature required for the production of aldehyde.

Catalyst	Temp., °C.
For Triphenylmethyl Ethyl Ether	
No catalyst	242
Finely divided copper	215
$Fe_2O_3 \cdot xH_2O$ dried at room temp.	205
$Fe_2O_3 \cdot xH_2O$ dried at 170°	205
$Fe_2O_3 \cdot xH_2O$ dried at red heat	205
ZnO	205
$Fe_2O_3 \cdot xH_2O \cdot ZnO$ dried at 170°	195
CuO	195
$BaCl_2$	195
Na_2HPO_4	195
$Al_2O_3 \cdot xH_2O$ dried at red heat	183
$Al_2O_3 \cdot xH_2O$ dried at 180°	142
$KHSO_4$	132
For Triphenylmethyl Methyl Ether	
No catalyst	267
Finely divided copper	242
$Al_2O_3 \cdot xH_2O$	205
$Al_2O_3 \cdot xH_2O$	157
$KHSO_4$	132

Action of Aluminum Chloride on Triphenyl Ethyl Ether.—Triphenylmethyl ethyl ether in carbon disulfide solution reacts with aluminum chloride free from hydrochloric acid to produce triphenylchloromethane and an aluminum chloro-ethylate.

$$2(C_6H_5)_3COC_2H_5 + 2AlCl_3 \longrightarrow (C_6H_5)_3CCl + (C_6H_5)_3CCl \cdot AlCl_3 + Al(OC_2H_5)_2Cl$$

To a solution of 28.8 g. (0.1 mole) of triphenylmethyl ethyl ether in 75 cc. of carbon disulfide in an Erlenmeyer flask with drying tube was added 13.5 g. (0.1 mole) of $AlCl_3$. Reaction began immediately, as evidenced by a slight warming and a darkening in the neighborhood of the aluminum chloride. After standing for twenty-four hours the carbon disulfide was decanted, filtered and evaporated; 15.6 g. of solid was obtained which was extracted with hot benzene. About 2 g. was insoluble in benzene. The soluble portion was found to be triphenylchloromethane. The residue in the reaction flask after decomposition with cracked ice yielded 11.6 g. of triphenylchloromethane.

It has been shown that $(C_6H_5)_3CCl \cdot AlCl_3$ reacts with ethers to give triphenylmethane.[3] If this molecular compound was formed as given in the equation, an additional amount of ether should give triphenylmethane; such proved to be true. An experiment similar to the one cited above was carried out, in which case, however, after the removal of the carbon disulfide by decantation, a second portion of the ether in carbon disulfide was added to the residue in the flask. After reaction there were obtained triphenylmethane and a tarry product. A third and fourth portion of the ether failed to undergo any change.

The material described as insoluble in benzene, which was obtained after the evaporation of the filtered carbon disulfide solution together with triphenylchloromethane, proved to be an almost white solid soluble in water. The aqueous solution gave positive tests for alcohol, chlorine and aluminum.

Anal. Calcd. for $Al(OC_2H_5)_2Cl$: Al, 17.75; Cl, 23.26. Found: Al, 17.40, 17.54; Cl, 23.65, 23.71.

Reaction of Ferric Chloride with Triphenylmethyl Ethyl Ether.—Ferric chloride brings about a decomposition of this ether different from that observed in the case of aluminum chloride. In the latter case the carbon–oxygen linkage to the triphenylmethyl radical is completely broken and triphenylchloromethane is formed. With ferric chloride about one-half of the product was triphenylcarbinol, in which this linkage remained intact.

Eleven and four-tenths grams (0.07 mole) of anhydrous ferric chloride and 20.2 g. (0.07 mole) of triphenylmethyl ethyl ether were allowed to react in 75 cc. of carbon disulfide. There was obtained 8 g. of material from the decanted carbon disulfide solution; this proved to be triphenylmethane and a tarry product. From the residue in the flask there was obtained 10 g. of triphenylcarbinol. When the reacting compounds were mixed in the proportion of 1 mole of ferric chloride to 3 moles of the ether, there was obtained besides triphenylmethane and triphenylcarbinol an amount of unchanged ether that indicated that the reaction took place between 1 mole of the ferric chloride and 1 mole of the ether.

Reaction of Aluminum Chloride and Ferric Chloride with Triphenylmethyl Acetate.—Fifteen and one-tenth grams (0.05 mole) of triphenylmethyl acetate was treated in carbon disulfide solution with 6.6 g. (0.05 mole) of aluminum chloride in the same manner as in the case of triphenylmethyl ethyl ether. Nine grams of solid was obtained from the carbon disulfide solution, which on crystallization from petroleum ether yielded triphenylchloromethane. The residue in the reaction flask was decomposed with ice and an additional four grams of triphenylchloromethane was collected. An experiment was carried out similarly in which ferric chloride was used instead of aluminum chloride. Triphenylcarbinol was the product of the reaction.

Summary

1. The products of the pyrolysis of ethers of the type $(C_6H_5)_3C–OR$ were shown to be triphenylmethane and either an aldehyde or ketone, formed as the result of the loss of hydrogen by the OR group. The temperatures at which decomposition occurs were found to vary with the structure of the alkyl radical. Change in this radical resulted in an alteration of the lability of the bond between oxygen and the triphenylmethyl group. If the ethers are arranged according to decreasing stability toward heat, the alkyl radicals fall in the order methyl, ethyl, *n*-butyl, *iso*amyl, *β*-phenylethyl, *n*-propyl, *iso*butyl, benzyl, *iso*propyl, *sec.*-butyl. This order, with one exception, is the same as that obtained as the result of the study of the lability of the oxygen bond in alcohols (H–OR) as measured by the velocity of the reactions between the latter and *p*-nitrobenzoyl chloride. The two independent methods based on different types of reactions lead to the same conclusion as to the effect of radicals on the lability of bonds.

2. The temperatures required to cause the decomposition of the ethers were found to be markedly affected by catalytic agents. The selective

action of catalyst in breaking a particular bond was shown by the action of aluminum chloride and ferric chloride on triphenylmethyl acetate: the former produced triphenylchloromethane and the latter triphenylcarbinol.

3. Aluminum chloride reacts with triphenylmethyl ethyl ether in the cold, the products being $(C_6H_5)_3CCl$ and $Al(OC_2H_5)_2Cl$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

SOME HIGHLY PHENYLATED ALIPHATIC NITRO COMPOUNDS

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Although aliphatic nitro compounds have been the subject of many excellent investigations they still present a number of problems of theoretical interest. Little is known about the factors that influence the stability of the *aci* forms and the manner in which these pass into true nitro compounds, the extent to which the nitro and iso-nitro groups are modified by conjugation with ethylenic linkages, the intimate structure of nitro and iso-nitro groups. Since the life of the *aci* forms of simple nitro compounds is short, we have studied a number of phenylated derivatives in the expectation that the saturated representatives would be more tractable than the simpler compounds which have been studied heretofore, and that a comparison between the unsaturated members and the correspondingly phenylated carbonyl compounds would be instructive.

Our starting materials were nitro styrene and nitro stilbene. Owing to the ease with which it polymerizes, the former proved comparatively useless for our purpose, but the latter enabled us to prepare and study still more highly phenylated saturated and unsaturated nitro compounds. It reacts with phenyl magnesium bromide as readily as does the corresponding unsaturated ketone—benzaldesoxybenzoin—and like the unsaturated ketone it forms, apparently exclusively, a 1,4-addition product

$$\underset{\text{I}}{C_6H_5CH{=}C(C_6H_5)NO_2} \longrightarrow \underset{\text{II}}{(C_6H_5)_2CHC(C_6H_5){=}N(OMgBr)O} \longrightarrow$$

$$\underset{\text{III}}{(C_6H_5)_2CHC(C_6H_5){=}N(OH)O}$$

From the product of the Grignard reaction it is easy to secure the corresponding *aci* nitro compound. In its chemical reactions this iso-nitro compound closely resembles its simpler analogs; it forms sodium, copper and silver salts; it gives the characteristic color reactions with ferric chloride and phenyl diazonium chloride; and it reacts with bromine in the usual manner. But this iso-nitro compound differs much from its simpler analogs both in the degree and in the quality of its instability. It can be isolated without too much difficulty in the form of a crystalline solid,