lization from petroleum ether (b.p. 38–56°) gave colorless needles, m.p. 81–82°. The infrared spectrum showed peaks at 2500–3000 (broad), 1680, 1430, 1250, and 930 cm.$^{-1}$.

2-Phenylpyrrolo[1,2-*c*]hydantoin (6).—A mixture of 5.60 g. (0.03 mole) of 2-pyrrolecarboxanilide (2),[4] 7.14 g. (0.06 mole) of phenyl isocyanate, and 1.50 g. of triethylamine (distilled from lithium aluminum hydride) was heated at 60–70° for 22 hr. The resulting solid was ground into a powder which was washed with petroleum ether, dried, and stirred thoroughly with 800 ml. of chloroform. The insoluble material (6.1 g., 95%) was shown to be N,N′-diphenylurea (3) by comparison of its infrared spectrum with that of an authentic sample. Crystallization from ethyl alcohol gave colorless needles, m.p. 238–240°. A mixture melting point with an authentic sample showed no depression. Evaporation of the filtrate to dryness under reduced pressure yielded 5.9 g. (92%) of 2-phenylpyrrolo[1,2-*c*]hydantoin (6). Crystallization from ethyl alcohol gave colorless crystals, m.p. 226–227°.

Anal. Calcd. for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20; mol. wt., 212. Found: C, 68.09; H, 3.89; N, 13.38; mol. wt., 208.

2-Phenylpyrrolo[1,2-*c*]hydantoin (6) from the Potassium Salt of 2-Pyrrolecarboxanilide (2) and Phosgene.—A solution of 9.30 g. (0.05 mole) of 2[4] in 70 ml. of tetrahydrofuran was stirred at reflux with 1.95 g. (0.05 g.-atom) of potassium until all of the metal had reacted. After dilution with 100 ml. of tetrahydrofuran, the temperature was brought down to 0° and 7 g. of phosgene dissolved in 100 ml. of tetrahydrofuran at 0° was added in the course of 15 min. The cooling bath was then removed, and the mixture was stirred overnight. After removal of the solvent under reduced pressure, the residue was treated with 250 ml. of ethyl alcohol, and the mixture was filtered. Crystallization of the precipitate from ethyl alcohol yielded 2.7 g. of 6, melting at 225–226°.

Similar treatment of the dipotassium salt of 2 (from 9.30 g. of 2 and 3.90 g. of potassium) afforded 3.75 g. of 6, m.p. 225–226°.

2-Phenylpyrrolo[1,2-*c*]hydantoin (6) from the Potassium Salt of 2-Pyrrolecarboxanilide (2) and Phenyl Isocyanate.—To a solution of the potassium salt of 2, made from 4.65 g. (0.025 mole) of 2, 0.97 g. (0.025 g.-atom) of potassium, and 20 ml. of tetrahydrofuran, was added 5.95 g. (0.050 mole) of phenyl isocyanate in one portion. The mixture was stirred for a few minutes, mixed with petroleum ether, and filtered. The precipitate was treated with water and the resulting solid was dried and stirred with an excess of chloroform. Filtration and evaporation of the filtrate to dryness yielded a solid which, on recrystallization from ethyl alcohol, gave 1.6 g. of 6, m.p. 225–227°.

Hydrolysis of 2-Phenylpyrrolo[1,2-*c*]hydantoin (6).—A mixture of 1 g. of 6, 2 g. of potassium hydroxide, and 20 ml. of ethyl alcohol was heated until a clear solution had been obtained. Cooling, dilution with cold water, and filtration gave 0.75 g. of a solid, m.p. 153–154°. This product was identified as 2-pyrrolecarboxanilide (2) by mixture melting point and comparison of the infrared spectra.

Reaction of 2-Phenylpyrrolo[1,2-*c*]hydantoin (6) with Aniline.—A mixture of 2 g. of 6 with 20 ml. of aniline was refluxed for 14 hr., cooled, and diluted with an excess of chloroform. Filtration afforded 1.65 g. of a solid, the infrared spectrum of which was identical with that of an authentic sample of N,N′-diphenylurea (3). Crystallization from ethyl alcohol gave colorless crystals, m.p. 238–239°, not depressed by an authentic sample of 3. The chloroform filtrate was washed with cold, dilute hydrochloric acid, then with water, and was evaporated to dryness under reduced pressure. Washing of the residue with petroleum ether yielded 1.30 g. of a solid, the infrared spectrum of which was identical with that of an authentic sample of 2. Crystallization from benzene–methanol (85:15) gave pure 2-pyrrolecarboxanilide, m.p. 153–154°.

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Cleavage of α,β-Unsaturated Ethers by Diisobutylaluminum Hydride

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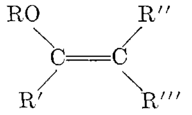
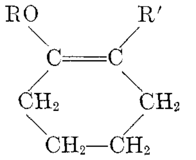
Only a few reports have appeared in the literature on the reaction of α,β-unsaturated ethers with organometallic compounds.

The alkyl vinyl ethers are cleaved[1] by lithium alkyls, yielding acetylene and aliphatic alcohols; α-ethoxystyrene and some related compounds are cleaved[2] by Grignard reagents, yielding olefins. Diisobutylaluminum hydride, at 30–35°, cleaves[3] vinyl *n*-butyl ether, forming ethylene.

In connection with some investigations on the stereospecific polymerization of vinyl ethers,[4] we have examined the reaction between diisobutylaluminum hydride and α,β-unsaturated ethers of the types I, II, and III.



Ia, R = alkyl; R′, R″, R‴ = H
b, R, R″ (or R‴) = alkyl;
R′, R‴ (or R″) = H
c, R, R″, R‴ = alkyl; R′ = H



II, R = alkyl; R′ = H

$$RO—C{\equiv}C—R'$$

III, R, R′ = alkyl

In agreement with the results obtained by Zakharkin and Savina in the case of *n*-butyl vinyl ether,[3] by mixing at 25° isobutyl vinyl ether or 2-ethylhexyl vinyl ether with diisobutylaluminum hydride, a remarkable temperature increase and a rapid gas evolution took place, the gas evolved being practically pure ethylene. At the same time, diisobutylaluminum isobutoxide, or diisobutylaluminum 2-ethylhexyloxide, was formed. However, the reaction did not occur when the temperature of the reagents was kept below 20°.

A smooth cleavage of isobutyl vinyl ether by diisobutylaluminum hydride occurred also in the presence of an excess of triisobutylaluminum, but temperatures higher than 50° were required.

1-Methyl-2-ethoxyethylene and 1-propyl-2-ethoxyethylene (Ib) (both mixtures of *cis* and *trans* isomers), when treated in isooctane solution at 50–100° with diisobutylaluminum hydride, yielded propylene or 1-

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[1] K. E. Piotrovskiĭ and M. P. Stotskaya, *Dokl. Akad. Nauk SSSR*, **135**, 868 (1960).

[2] C. M. Hill, R. A. Walker, and M. E. Hill, *J. Am. Chem. Soc.*, **73**, 1663 (1951).

[3] L. I. Zakharkin and L. A. Savina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 444 (1959).

[4] In a series of polymerization experiments of some vinyl ethers, carried out in the presence of $TiCl_3$ and an excess of $Al(i\text{-}C_4H_9)_3$ at 100°, small quantities of polyethylene were obtained. On the basis of previous[3] and present findings, the above result can be accounted for admitting that, because of the presence of $Al(i\text{-}C_4H_9)_2H$ deriving from $Al(i\text{-}C_4H_9)_3$ by thermal decomposition, the monomer decomposed giving rise to ethylene which then polymerized.

pentene, respectively, and diisobutylaluminum ethoxide.

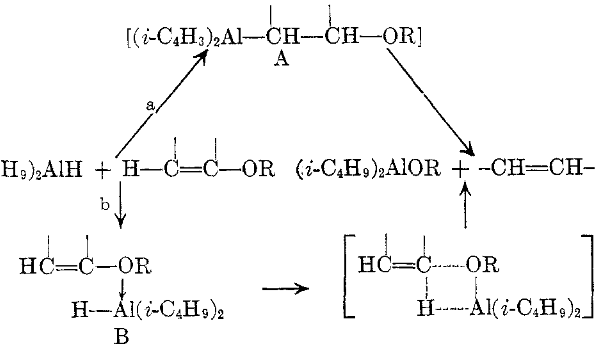
Under the experimental conditions used, owing to the reaction[5] of olefins with diisobutylaluminum hydride, not more than 40–50% of the theoretical amount of the olefins was recovered. In fact, starting from isobutyl vinyl ether and 1-methyl-2-ethoxyethylene, fairly large quantities of ethane or propane, respectively, were found among the hydrolysis products of the aluminum compounds.

From 1-ethoxy-cyclohexene (II), cyclohexene was obtained; on the contrary, no reaction was noticed in the case of 1-methyl-1-ethyl-2-ethoxyethylene (Ic), the ether being quantitatively recovered by distillation from the mixture with diisobutylaluminum hydride.

Under conditions similar to those adopted for the alkenyl ethers, 1-methoxy-1-hexyne (III) gave 1-hexyne and diisobutylaluminum methoxide, a result which closely resembles that obtainable from 1-alkyl-2-alkoxyethylenes.

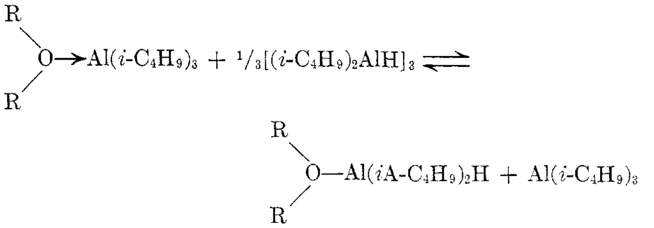
With regard to the cleavage of alkenyl and cycloalkenyl ethers, both the mechanisms a and b reported in Scheme I can be proposed. The former involves the initial addition of the diisobutylaluminum hydride to the unsaturated ether followed by a β elimination of the type observed in β-chloroalkylborons,[6] and postulated in the reaction between magnesium and β-halo ethers[7] or β-haloamines.[8] The latter, which is analogous to the mechanism proposed[2,9] for the cleavage of unsaturated ethers by Grignard reagents, involves the formation of a coordination complex (B) followed by elimination of the olefin through a four-center transition state.

SCHEME I



All the attempts to isolate the adduct (A) have failed. Cautiously adding isobutyl vinyl ether to diisobutylaluminum hydride at 0° and decomposing the organometallic compound with methanol after keeping the solution at 20° yielded no trace of the saturated ether which should arise from the methanolysis of the adduct A.

On the other hand, taking in account the fact that in the presence of an excess of $Al(i\text{-}C_4H_9)_3$ the complex B can be present only in very small amount, as the equilibrium should be completely displaced toward the left,[10]



$$R_2O \rightarrow Al(i\text{-}C_4H_9)_3 + {}^1/_3[(i\text{-}C_4H_9)_2AlH]_3 \rightleftharpoons R_2O—Al(iA\text{-}C_4H_9)_2H + Al(i\text{-}C_4H_9)_3$$

the occurrence of cleavage of isobutyl vinyl ether under the above conditions seems to be more satisfactorily explained on the basis of mechanism a, although mechanism b cannot be completely ruled out. In fact, traces of complex B in equilibrium with other species could be sufficient to give rise to a slow cleavage of the unsaturated ether.

Finally, the failure of the reaction in the case of 1-methyl-1-ethyl-2-ethoxyethylene is in our opinion more consistent with mechanism a than with mechanism b.[11] In this case, in fact, the addition would lead to a tertiary group bound to aluminum and it is known[12] that this type of addition is prevented by steric hindrance.

In conclusion, although mechanism b cannot be discarded on the basis of the present experimental results, at the present stage of our research, mechanism a, which has been already suggested[3] for the cleavage of vinyl n-butyl ether by diisobutylaluminum hydride, appears to us more probable.

Experimental Section

Gas chromatographic qualitative and quantitative analysis were performed with helium as carrier gas on a Perkin-Elmer Model 154 chromatograph equipped with a Perkin-Elmer A column (diisodecyl phthalate on Celite). Product identification was made by comparison of retention times of known compounds and confirmed by infrared analysis. The composition of the gas mixture was calculated by the area under the peak method, the peak areas being determined by half-width and peak-height measurements.

The infrared spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer.

Materials.—The vinyl ethers were prepared by vinylation[13] of the corresponding alcohols with acetylene. 1-Methyl-2-ethoxyethylene, 1-propyl-2-ethoxyethylene, 1-methyl-1-ethyl-2-ethoxyethylene, and 1-ethoxycyclohex-1-ene were prepared by pyrolysis in the presence of p-toluensulfonic acid of the corresponding acetals, according to the procedure of Farina, Peraldo, and Bressan.[14]

The purification of the above unsaturated ethers was carried out immediately before the experiments by refluxing the ethers several hours on Na metal, or on a liquid Na–K alloy, and subsequent distillation.

1-Methoxy-1-hexyne was prepared by the method of Nooi and Arens.[15]

Diisobutylaluminum hydride was prepared by heating[16] purified triisobutylaluminum[17] at 120–130° for 2.5 hr., under

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(5) K. Ziegler, *Angew. Chem.*, **68**, 721 (1956).

(6) M. F. Hawthorne and J. A. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

(7) R. Tallman, *ibid.*, **56**, 126 (1934).

(8) A. N. Nesmeyanov, R. K. Freĭdlina, and E. I. Kan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 531 (1950).

(9) C. M. Hill, L. Haynes, D. E. Simons, and M. E. Hill, *J. Am. Chem. Soc.*, **75**, 5408 (1953).

(10) E. G. Hoffmann and G. Schomburg, *Z. Elektrochem.*, **61**, 1101 (1957).

(11) According to the suggestion of a referee, whom we thank, it is also conceivable that 1-methyl-1-ethyl-2-ethoxyethylene is not cleaved by $Al(i\text{-}C_4H_9)_2H$, because a four-center transition state (mechanism b) would demand in this case that a tertiary carbon atom sustain undesirable negative charge.

(12) H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 217.

(13) W. Reppe, *et al.*, *Ann.*, **601**, 81 (1957).

(14) M. Farina, M. Peraldo, and G. Bressan, *Chim. Ind.* (Milan), **42**, 967 (1960).

(15) J. R. Nooi and J. F. Arens, *Rec. trav. chem.*, **78**, 284 (1959).

(16) K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Steudel, *Ann.*, **629**, 53 (1960).

(17) Kindly supplied by the Montecatini Co., Milan, Italy.

20-mm. pressure. The monohydride content in the product, calculated on the basis of the amount of isobutylene evolved during the reaction, was about 95%.

Isooctane (Phillips Petroleum Co., pure grade), used as solvent, was purified by distillation on Na metal under dry nitrogen.

Reaction of Alkyl Vinyl Ethers with Diisobutylaluminum Hydride.—Isobutyl vinyl ether (2.37 g., 0.0237 mole, b.p. 83.5°, $n^{20}\text{D}$ 1.3966) was added under nitrogen, at 25°, to 3.90 g. (0.0275 mole) of diisobutylaluminum hydride. The addition caused a rapid gas evolution which ceased after a few minutes. In order to complete the reaction, the mixture was heated at 120° for 1.5 hr. After cooling the liquid product was diluted with 15 ml. of anhydrous diethyl ether and, cautiously adding drop by drop, 1.9 ml. of water.

The gases evolved during the hydrolysis, collected and analyzed by gas chromatography, contained 0.045 mole of isobutane and 0.009 mole of ethane. Small quantities of isobutylene and *n*-butane were also present.

By extracting the hydrolysis products with ether, 1.58 g. (0.0214 mole) of isobutyl alcohol was recovered.

The gases evolved during the reaction between diisobutylaluminum hydride and isobutyl vinyl ether were collected and analyzed by infrared spectroscopy and gas chromatography. The analyses revealed that the gases consisted almost exclusively of ethylene (0.007 mole, yield 29%).

In other experiments carried out in the presence of $\text{Al}(i\text{-C}_4\text{H}_9)_3$ [moles of $\text{Al}(i\text{-C}_4\text{H}_9)_3$/moles of vinyl ether = 1.0 or 5.1], no gas evolution has been noticed below 50 or below 70°, respectively.

Using 2-ethylhexyl vinyl ether (0.0125 mole), 0.0085 mole of ethylene was recovered (68% yield).

Reaction of 1-Methyl-2-ethoxyethylene with Diisobutylaluminum Hydride.—A solution of 2.20 g. (0.0256 mole) of 1-methyl-2-ethoxyethylene (b.p. 69–75°, $n^{20}\text{D}$ 1.3980) in 10 ml. of isooctane was heated under nitrogen at 50° and 5.9 g. (0.042 mole) of diisobutylaluminum hydride was then added with stirring over a period of 1 hr. During the addition, the temperature was gradually raised to 100°. Unreacted alkenyl ether, which distilled, was again introduced into the reaction flask after cooling to 50°, and the reaction was completed, maintaining the mixture at 50° for 1 hr. and then refluxing for 0.5 hr.

The evolved gas contained 0.011 mole of propylene (44% yield).

By hydrolysis of the residual liquid, 0.005 mole of propane was obtained.

Reaction of 1-Propyl-2-ethoxyethylene with Diisobutylaluminum Hydride.—Diisobutylaluminum hydride (4.26 g., 0.0300 mole) was added with stirring, over 1 hr., to a boiling solution of 2.3 g. (0.020 mole) of 1-propyl-2-ethoxyethylene (b.p. 121.5–122.5°, $n^{20}\text{D}$ 1.4138) in 10 ml. of isooctane. Two liquid fractions were collected, weighing 0.45 and 0.88 g., respectively. Gas chromatographic analysis showed that the first fraction was predominantly 1-pentene, and the second fraction was 80% isooctane and 20% 1-pentene (35% yield of 1-pentene).

Reaction of 1-Ethoxycyclohexene with Diisobutylaluminum Hydride.—Diisobutylaluminum hydride (16.5 g., 0.116 mole) was added with stirring, over 1.5 hr., to a boiling solution of 7.21 g. (0.0572 mole) of 1-ethoxycyclohexene [b.p. 61° (18 mm.), $n^{25}\text{D}$ 1.4552] in 30 ml. of isooctane. The addition rate and heating were so regulated as to achieve a slow distillation of the reaction product. Heating was continued until *ca.* 31 ml. of distillate was obtained. Redistillation through a spiral-packed column gave the following fractions: (A) 1.68 g., b.p. 88–94°, $n^{25}\text{D}$ 1.4158; (B) 2.96 g., b.p. 94–99°, $n^{25}\text{D}$ 1.3985; and (C) 2.20 g., b.p. 99–99.5°, $n^{25}\text{D}$ 1.3901. Gas chromatographic and infrared analysis indicated that such fractions consisted almost exclusively of cyclohexene and isooctane, the total amount of the former being 1.5 g. (0.018 mole) (32% yield).

Reaction of 1-Methoxy-1-hexyne with Diisobutylaluminum Hydride.—Diisobutylaluminum hydride (7.19 g., 0.0506 mole) was added over 1 hr. to a stirred solution of 3.80 g. (0.0339 mole) of 1-methoxy-1-hexyne [b.p. 75° (77 mm.), $n^{20}\text{D}$ 1.4240] in 10 ml. of anhydrous isooctane. A slow distillation was achieved during the addition of the hydride by careful heating. Redistillation through a spiral-packed column gave a fraction, b.p. 71–75°, $n^{25}\text{D}$ 1.3942, which was 80% 1-hexyne, as shown by gas chromatographic and infrared analysis (32% yield).

Attempted Synthesis of the Adduct (A) between Diisobutylaluminum Hydride and Isobutyl Vinyl Ether.—Isobutyl vinyl ether, 4.48 g. (0.0448 mole), $n^{20}\text{D}$ 1.3966, was added at 0° with stirring to an equimolar amount of diisobutylaluminum hydride dissolved in 10 ml. of isooctane. The solution was then slowly heated and kept at 20° for 1 hr. No gas evolution was observed.

Cautious addition at 10–15° of an excess of pure methanol and subsequent distillation yielded a mixture which, as shown by gas chromatographic analysis, consisted of methanol, isooctane, traces of isobutyl alcohol, and isobutyl vinyl ether. The peak given by the last compound disappeared completely from the chromatogram after refluxing the mixture with dilute sulfuric acid.

Studies of Quinoid Structures. VII.[1] Reaction of Benzonitrile Oxide with *o*-Quinones

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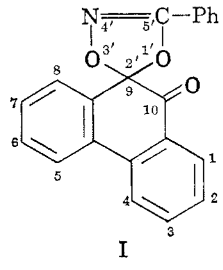
The 1,3-dipolar addition of nitrile oxides with *p*-quinones was first observed by Quilico, *et al.*,[2] to lead to condensed isoxazoles. The formation of 1,3,4-dioxazoles by the addition of nitrile oxides to suitably activated carbonyl groups has been reported by Huisgen and Mack.[3] In this Note we describe the reaction of benzonitrile oxide with *o*-quinones to give dioxazoles I and II and the reaction with *o*-quinonimines to give oxadiazoles. The yellow product from phenanthraquinone was shown to be the 1:1 adduct, namely 9(10)-phenanthrone-10(9)-spiro(4′,5′-dehydro-5′-phenyl)-1′,3′,4′-dioxazole (I). The infrared($\nu_{\text{C=O}}$ at 1689 cm.$^{-1}$ [4] and $\nu_{\text{N-O}}$ at 1345 cm.$^{-1}$) and n.m.r. data (τ = 1.8–2.7 p.p.m.), characteristic for aromatic protons only, are consistent with this structure. The adduct gave a 2,4-dinitrophenylhydrazone but no product with *o*-phenylenediamine (*i.e.*, absence of *o*-quinoid structure). Oxidation of I with chromic anhydride gives phenanthraquinone.



I

The reactivity of one carbonyl group only in phenanthraquinone has been observed in several other cases: *e.g.*, (i) with nitromethane it gives 9-keto-10-nitromethyl-9,10-dihydro-10-phenanthrol,[5] (ii) with diazo-

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[1] Part VI: W. I. Awad, A. K. Fateen, and M. A. Zayed, *J. Org. Chem.*, **26**, 2112 (1961).

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[3] R. Huisgen and W. Mack, *Tetrahedron Letters*, 583 (1961); see also *Angew. Chem.*, **75**, 614 (1963).

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