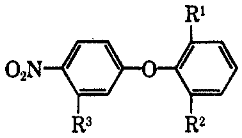
TABLE I

2,6-DIALKYLPHENYL 4-NITROPHENYL ETHERS



No.	R¹	R²	R³	Mp, °C or bp (mm)	Yield, %	λ_{max}, mμ (ε)	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1	Me	Me	H	61–62	82	300 (15,300)	$C_{14}H_{13}NO_3$	69.12	5.39	5.76	69.29	5.43	5.98
2	*i*-Pr	*i*-Pr	H	92–93	75	300 (13,200)	$C_{18}H_{21}NO_3$	72.21	7.07	4.68	72.11	6.81	4.61
3	*sec*-Bu	*sec*-Bu	H	170 (5)	70	300 (15,300)	$C_{20}H_{25}NO_3$	73.36	7.70	4.28	73.38	7.70	4.42
4	Me	*t*-Bu	H	96	20	302 (12,000)	$C_{17}H_{19}NO_3$	71.56	6.71	4.91	71.70	6.61	5.15
5	*i*-Pr	*i*-Pr	Me	90–91	60	296 (6,000)	$C_{19}H_{23}NO_3$	72.82	7.40	4.47	73.06	7.26	4.59
6	*sec*-Bu	*sec*-Bu	Me	63–64	62	296 (7,500)	$C_{21}H_{27}NO_3$	73.87	7.97	4.10	74.11	7.65	4.12

tion) and extracted with chloroform.[13] The chloroform layer was washed twice with dilute hydrochloric acid and twice with water. After drying, the chloroform was removed under reduced pressure and the residue distilled under vacuum, the fraction distilling above 160° (5 mm) being collected. The resultant pale yellow oil was crystallized from ethanol.

5-Chloro-2-nitrotoluene was prepared by a modification of the method of Wibaut.[14] Fuming nitric acid (200 g, *d* 1.52) was added dropwise with stirring during 90 min to *m*-chlorotoluene (50 g), maintaining the temperature below 5°. After stirring for a further 2 hr at 0°, the mixture was refrigerated overnight, then poured onto crushed ice. The precipitated oil was extraced with ether and washed four times with 10% sodium bicarbonate solution and twice with water. After drying ($CaCl_2$), the ether was removed under reduced pressure to give 60 g of nitrated product. The 5-chloro-2-nitrotoluene predominated in the first yellow fractions obtained by elution from an acid-washed alumina column with 6% benzene in petroleum ether (bp 40–60°). The crude isomeric 3-chloro-4-nitrotoluene was present in later fractions. The 5-chloro-2-nitrotoluene obtained in this manner (40 g) contained a small proportion of *m*-chlorotoluene as indicated by thin layer chromatography and nmr spectroscopy, but could be used as such for the diphenyl ether condensation reaction. For analytical purposes a pure sample was obtained by crystallization from ethanol at low temperature: mp 24° (lit.[14] mp 24.9°).

Anal. Calcd for $C_7H_6ClNO_2$: C, 48.97; H, 3.49; N, 8.16. Found: C, 49.00; H, 3.50; N, 7.99.

2,6-Dialkylphenyl 3-methyl-4-nitrophenyl ethers (5, 6) were prepared in the same manner as **1–4**, substituting 5-chloro-2-nitrotoluene for the *p*-chloronitrobenzene. Both were isolated as crystalline solids from ethanol, following vacuum distillation.

2,6-Di-*t*-butyl-4-(*p*-nitrophenyl)phenol (7).—A mixture of 2,6-di-*t*-butylphenol (24.7 g, 0.12 mole), *p*-chloronitrobenzene (15.7 g, 0.10 mole), potassium hydroxide (5.6 g, 0.10 mole), and dimethyl sulfoxide (150 ml) was heated at 90° with stirring for 24 hr. The resulting dark blue solution was poured into dilute hydrochloric acid and extracted with chloroform. After drying, the chloroform was removed under reduced pressure and the dark oil remaining was crystallized three times from ethanol to yield (68%) the biphenyl analog **7**: mp 155–156°; $\lambda_{max}^{C_2H_5OH}$ 346 mμ (ε 15,100).

Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.36; H, 7.70; N, 4.28. Found: C, 73.70; H, 7.52; N, 4.55.

Registry No.—**1**, 15158-13-1; **2**, 15158-14-2; **3**, 15138-26-8; **4**, 15138-27-9; **5**, 15138-28-0; **6**, 15138-29-1; **7**, 15138-30-4.

Acknowledgment.—The authors are indebted to Mr. A. Ishimoto for the preparation of 5-chloro-2-nitrotoluene.

[13] 2,6-Diisopropylphenyl 4-nitrophenyl ether solidified when the reaction mixture was poured into water. The precipitate was crystallized from ethanol.

[14] W. P. Wibaut, *Rec. Trav. Chim. Pays-Bas*, **32**, 288 (1913).

The Reaction of Tetrakis(dimethylamino)titanium with Tetramethyloxamide

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It has been reported that titanium tetramides aminate carboxylic acid derivatives, forming vinylidene diamines or *gem*-triamines.[1,2] From consideration of these results it would be predicted that oxalic acid derivatives would be converted by titanium amides into hexaminoethanes, presently an unknown class of compound. We have now found this not to be the case; instead, carbon–carbon bond cleavage accompanies amination in the oxalates.

Tetrakis(dimethylamino)titanium (**1**) reacts with 2 moles of tetramethyloxamide[3] (**2**) very slowly at room temperature and more rapidly at 80°, either neat or in solution (ether, benzene, or cyclohexane–dioxane) to form 2 moles of tetramethylurea (**3**), 1 mole of tris(dimethylamino)methane[2] (**4**), and a deep red, ill-defined substance containing complexed titanium. However, when **1** and **2** are allowed to react in the presence of excess dimethylamine, the stoichiometry given in eq 1 is observed. Titanium dioxide precipitates under these conditions.

$$Ti(NMe_2)_4 + 2(Me_2NCO)_2 \xrightarrow{Me_2NH} TiO_2 + 2(Me_2N)_2CO + 2(Me_2N)_3CH \quad (1)$$

When the course of the reaction is followed by nmr spectroscopy, a resonance not attributable to any of the reactants or products appears as the reactants begin to disappear, and then disappears after the reactants are used up and products appear. This resonance is presumed to be due to the presence of an intermediate in the amination reaction; its chemical shift (τ 7.60 in ether) is consistent with a structure containing two or more hindered dimethylamino

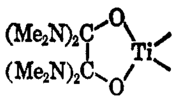
[1] H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, **88**, 850 (1966).

[2] H. Weingarten and W. A. White, *J. Org. Chem.*, **31**, 2874 (1966).

[3] Other oxalic acid derivatives would be converted into this amide by **1** before further reaction took place.[2]

groups on a single carbon atom [*cf.* $C(NMe_2)_4$, τ 7.4,[4] $HC(NMe_2)_3$, 7.7[2]].

It is reasonable to postulate that the reaction proceeds *via* initial coordination of **2** with **1**, possibly followed by transfer of two dimethylamino ligands from titanium to carbon to form an intermediate 1,1,2,2-tetrakis(dimethylamino)-1,2-ethanediolato complex (**5**). This complex can then slowly undergo C–C and Ti–O bond scission (perhaps by displacement) with expulsion of **3**, followed by rapid proton abstraction from **2** or dimethylamine (or perhaps solvent) to form a complex containing the group $(Me_2N)_2CH\text{-}O\text{-}Ti$. Transfer of a dimethylamide from Ti to C then gives **4**.



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With dimethylamine as the proton source, the species remaining after displacement of **4** will be formally $TiO(NMe_2)_2$ which can continue the reaction either by disproportionation[5] into **1** and TiO_2 or by itself. However, if **2** (or solvent) is the proton source, only one dimethylamide then remains per titanium atom, and this one dimethylamide will be sufficient only to effect the transformation of **2** into **3**, leaving behind the complex species containing titanium, oxygen, carbon, and (from their color) nitrogen which are observed.

There is not enough evidence available to suggest whether the failure to form an hexaminoethane is the result of inherent lability of that product or the result of steric, electronic, or other factors operating in the amination reaction, but it is clear that the result sets one limit on the scope of this very useful, novel reaction.

Experimental Section

Tetramethyloxamide and tetrakis(dimethylamino)titanium were prepared by W. A. White by standard methods.[2,6] Benzene solvent (Mallinckrodt AR) was distilled from calcium hydride, and ether and dioxane (both Mallinckrodt AR) from potassium-benzophenone ketyl, all in a nitrogen atmosphere. Cyclohexane from Matheson was distilled from concentrated sulfuric acid and washed over "activity I" neutral alumina. Dimethylamine was Eastman "White Label," used as received.

Nmr spectra were obtained using either a Varian A-60 or A-56/60 spectrometer with tetramethylsilane (TMS) as internal standard. Infrared spectra were obtained on neat films using a Beckman IR-4 spectrophotometer.[6]

All transfers of reagents were carried out in an efficient, nitrogen-filled drybox.

Nmr scale reactions were carried out by making up separate solutions of the reactants to known concentrations (w/v) and then mixing the appropriate quantities of the standard solutions. Relative concentrations were checked by integration of nmr spectra. In this fashion reactions of initial relative concentrations of 4:1, 2:1, and 1:1 oxamide–Ti were followed in benzene solvent. (Total reaction time was 4 days at 80°.)

Larger scale reactions were carried out by mixing appropriate quantities (0.01 mole of limiting reagent) of the reagents, adding solvent, and heating at reflux until the reaction was complete. (The reactions were monitored by nmr.) In this fashion 2.5:1 oxamide–Ti reactions were carried out in cyclohexane–dioxane (24 hr at 90°) and ether–dimethylamine (almost complete in 16 days at *ca.* 25°). The products were isolated by stripping off solvent and distilling at reduced pressure.

Tetramethylurea (**3**) was identified by its nmr and infrared spectra. The triaminomethane (**4**) was identified by its characteristic nmr spectrum[2] and the superposability of the infrared spectra of an authentic mixture of **3** and **4** with that exhibited by a mixture of the two obtained by distillation of one reaction mixture.

Registry No.—**1**, 3275-24-9; **2**, 1608-14-6.

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[4] H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, **88**, 2885 (1966).

[5] H. Weingarten and J. R. Van Wazer, *ibid.*, **87**, 724 (1965).

[6] We wish to thank Mr. W. A. White for the preparation of these compounds and Mrs. N. K. Edelman for the measurement of spectra.

The Reaction of Unsaturated Ketones with Polynitro Addends

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There has been relatively little work published on the reactions of divinyl ketone (I) despite its position as the simplest compound containing the dienone system. In a recent paper, deJongh and Winberg[1] described the use of I in the synthesis of dispiro ketones, Arbuzov, Klimov, and Korolev[2] have prepared the interesting compound bis(5-norbornen-2-yl) ketone by a Diels–Alder reaction of divinyl ketone with cyclopentadiene, and Nazarov and coworkers have studied divinyl ketone and its derivatives as synthetic intermediates.[3]

Because of the potential of I as an acceptor molecule in Michael reactions, the available preparative methods were examined. Divinyl ketone has been prepared by the dehydrochlorination of di(β-chloroethyl) ketone,[4] by the thermal decomposition of di(β-methoxy) ketone,[5] by the oxidation of divinylcarbinol,[6] and by the thermal decomposition of the dihydrochloride salt of 1,5-bis(diethylamino)-3-pentanone.[7] The yields of pure ketone from all of these methods in this investigation were erratic and in general rather poor, ranging from about 5 to 25%. Since there is some evidence that the low yields may be due to the further reaction of divinyl ketone as it is formed,[6] attention was then directed toward the synthesis of ketals of I. The ketals should be stable to basic reaction conditions and to storage and yet should be a ready source of the unsaturated ketone.

The method of Garbisch for the preparation of cyclic dienone ketals[8] proved to be an easy and reliable method for the synthesis of 2,2-divinyl-1,3-dioxolane *via* bromination in ether of 2,2-diethyl-1,3-dioxolane (80% yield) followed by dehydrobromination with alcoholic caustic (60% yield). The ketal, as expected, was stable and could be readily hydrolyzed with dilute acid as required.

[1] H. A. P. deJongh and H. Winberg, *Tetrahedron*, **20**, 2553 (1964).

[2] Y. A. Arbuzov, W. M. Klimov, and S. M. Korolev, *Zh. Obshch. Khim.*, **32**, 3681 (1962).

[3] See I. N. Nazarov and S. I. Zav'yalov, *ibid.*, **23**, 1703 (1953), for pertinent references.

[4] J. Nelles, U. S. Patent 2,105,792 (January 18, 1938).

[5] I. N. Nazarov and I. V. Torgov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 419 (1946).

[6] S. F. Reed, *J. Org. Chem.*, **27**, 4116 (1962).

[7] G. S. Mironov, M. I. Farberov, and I. M. Orlova, *Zh. Obshch. Khim.*, **33**, 1512 (1963).

[8] E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2019 (1965).