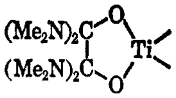
groups on a single carbon atom [*cf.* $C(NMe_2)_4$, τ 7.4,[4] $HC(NMe_2)_3$, 7.7[2]].

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 $(Me_2N)_2CH-O-Ti$. 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).

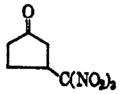
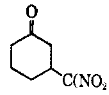
[6] S. F. Reed, *J. Org. Chem.*, **27**, 4116 (1962).

[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).

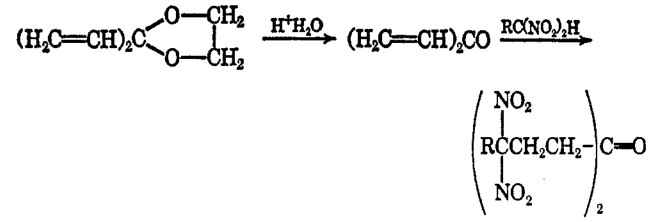
TABLE I

PROPERTIES OF POLYNITRO ADDUCTS OF UNSATURATED KETONES

Addend	Product[e]	Yield,[a] %	Mp, °C	Infrared maximum,[c] cm^{-1} -C=O	-NO$_2$	Calcd, % C	H	N	Found, % C	H	N
$(NO_2)_3CH$	$[(NO_2)_3CCH_2CH_2]_2C{=}O$[d]	70	121–122	1730	1594, 1355	21.88	2.10	21.88	22.25	2.26	21.86
$(NO_2)_2FCH$	$[(NO_2)_2FCCH_2CH_2]_2C{=}O$	51	77–78	1732	1595, 1317	25.45	2.42	16.97	25.85	2.42	16.69
$CH_3CH_2(NO_2)_2CH$	$[CH_3CH_2C(NO_2)_2CH_2]_2C{=}O$	70	97–98	1730	1565, 1372	37.71	5.14	16.00	37.99	4.99	16.02
$N{\equiv}C(NO_2)_2CH$	$[N{\equiv}C{\cdot}C(NO_2)_2CH_2CH_2]_2C{=}O$	25	104–105	1732	1600, 1297	31.39	2.32	24.41	...	...	23.79
$(NO_2)_2ClCH$	$[ClC(NO_2)_2CH_2CH_2]_2C{=}O$	...	86–87	1728	1586, 1305	23.14	2.20	15.42	23.11	2.23	15.14
$(NO_2)_3CH$		66	70	1733	1572, 1283	30.90	3.00	18.02	31.02	3.42	17.95
$(NO_2)_3CH$		87	53	1686[b]	1550,[b] 1281[b]	33.60	3.64	17.01	33.94	3.49	17.07

[a] Based upon unsaturated ketal. [b] Potassium bromide pellet. [c] Infrared data were obtained in methylene chloride solutions unless otherwise noted. [d] M. E. Hill, D. L. Ross, and C. L. Coon (personal communication, Stanford Research Institute) first prepared this compound by the addition of nitroform to divinyl ketone. [e] Respective registry no.: 15353-11-4, 15353-12-5, 15353-13-6, 15353-14-7, 15353-15-8, 15353-16-9, 15353-17-0.

For the present purpose, a prehydrolysis was not necessary. The slow addition of the acidic polynitro addend to an aqueous methanol solution of 2,2-divinyl-1,3-dioxolane gave good yields of the respective diadducts.



R = F, Cl, $-NO_2$, $-C{\equiv}N$, Et

The order of addition is important since the yields of the diadduct were markedly lower when the ketal was added to the addend solution, possibly because of the reaction of the polynitro carbanions with intermediate carbonium ions formed during the hydrolysis of the ketal.

The diadduct is apparently the main addition product of the reaction since the attempted preparation of the monoadduct of nitroform with the ketal led only to 1,1,1,7,7,7-hexanitro-4-heptanone, whatever the ratio of reactants. Presumably the inductive effect of the trinitromethyl group increases the rate of addition of the second group. Some credence is given to this viewpoint by a comparison of the carbonyl stretching frequencies for 2-pentanone (1717 cm^{-1}) and for 5,5,5-trinitro-2-pentanone (1736 cm^{-1}) in carbon tetrachloride.

The method was extended to the synthesis of 3-trinitromethylcyclohexanone and 3-trinitromethylcyclopentanone by the reaction of nitroform with 2-cyclohexenone ethylene ketal[8] and 2-cyclopentenone ethylene ketal.[8] An 87% yield of the cyclohexenone adduct was obtained by the addition of nitroform to an aqueous methanol solution of the ketal. For reverse addition the yield was lowered to 55%. However, a 64% yield of 3-trinitromethylcyclopentanone was obtained by the addition of the ketal to a solution of nitroform, while the reverse addition gave a comparable yield of 66%. In this case the rate of hydrolysis of the ketal is faster than the rate of formation of side products. This result is in keeping with the concept of *I* strain[9] wherein nonbonded interactions are relieved through the hydrolysis of the cyclopentanone ketal.

The compounds which were synthesized in this study and their properties are presented in Table I. No attempts were made to optimize the yields, which ranged from 25 to 87%. The method of preparation, while of limited general applicability, should be of value for preparing adducts of other reactive unsaturated ketones.

Experimental Section

Caution! Reasonable care and precautions should be taken when handling polynitro compounds. One attempted reaction of nitroform with a solution of impure divinyl ketone resulted in an explosion at refrigerator temperature.

2,2-Divinyl-1,3-dioxolane.—A solution of 2,2-bis(1-bromoethyl)1,3-dioxolane[10] (70.0 g, 0.243 mole) and 60.0 g (1.5 moles) of sodium hydroxide in 500 ml of methanol was refluxed for 72 hr. After cooling, the solution was poured into 1 l. of water saturated with sodium chloride which was then extracted with three 100-ml portions of pentane. After drying the combined extracts, the pentane was removed under reduced pressure. Distillation of the residue gave 18.4 g (60%) of 2,2-divinyl-1,3-dioxolane: bp 60° (43 mm); $n^{24}D$ 1.4228. The nmr (CCl_4) spectrum showed a complex multiplet centered at 5.5 ppm (vinyl protons) and a sharp singlet at 3.9 ppm (ethylene protons). The integration ratio was 6:4. The purity of the ketal was judged to be 99+% by gas chromatographic analysis.

Example of the Method for Preparation of Divinyl Ketone Adducts.—A solution of nitroform (9.06 g, 0.06 mole) in 5 ml of 50% aqueous methanol was added dropwise to an agitated solution of 2,2-divinyl-1,3-dioxolane (3.78 g, 0.03 mole) in 30 ml of 50% aqueous methanol. After stirring overnight, the crude orange product was isolated by filtration and recrystallized from ethanol to give 8.05 g (70%) of diadduct, mp 121–122°.

3-Trinitromethylcyclohexanone.—A solution of nitroform (6.0 g, 0.04 mole) in 10 ml of 50% aqueous methanol was added dropwise to a stirred solution of 2-cyclohexenone ethylene ketal (6.0 g, 0.04 mole) in 50 ml of 50% aqueous methanol. The mixture was agitated for 3 hr at room temperature. The lower yellow oily layer was then extracted with methylene chloride. The methylene chloride extracts were washed with water and dried. Evaporation of the solvent under reduced pressure yielded 8.0 g of a crude light yellow oil. Crystallization from hexane gave a white crystalline product in 87% yield: mp 53°;

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(9) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265.

(10) The dibromo compound was prepared in 80% yield by bromination of an ethereal solution of 2,2-diethyl-1,3-dioxolane following the general directions of Garbisch.[8]

nmr δ CCl_4 3.50 (1 H, broad methine multiplet), 1.8–2.7 (8 H, complex multiplet for the ring methylene protons).

3-Trinitromethylcyclopentanone.—A solution of 2-cyclopentenone ethylene ketal (5.0 g, 0.04 mole) in 10 ml of 50% aqueous methanol was added to a solution of nitroform (6.0 g, 0.04 mole) in 50 ml of 50% aqueous methanol. The title compound was isolated and purified in the same manner as described for 3-trinitromethylcyclohexanone. The yield was 64%: mp 70°; nmr δ CCl_4, 3.9 (1 H, broad methine multiplet), 2.5 (6 H, multiplet for the ring protons).

Registry No.—2,2-Divinyl-1,3-dioxolane, 15353-18-1.

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Electron-Impact Fragmentations of $\Delta^{1(7)}$-Menthenone-2 and $\Delta^{8(9)}$-Menthenone-2

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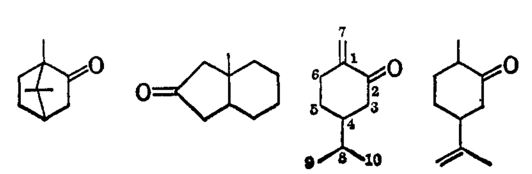
Details of the behavior of camphor (I) upon electron impact have been reported by Weinberg and Djerassi.[1] They have observed that (1) all of the major peaks in the mass spectrum of camphor are due to hydrocarbon species and the carbonyl group does not compete effectively with the hydrocarbon framework in directing the fragmentation of this molecule; (2) camphor and its isomer, *trans*-8-methylhydrindan-2-one (II), display very similar mass spectra, the principal difference residing only in the relative intensity of certain peaks; and (3) many of the fission reactions are best rationalized by postulating migrations of double bonds, alkyl groups, or hydrogen.



I II III IV

In connection with our pyrolysis study,[2] mass spectra of two further isomers of camphor, $\Delta^{1(7)}$-menthenone-2 (III) and $\Delta^{8(9)}$-menthenone-2 (IV) were obtained, which are reproduced in Figures 1 and 2, respectively.[3] Although the mass spectral peak positions of these compounds are generally similar to those of camphor, detailed study using deuterium-labeling and high-resolution techniques shows that much difference exists among the electron-impact fragmentation reactions of these compounds.

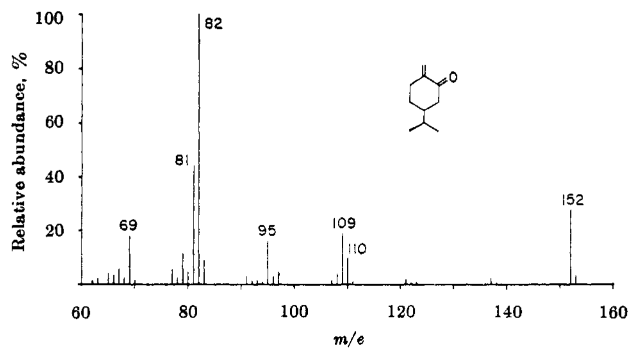


Figure 1.—Mass spectrum of $\Delta^{1(7)}$-methenone-2 (III).

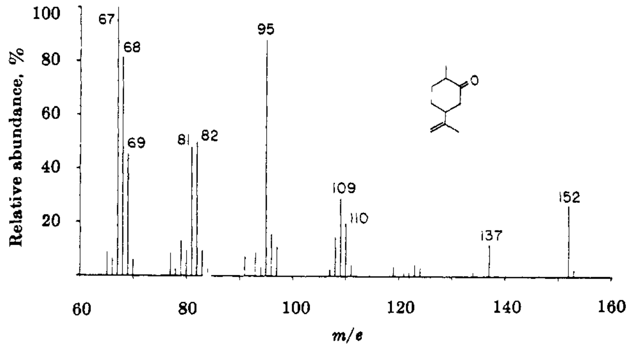


Figure 2.—Mass spectrum of $\Delta^{8(9)}$-methenone-2 (IV).

The principal mass spectral peaks (elemental compositions) of III determined by high-resolution measurement[4] are listed in Table I. High-resolution measurement was also carried out with III-3,3-d_2 and peaks were correlated to those of the nondeuterated analog. Unlike the case with camphor, most of the peaks are found to be doublets—a hydrocarbon ion peak and an oxygen-containing ion peak. It might be possible to write fragmentation mechanisms from these data, but there is not sufficient evidence to exclude alternatives explicitly and we avoid giving fragmentation mechanism in unwarranted detail.

TABLE I[a,b]
PRINCIPAL MASS SPECTRAL PEAKS OF III AND THEIR DEUTERIUM SHIFTS IN THE 3,3-d_2 ANALOG

Elemental compositions	
III	III-3,3-d_2
C_8H_{14} (110)	C_8H_{14} (110)
$C_7H_{10}O$ (110)	$C_7H_8D_2O$ (112)
C_8H_{13} (109)	$C_8H_{11}D_2$ (111)
C_7H_9O (109)	$C_7H_7D_2O$ (111)
C_7H_{11} (95)	C_7H_{11} (95)
C_6H_7O (95)	$C_6H_5D_2O$ (97)
C_5H_6O (82)	C_5H_6O (82), C_5H_5DO (83), $C_5H_4D_2O$ (84)
C_6H_9 (81)	$C_6H_7D_2$ (83)
C_5H_9 (69)	C_5H_9 (69)
C_4H_5O (69)	C_4H_5O (69)

[a] High-resolution mass spectra were recorded on a photographic plate and the peak intensities were not determined quantitatively. It is definitely shown, however, that the elemental compositions and their deuterium shifts shown in the table constitute the major portions of the spectra. [b] Figures in the parentheses designate *m/e*.

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[1] D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

[2] T. Sato, K. Murata, A. Nishimura, T. Tsuchiya, and N. Wasada, *Tetrahedron*, **23**, 1791 (1967).

[3] The mass spectra were determined on a CEC 21-103C mass spectrometer, the electron energy being 70 eV.

[4] The mass spectra were determined on a CEC 21-110B mass spectrometer, the electron energy being 70 eV.