Intermediates in Nucleophilic Aromatic Substitution. Part XIII.[1,2] Kinetic and Proton Magnetic Resonance Investigations of the Interaction of Methoxide Ions with 1-Methoxy-2,4,7-trinitronaphthalene

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The rate constants (k_1) for the formation of the 1,1-dimethoxy-complex of 1-methoxy-2,4,7-trinitronaphthalene in methanol at 7·95, 15·35, and 25·00 °C have been determined spectrophotometrically by following the increase in absorbance at 480 nm as a function of time in $5·0 \times 10^{-5}$M solutions of 1-methoxy-2,4,7-trinitronaphthalene in the presence of methoxide ions [$(0·56—14·0) \times 10^{-3}$M]. The rate constants ($k_{-1}$) for the decomposition of the complex have been determined directly at the same three temperatures by following the decrease in the absorbances of dilute methanolic solutions of the isolated complex. From these values the equilibrium constant, and the energy and entropy of activation for the formation of the complex ($1·09 \times 10^5$ l mol^{-1}, 13·3 kcal mol^{-1}, and −8·0 cal mol^{-1} K^{-1}, respectively) and the energy and entropy of activation for its decomposition (20·3 kcal mol^{-1} and −7·2 cal mol^{-1} K^{-1}) have been calculated. The stability of this complex is discussed in comparison with other Meisenheimer complexes. The structure of the 1,1-dimethoxy-complex of 1-methoxy-2,4,7-trinitronaphthalene has been established from ^{1}H n.m.r. spectra of both the isolated and the complex generated *in situ*. The ^{1}H n.m.r. parameters of the complex and its parent ether are discussed and contrasted with those for other naphthalene complexes.

IN previous PARTS we have discussed the stabilities and structure of the naphthalene σ, or Meisenheimer, complexes (1) and (2), which are formed on the addition of methanolic methoxide ions to 1-methoxy-2,4-dinitronaphthalene[3] and 1-methoxy-2,4,5-trinitronaphthalene.[4] The equilibrium constant for the formation of (2) (M = Na) in methanol at 25·00 °C is 127 times greater than that for the formation of (1).[4] Introduction of a third nitro-group in the 6-position of 2,4-dinitroanisole,

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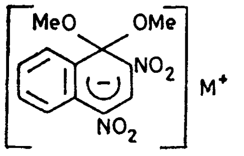
[1] Part XII, E. J. Fendler, J. H. Fendler, N. L. Arthur, and C. E. Griffin, *J. Org. Chem.*, 1972, **37**, 812.

[2] For recent reviews on Meisenheimer complexes and their relevance in nucleophilic aromatic substitution see: (*a*) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, 1966, **16**, 61; (*b*) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev.*, 1968, **22**, 123; (*c*) P. Buck, *Angew. Chem. Internat. Edn.*, 1969, **8**, 120; (*d*) J. Miller, 'Aromatic Nucleophilic Substitutions,' Elsevier, Amsterdam, 1968; (*e*) M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211; (*f*) F. Pietra, *Quart. Rev.*, 1969, **23**, 504; (*g*) M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

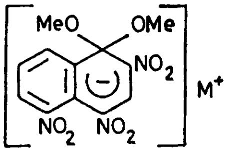
[3] J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, 1968, **33**, 977.

[4] J. H. Fendler and E. J. Fendler, *J. Org. Chem.*, 1970, **35**, 3378.

on the other hand, enhances the Meisenheimer complex stability by eight orders of magnitude.[5-7] These results have been rationalized in terms of contributions from differences in the electron density at the seat of substitution of the aromatic reactant, in the extent of electron delocalization by the aromatic substituents, and in the steric requirements of the initial and transition states.[4] The proximity of the 4- and 5-nitro-groups in 1-methoxy-2,4,5-trinitronaphthalene could result in a decrease in the extent of electron delocalization in the complex owing to non-coplanarity of the nitro-groups with the π-system. In order to substantiate this assumption and to investigate further the transmission of electronic effects from one ring to the other in substituted naphthalenes, we have determined kinetic and thermodynamic parameters for the formation and decomposition of the dimethoxy-complex (3) of 1-methoxy-2,4,7-trinitronaphthalene (4). Additionally, proton magnetic resonance parameters have been obtained both for the isolated and for the *in situ* generated complex (3).



M = Na or K
(1)



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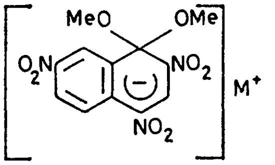

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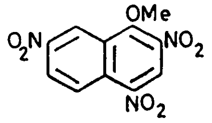
(3)



(4)

EXPERIMENTAL

The reagents and solvents were prepared, purified, and standardized as previously described.[8] 2,4,7-Trinitro-1-naphthol was prepared by a modified procedure of Consden and Kenyon.[9] 2,4-Dinitro-1-naphthol (35·00 g; 0·1495 mol) (Eastman reagent grade) was added slowly with stirring to a solution at *ca.* 3 °C containing fuming nitric acid (*d* 1·52; 70 ml) and glacial acetic acid (70 ml). The reaction mixture was allowed to reach room temperature slowly and was stirred for 18 h. at 25—28 °C (maintained by occasional external cooling).† The reaction mixture was filtered through a medium porosity sintered-glass filter to remove the major nitration product, 2,4,5-trinitro-1-naphthol, and the filtrate was poured on 400 ml of ice–water. The yellow precipitate was filtered off, washed with a small amount of cold water, and dried *in vacuo* (P_2O_5). After recrystallization from acetic acid and drying *in vacuo* (P_2O_5), 2·30 g (5·5% yield) of 2,4,7-trinitro-1-naphthol was obtained which decomposed at 142—144 °C [lit.,[9] 145 °C (decomp.)]. A subsequent preparation by the same procedure yielded 9·3% of pure product after recrystallization from glacial acetic acid.

Pyridinium 2,4,7-trinitro-1-naphthoxide was prepared by the addition of pyridine (2·00 ml; 24·8 mmol) to a stirred solution of 2,4,7-trinitro-1-naphthol (1·20 g; 4·30 mmol) in dry benzene (100 ml). After cooling to *ca.* 8 °C the yellow precipitate was filtered off, washed with dry benzene, and dried *in vacuo* (P_2O_5) yielding 1·49 g (96·7%) of product, m.p. 185—186 °C (lit.,[10] m.p. 184 °C crude, 187 °C after recrystallization from methanol).

1-Chloro-2,4,7-trinitronaphthalene was prepared by the portionwise addition of pyridinium 2,4,7-trinitro-1-naphthoxide (6·03 g) to phosphoryl chloride (20 ml) with stirring at room temperature. After dissolution of the pyridinium salt, the solution was heated for 50 min to 73 °C during which time a flocculent precipitate formed. The reaction mixture was cooled and poured on ice–water; the yellow precipitate was pulverized, filtered off, washed with water, and dried *in vacuo* (P_2O_5). After recrystallization from methanol the dark yellow crystals of 1-chloro-2,4,7-trinitronaphthalene had m.p. 119—120 °C (lit.,[10] m.p. 113 °C from methanol, m.p. 110—118 °C from other solvents).

1-Methoxy-2,4,7-trinitronaphthalene (4) was prepared by the dropwise addition of 5·05M-potassium methoxide (0·65 ml, *i.e.*, 3·27 mmol) in methanol to a hot solution of 1-chloro-2,4,7-trinitronaphthalene (1·00 g; 3·36 mmol) in anhydrous methanol (35 ml). The mixture was refluxed for 30 min. cooled to *ca.* 0 °C with an ice-bath, and the product filtered off, washed with anhydrous methanol, and dried *in vacuo* (P_2O_5), m.p. 139·5—140 °C (lit.,[10] m.p. 140·5 °C after 3 recrystallizations from methanol).

The dimethoxy-complex (3) of 1-methoxy-2,4,7-trinitronaphthalene was prepared by the addition of 0·12 ml of 4·53M-potassium methoxide in methanol (0·12 ml, *i.e.*, 0·516 mmol) to a warm saturated solution (containing a small amount of undissolved solid) of (4) (0·1466 g; 0·50 mmol) in dry dioxan (1·0 ml). After the reaction mixture had been flushed with dry nitrogen and allowed to stand for *ca.* 3 min, the red crystals were filtered off under nitrogen and washed with dry benzene (2 × 10 ml) and anhydrous ether (2 × 10 ml). After being dried *in vacuo* (P_2O_5) the crystals decomposed at *ca.* 240 °C.

The attainment of the equilibrium for the formation of complex (3) from 1-methoxy-2,4,7-trinitronaphthalene (4) and sodium methoxide in methanol was followed at 480 nm in the thermostatted cell compartment of a Beckman Kintrac VII spectrophotometer. The temperature was monitored inside the cells and was maintained within ±0·02 °C. The mixing techniques utilized for fast reactions have been described.[7]

The rate constants for the decomposition of the isolated

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† This procedure was attempted unsuccessfully twice with the use of practical grade 2,4-dinitro-1-naphthol. In both instances after stirring for 1—2 h, the externally cooled reaction became extremely exothermic resulting in the evolution of large quantities of nitrogen oxides. The starting material was found from its ^{1}H n.m.r. spectrum to contain an appreciable quantity of the 2-naphthol as well as traces of other impurities.

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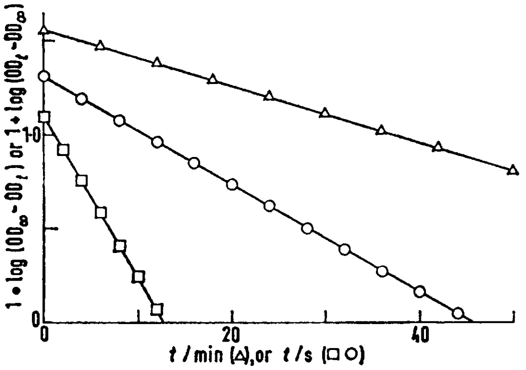
[7] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.* 1969, **34**, 689.

[8] W. E. Byrne, E. J. Fendler, J. H. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1967, **32**, 2506.

[9] R. Consden and J. Kenyon, *J. Chem. Soc.*, 1935, 1591.

[10] D. S. Gilbert, Thesis, Leicester College of Technology, Leicester, 1963.

crystalline complex (3) in methanol were obtained by following the rates of decrease in absorbance at 480 nm of appropriate solutions of (3) in the thermostatted cell compartment of the spectrophotometer. Good first-order kinetics, up to 95% reaction, were observed both for the equilibrium attainment for the formation of (3) and for the decomposition of solid (3). Typical first-order plots are given in the Figure.



Plot (△) of log ($OD_\infty - OD_t$) against time/min for the decomposition of complex (3) in methanol at 25·00 °C. Plots of log ($OD_t - OD_\infty$) against time/s for the attainment of equilibrium for complex (3) in methanol at 15·35 °C: ○ [NaOMe] = $1·96 \times 10^{-3}$M; □ [NaOMe] = $5·60 \times 10^{-3}$M

^1H N.m.r. spectra at 60 MHz were obtained on a modified Varian Associates A-60 spectrometer at 38 and 31 °C and those at 100 MHz were obtained on a modified Varian Associates HA-100 spectrometer with a Hewlett–Packard model 200 ABR audio-oscillator and frequency counter at 32 °C. All spectra were determined on solutions in [$^2H_6$]-dimethyl sulphoxide or CD_3CN with tetramethylsilane as an internal standard; chemical shifts are given on the δ scale in p.p.m. relative to tetramethylsilane (δ = 0 p.p.m.) and are accurate to ±0·007 at 100 MHz and ±0·02 at 60 MHz.

RESULTS AND DISCUSSION

Addition of sodium methoxide to dilute methanolic solutions of 1-methoxy-2,4,7-trinitronaphthalene (3) results in the formation of a red colour, with an absorption maximum at 480 nm [$\epsilon_{480\,\text{nm}} = (2·5 \pm 0·1) \times 10^4$ cm^{-1} l mol^{-1}]. The absorbance of $5·0 \times 10^{-5}$M methanolic solutions of (4) at this wavelength remain constant over a wide range of methoxide ion concentrations indicating completion of the equilibrium (1). In the concentration

$$(4) + \text{NaOMe} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (3) \qquad (1)$$

range of (0·56—14·0) × 10^{-3}M methanolic NaOMe it was possible, however, to follow the attainment of the equilibrium at a given temperature by measuring the absorbance increase at 480 nm as a function of time. Under the experimental conditions ([4] ≪ [NaOMe]), the observed first-order rate constant for equilibrium attainment, k_{obs}, is given by [1] equation (2) where k_1 is

$$k_{\text{obs}} = k_1[\text{NaOMe}] + k_{-1} \qquad (2)$$

the second-order rate constant for the formation of compound (3) and k_{-1} is the first-order rate constant for its decomposition. Table 1 gives the data for the interaction of methoxide ion with compound (4) at 7·95, 15·35, and 25·00 °C. Plots of k_{obs} against [NaOMe] give good straight lines [equation (2)] at all three temperatures, from the slopes of which the k_1 values have been calculated. Since the intercepts of the straight lines in these plots are extremely small and hence would incorporate large errors into the k_{-1} values obtained therefrom, k_{-1} values have been obtained directly from measurements of the rate of decrease in the absorbance of isolated complex (3) dissolved in pure methanol at the appropriate temperature. The rate constants for the formation, k_1, and decomposition, k_{-1}, of (3) as well as the Arrhenius parameters are given in Table 1.

TABLE 1

Interaction of 1-methoxy-2,4,7-trinitronaphthalene ($5·0 \times 10^{-5}$M) with methanolic sodium methoxide)

t/°C	10^3[NaOMe]/ M	$10^2 k_{\text{obs}}$/ s^{-1}	k_1 [a] / l mol^{-1} s^{-1}	$10^4 k_{-1}$ [b] / s^{-1}	$10^{-5} K$ [c] / l mol^{-1}
7·95	0·00		16·4	0·76	2·15
	2·80	4·20			
	4·20	7·13			
	5·60	9·40			
	8·40	13·8			
	9·80	15·7			
	11·2	18·6			
	12·6	20·4			
	14·0	22·9			
15·35	0·00		34·6	2·09	1·65
	1·40	4·80			
	1·96	6·67			
	2·24	8·21			
	2·52	8·86			
	2·80	9·40			
	4·20	14·5			
	5·60	19·4			
25·00	0·00		62·0	5·70	1·09
	0·56	3·20			
	0·82	5·00			
	1·40	8·60			
	1·64	10·4			
	1·96	12·0			
	2·24	13·5			
	2·80	17·0			

$E_1 = 13·3 \pm 0·8$ kcal mol^{-1}. $E_{-1} = 20·3 \pm 0·8$ kcal mol^{-1}. $\Delta S_1^{\ddagger} = -8·0 \pm 2·0$ cal mol^{-1} K^{-1} [d]. $\Delta S_{-1}^{\ddagger} = -7·2 \pm 2·0$ cal mol^{-1} K^{-1}.

[a] Obtained from the slope of plots of k_{obs} against [NaOMe]/M. [b] Mean of six runs (each within ±3%) obtained by following the decomposition of solid complex (3) in methanol. [c] $K = k_1/k_{-1}$. [d] At 25·00 °C.

In methanol, compound (4) undergoes ‘ solvolysis ’ to form the naphthol, but the rate of naphthol formation is several orders of magnitude slower than the slowest rate observed for the equilibrium attainment of (3).[10]

Kinetic and thermodynamic data for the formation and decomposition of complexes (1)—(3) at 25·00 °C are combined in Table 2. Equilibrium constants for the complexes increase in the order (1) < (2) < (3). This order of complex stability is the result of an increase in k_1 and a decrease in k_{-1}, the magnitude of the difference in the rate constants in going from (1) to (3) being greater for the forward (k_1) than for the reverse (k_{-1}) reaction. Comparison of the values for complexes (2) and (3) reveals, however, that the increase in k_1 is almost paralleled by the decrease in k_{-1}. It appears, therefore, that any steric interactions between the nitro-groups in the 4- and 5-positions of 1-methoxy-2,4,5-trinitronaphthalene influence the formation of the complex (2) to about the same extent as they do its decomposition. The absence of a nitro-group *peri* to C(4) in (4) and its complex (3) affords a more meaningful interpretation of the influence of an additional nitro-group in the dinitro-naphthalene and -benzene complexes than previously available from comparison of (1) and (2) with the 1,1-dimethoxy-complexes of 2,4-dinitroanisole and 2,4,6-trinitroanisole. The equilibrium-constant ratio for the formation of the methoxy-Meisenheimer complexes of these anisoles is 10^8 as compared with $K_{(3)}/K_{(1)} = 495$ and $K_{(2)}/K_{(1)} = 133$. This difference is primarily the consequence of significant electron delocalization over the nitro-group and π-system in the second ring and a smaller inductive effect of the additional nitro-group in the naphthalenes.

TABLE 2

Kinetic and thermodynamic parameters for the formation and decomposition of di- and trinitro-substituted Meisenheimer complexes in methanol at 25·00 °C [a]

	Complex		
	(1) [b]	(2) [c]	(3)
k_1/l mol^{-1} s^{-1}	0·90	32·8	62·0
10^3k_{-1}/s^{-1}	4·00	1·12	0·57
$10^{-3}K$/l mol^{-1}	0·220	29·3	109
E_1/kcal mol^{-1}	13·8	12·2	13·3
$\Delta S_1^{\ddagger}$/cal mol^{-1} K^{-1}	−17·0	−12·5	−8·0
E_{-1}/kcal mol^{-1}	16·5	18·6	20·3
$\Delta S_{-1}^{\ddagger}$/cal mol^{-1} K^{-1}	−18·0	−11·7	−7·2

[a] Errors in $E = \pm 0·8$ kcal mol^{-1} and in $\Delta S^{\ddagger} = 2·0$ cal mol^{-1} K^{-1}. [b] Ref. 3. [c] Ref. 4.

The greater stability of complex (3) than of (1) and (2) results primarily from an increase in the entropy of activation for the formation of the complex and from a combination of enthalpy and entropy factors for its decomposition. Similar thermodynamic behaviour has been observed for several other Meisenheimer complexes.[1,2]

In order to substantiate the postulated structure of complex (3), to observe any relatively long-lived transients during its formation, and to shed some light on the electron distribution in complex (3) as compared with the trinitro- and dinitro-complexes (2) and (1), we examined the ^{1}H n.m.r. spectra of the ether (4) and its isolated and *in situ*-generated methoxy-complex. The ^{1}H n.m.r. parameters for the ether (4), its synthetic precursors, and its dimethoxy-complex (3) in [^{2}H$_6$]-dimethyl sulphoxide and/or CD_3CN solutions are in Table 3. The observed resonance frequencies for H(5), H(6), and H(8) of compound (4) at 60 MHz comprise an AMX-type spectrum in CD_3CN (*i.e.*, an ABX case which approximates a first-order AMX one with the exception of the intensities) whereas in [^{2}H$_6$]dimethyl sulphoxide an ABX pattern is found at both 60 and 100 MHz. In the case of the dimethoxy-complex (3) of (4) in [^{2}H$_6$]-dimethyl sulphoxide, however these resonance frequencies exhibit the less complex AMX-type pattern primarily as a consequence of the greater difference between the chemical shifts of H(5) and H(6). The spectral parameters (chemical shifts, coupling constants, and integrated intensities) are completely consistent with the postulated 1 : 1-complex structure [*i.e.* (3)]. Rehybridization of C(1) from sp^2 in (4) to sp^3 in (3) results in an upfield shift ($\Delta\delta = 1·44$ p.p.m. in [^{2}H$_6$]dimethyl sulphoxide) of the methoxy proton resonance very similar to those observed for (1) ($\Delta\delta = 1·33$ p.p.m.)[3] and (2) ($\Delta\delta = 1·39$ p.p.m.)[4] and apparently characteristic of 1,1-dialkoxy-benzene and -naphthalene Meisenheimer complexes.[2,7,8,11] Not unexpectedly the magnitude of this upfield shift ($\Delta\delta$) shows very little sensitivity to differences in electron density at C(1). Conversely the values for the aromatic protons have been found to reflect the relative charge densities in 1,1-dialkoxy-cyano-,[12] cyanonitro-,[7,11] and nitro-substituted[8] cyclohexadienylide ions. For the naphthalene compounds the relationship is less straightforward owing to anisotropic contributions to the chemical shifts, especially those arising from *peri*-interactions, and to electron delocalization over both rings. The H(6) and H(8) resonances of complex (3) show the expected upfield shifts ($\Delta\delta = 0·43$, $0·46$ and $0·53$, $0·67$ p.p.m., respectively) whereas those of H(3) and H(5) shift downfield ($\Delta\delta = -0·19$, $-0·24$ and $-0·19$, $-0·21$ p.p.m.,

TABLE 3

^{1}H N.m.r. parameters for 1-X-2,4,7-trinitronaphthalenes and the methoxy-complex (3) of 1-methoxy-2,4,7-trinitronaphthalene [a]

	X = OH	X = Cl	X = OMe		Complex (3)	
Solvent	$(CD_3)_2$-SO [b]	CD_3CN	CD_3CN	$(CD_3)_2SO$	$(CD_3)_2SO$ [d]	
δ_3	9·19	8·81	8·89	9·05, 9·10 [c]	9·29 (9·32)	9·29 [c]
δ_5	8·91	8·75	8·80	8·74, 8·71 [c]	8·93 (8·94)	8·92 [c]
δ_6	8·35	8·54	8·54	8·65, 8·62 [c]	8·19 (8·19)	8·19 [c]
δ_8	9·08	9·36	9·24	9·15, 9·00 [c]	8·48 (8·51)	8·47 [c]
δ_{OMe}			4·23	4·26, 4·23 [c]	2·81 (2·83)	2·80 [c]
J_{56}	9·5	9·5	9·5	9·5, 9·5 [c]	9·3 (9·3)	9·4 [c]
J_{58}	~0·4		0·8	~0·4, 0·7 [c]	~0·4 (~0·4)	0·35 [c]
J_{68}	~2·6	~2	2·2	2·6, 2·3 [c]	2·6 (2·6)	2·8 [c]

[a] At 60 MHz and 38 °C unless specified otherwise. [b] At 31 °C. [c] At 100 MHz and 32 °C. [d] Values in parentheses were obtained in the *in situ* formation of the complex (3) by the dropwise addition of 4·53M-potassium methoxide in methanol to a *ca.* 2M solution of (4) in [^{2}H$_6$]dimethyl sulphoxide.

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[11] E. J. Fendler, J. H. Fendler, C. E. Griffin, and J. W. Larsen, *J. Org. Chem.*, 1970, **35**, 287.

[12] E. J. Fendler, W. Ernsberger, and J. H. Fendler, *J. Org. Chem.*, 1971, **36**, 2333.

respectively). The increases in electron density at the 6- and 8-positions and the decrease at C(3) of the complex relative to the ether are explicable in terms of canonical contributions and localization of the negative charge primarily in the nitro-groups in agreement with earlier observations for complexes (1)[3] and (2)[4] and with the results of HMO calculations.[13]

The interaction between methoxide ions and the ether (4) also was examined by rapidly recording the ^1H n.m.r. spectra of solutions of (4) in [$^2H_6$]dimethyl sulphoxide to which 4·53M-potassium methoxide in methanol was successively added dropwise. In successive spectra the resonances of the ether (4) decreased in intensity with the concurrent appearance and increase in intensity of those of the complex (3) and methanol until those of the former were no longer discernible (see Table 3). With our experimental conditions no species other than (3), such as a complex resulting from attack of methoxide ion at C(3) or ' solvolysis ' products, could be detected; however, spectra of samples of both the isolated and *in situ*-generated (3) showed some decomposition on standing for longer than 24 h, possibly as the consequence of absorption of water by the dimethyl sulphoxide.

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