Can *N*-Acylazetones ever be Obtained? The Reaction between Di-t-butoxyethyne and Benzoyl Isocyanate leading to 2-Phenyl-4,5-di-t-butoxy-1,3-oxazin-6-one†

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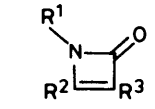
Di-t-butoxyethyne (**14**) reacts with benzoyl isocyanate (**13**) affording 2-phenyl-4,5-di-t-butoxy-1,3-oxazin-6-one (**15**) and *N*-benzoyl-4-hydroxy-3,5,6-tri-t-butoxy-2-pyridone (**16**). The crystal structure of (**15**) has been determined by *X*-ray diffraction. The formation of (**15**) and (**16**) is explained in terms of the intermediacy of *N*-benzoyl-3,4-di-t-butoxyazet-2(1*H*)-one (**8**) in equilibrium with the corresponding iminoketene (**17**). The equilibria between some model azet-2-ones (**20**)—(**23**) and *N*-formylazet-2-ones (**24**)—(**27**) and the corresponding iminoketenes (**28**)—(**35**), as well as the conversion of the *N*-formyliminoketenes (**32**)—(**35**) into the 1,3-oxazin-6-ones (**40**)—(**43**), have been studied by the MNDO procedure. The results of this study suggest the impossibility of preparing *N*-acylazet-2-ones by [2 + 2] cycloadditions of acetylenes with acyl isocyanates.

Azetones (**1**) have attracted considerable interest both from a theoretical point of view, as a potential new class of antiaromatic substances, or from a more practical perspective, as potential intermediates in the synthesis of β-lactam antibiotics.

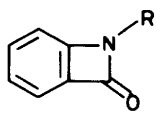
Whereas benzazetones (**2**) have been known for a number of years,[1] the first proof of the formation of simple azetones has been provided only recently by Olofson and his co-workers,[2] closing a long series of announcements of success in the synthesis of these substances generally followed by disproofs of the azetone structures initially assigned.[3]

Some doubt still remained concerning whether *N*-acylazetones could be synthesised. Arbuzov and his co-workers had reported the formation of *N*-benzoylazetones (**3**),[4a] (**4**),[4a] (**5**),[4b] (**6**),[4b] and (**7**)[4c] from the reactions of benzoyl isocyanate (**13**) with several alkynes. Lattrell[5] and Dehmlow,[6] however, were subsequently unable to reproduce these results, and Arbuzov attributed Lattrell's failure to the nature of the glass equipment used.[7] In any case, no alternative structures have been proposed for compounds (**3**)—(**7**). On the other hand, Martin and his co-workers have reported the formation of the 1,3-oxazin-4-one (**9**) in the reaction of (**13**) with ethoxyethyne.[8]

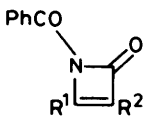
In order to elucidate this matter, we decided to study the reaction of di-t-butoxyethyne (**14**), the only stable acetylene diether described so far,[9] with benzoyl isocyanate (**13**). The presumed primary product, 1-benzoyl-3,4-di-t-butoxyazet-2(1*H*)-one (**8**) could be stabilised in principle by a combination of steric and electronic factors. The steric effect exerted by the bulky t-butoxy groups, which is responsible for the thermal stability of compounds such as (**11**)[10] and (**12**),[11] as well as of di-t-butoxyethyne (**14**) itself, would protect the azetone (**8**) from intermolecular interactions.



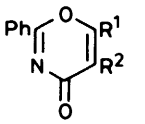
(**1**)



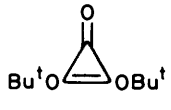
(**2**)



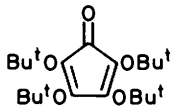
(**3**) R^1 = Ph, R^2 = H
(**4**) R^1 = CH_2OAc, R^2 = H
(**5**) R^1 = CH_2OMe, R^2 = H
(**6**) R^1 = CO_2Me, R^2 = H
(**7**) R^1 = R^2 = Ph
(**8**) R^1 = R^2 = OBu^t



(**9**) R^1 = OEt, R^2 = H
(**10**) R^1 = R^2 = OBu^t



(**11**)

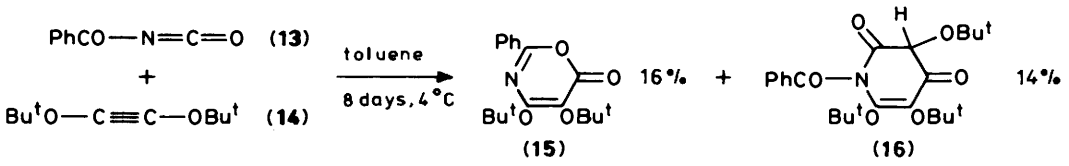


(**12**)

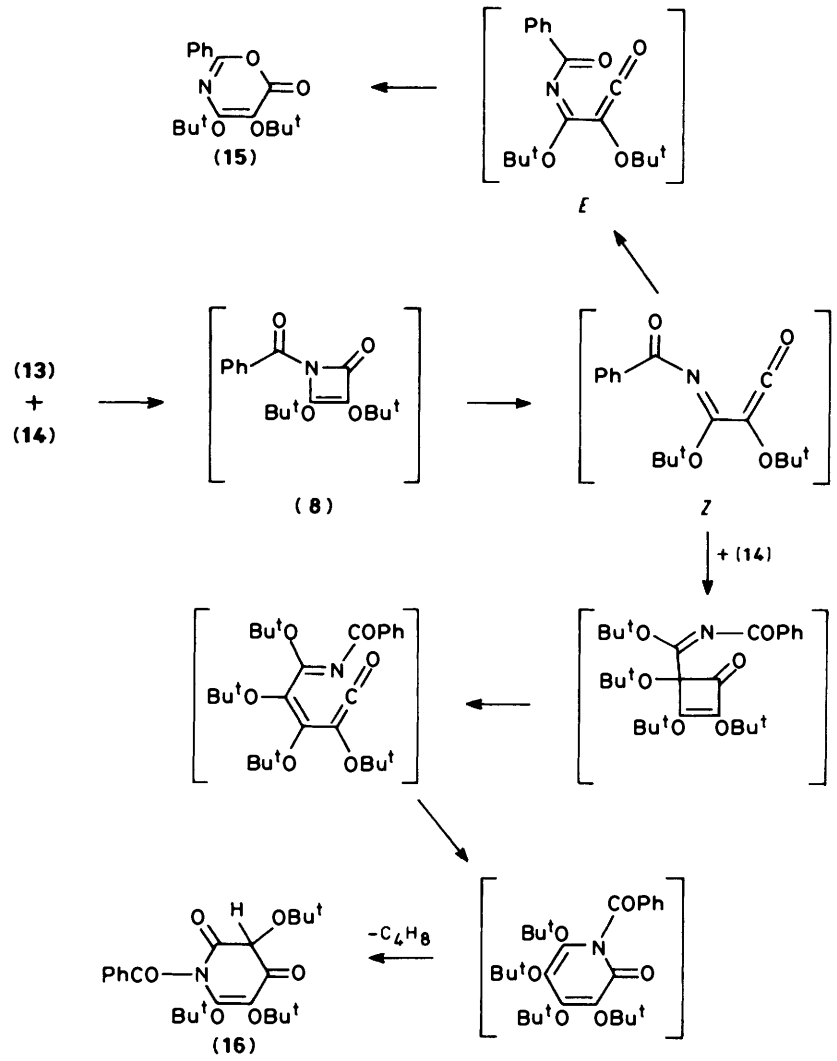
Results and Discussion

When di-t-butoxyethyne (**14**) reacted with benzoyl isocyanate (**13**) in dilute toluene solution for 8 days at 4 °C, until the acetylene (**14**) had almost all disappeared, a considerable amount of oligomeric material was formed. Repeated purification of the crude mixture by column chromatography led to the isolation of two products. The less polar one, isolated in 16% yield, was a 1:1 adduct of (**13**) and (**14**), the spectral characteristics of which ruled out both the azetone structure

† *Supplementary data available* (SUP 56547, 22 pp.): thermal parameters for compound (**15**); MNDO calculations data. For details of Supplementary Publications see Instructions for Authors (*J. Chem. Soc., Perkin Trans. 2*, 1986, Issue 1).



Scheme 1.

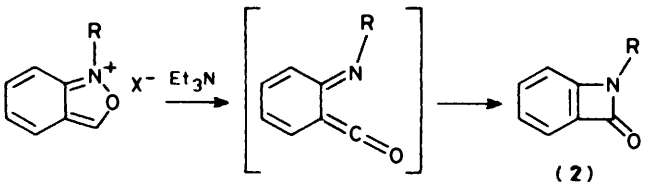


Scheme 2.

(**8**), the primary product of a [2 + 2] cycloaddition,[4] and the 1,3-oxazin-4-one structure (**10**), arising from a [4 + 2] cycloaddition involving the acyl substituent of the isocyanate moiety.[8] On the other hand, i.r. bands at 1 760, 1 610, and 1 580 cm^{-1} agreed well with those reported for substituted 2-aryl-1,3-oxazin-6-ones,[12] so the structure (**15**) of 2-phenyl-4,5-di-t-butoxy-1,3-oxazin-6-one was tentatively assigned to it. A single-crystal *X*-ray analysis of a crystal of (**15**) (see later) confirmed the assigned structure.

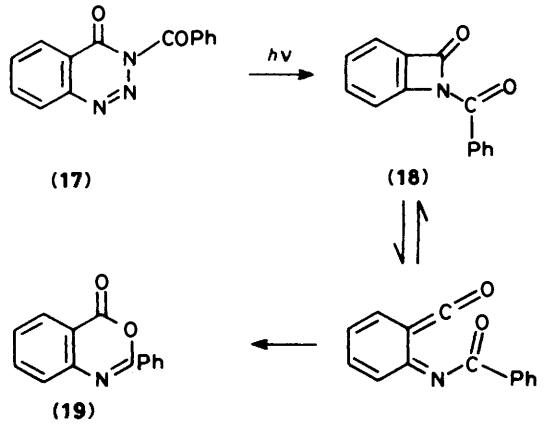
The more polar product, obtained in 14% yield, was a 1:2 adduct of (**13**) and (**14**), formed with loss of one molecule of 2-methylpropene, to which the structure (**16**) of *N*-benzoyl-4-hydroxy-3,5,6-tri-t-butoxy-2-pyridone was assigned on the basis of spectral characteristics.

The formation of such a 1,3-oxazin-6-one derivative as a product of cycloaddition between an alkyne and an acyl isocyanate has no literature precedent, but parallels the reported formation of 6-chloro-1,2,3-oxathiazine 2,2-dioxides in the reaction of alkynes with chlorosulphonyl isocyanate.[6,13] In both cases, the carbon–nitrogen double bond of the starting isocyanate is completely cleaved during the reaction, indicating the intermediacy of an azetone, which then rearranges to the six-membered ring derivative (**15**), *via* an iminoketene intermediate. On the other hand, the formation of (**16**) can be easily explained from the aforementioned iminoketene intermediate by a mechanism similar to that postulated by Danheiser and Gee for the formation of highly substituted benzene derivatives from cyclobutenones and alkynes[14] (Scheme 2). This mechanism probably applies also to the formation of 4,6-bisdimethylamino-3,5-diphenyl-2-pyridone from chlorosulphonyl isocyanate and



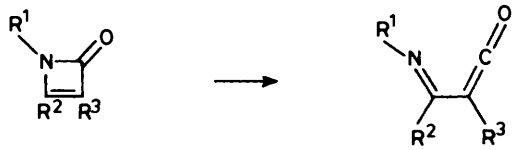
(2)

Scheme 3.



(17) (18) (19)

Scheme 4.



(20)	$R^1 = R^2 = R^3 = H$	(28)
(21)	$R^1 = R^3 = H, R^2 = OH$	(29)
(22)	$R^1 = R^2 = H, R^3 = OH$	(30)
(23)	$R^1 = H, R^2 = R^3 = OH$	(31)
(24)	$R^1 = CHO, R^2 = R^3 = H$	(32)
(25)	$R^1 = CHO, R^2 = OH, R^3 = H$	(33)
(26)	$R^1 = CHO, R^2 = H, R^3 = OH$	(34)
(27)	$R^1 = CHO, R^2 = R^3 = OH$	(35)

Scheme 5.

1-dimethylamino-2-phenylethyne.[15] In our case, the final loss of 2-methylpropene leading to (**16**) may be facilitated by the mutual steric interactions of the four adjacent t-butoxy groups.

Our results show once again the importance of the relationship between azetones and iminoketenes. In fact, Olofson, on the basis that *N*-alkylazetones in solution are probably in equilibrium with minute amounts of the corresponding iminoketenes,[1g] devised his syntheses of *N*-alkylbenzazetones (**2**)[1f] and of *N*-alkylazetones (**1**)[2] which includes, as the key step, the ring closure of an assumed iminoketene intermediate (see Scheme 3). On the other hand, Ege reported that *N*-benzoylbenzazetone (**18**), generated by photolysis of 3-benzoyl-1,2,3-benzotriazin-4(3*H*)-one (**17**), was transformed into 2-phenyl-1,3-benzoxazin-6-one (**19**) *via* an *N*-benzoyliminoketene[1b] (see Scheme 4).

According to these observations, the presence of an *N*-benzoyl substituent on an iminoketene can exert a dramatic effect on the behaviour of this intermediate. This effect can be due either to a modification of the relative stabilities of the azetone and iminoketene forms or, simply, to the existence of a reaction path with low activation energy leading to the more stable 1,3-oxazin-6-one system.

Table 1. MNDO-calculated activation energies $\Delta H^{\ddagger}$ and reaction enthalpies ΔH_r° for the conversion of azetones (**20**)—(**27**) into the corresponding (*E*)-iminoketenes

Reaction	$\Delta H^{\ddagger}$/kcal mol^{-1}	ΔH_r°/kcal mol^{-1}
(20) ⟶ (28)	19.6	−9.9
(21) ⟶ (29)	15.7	−9.4
(22) ⟶ (30)	22.3	−3.3
(23) ⟶ (31)	17.7	−4.1
(24) ⟶ (32)	16.2	−7.6
(25) ⟶ (33)	12.1	−8.7
(26) ⟶ (34)	18.0	1.5
(27) ⟶ (35)	13.6	−4.1

Table 2. MNDO-calculated activation energies $\Delta H^{\ddagger}$ and reaction enthalpies ΔH_r° for the isomerisation of *N*-formyliminoketenes (**32**)—(**35**)

Reaction	$\Delta H^{\ddagger}$/kcal mol^{-1}	ΔH_r°/kcal mol^{-1}
(32) ⟶ (36)	11.8	3.1
(33) ⟶ (37)	13.6	0.8
(34) ⟶ (38)	8.1	−3.9
(35) ⟶ (39)	13.5	1.2

In order to elucidate this reaction, we undertook a theoretical study of the conversion of some model azetones and *N*-formylazetones into the corresponding iminoketenes, by the semiempirical SCF-MO MNDO method.[16] In the case of the *N*-formyl derivates, the subsequent conversion into 1,3-oxazin-6-ones was also investigated.

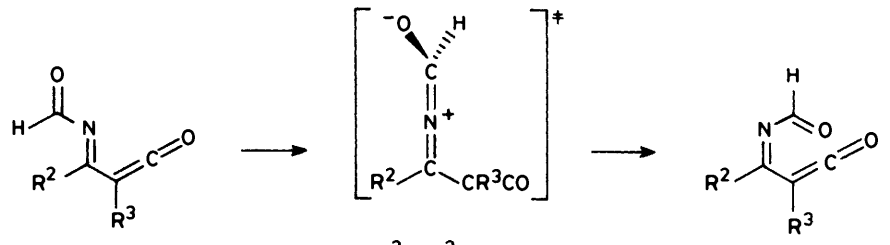
MNDO Calculations.—The azetones (**21**)—(**23**) and the *N*-formylazetones (**25**)—(**27**) were selected as models for the products of [2 + 2]cycloaddition of acetylenic monoethers and diethers with alkyl and acyl isocyanates; the unsubstituted compounds (**20**) and (**24**) were included for comparison.

The conversion of (**20**)—(**27**) into the corresponding (*E*)-iminoketenes (**28**)—(**31**) and (*E*)-*N*-formyliminoketenes (**32**)—(**35**) was studied by the normal reaction co-ordinate method, the corresponding transition states being located and characterised. The calculated activation energies $\Delta H^{\ddagger}$ and reaction enthalpies ΔH_r° are summarised in Table 1. Some important inferences can be drawn from these data.

In the first place, the activation energies for the ring-opening process are in all cases rather low, indicating that the equilibrium between azetone and (*E*)-iminoketene can be established even at low temperatures. In this context, it is important to realise that the presence of a *N*-formyl substituent uniformly produces a lowering of 3—4 kcal mol^{-1} in the activation energies relative to the unsubstituted compound. Accordingly, it is expected that *N*-acylazetones can equilibrate with the corresponding (*E*)-*N*-acyliminoketenes with even greater facility.

On the other hand, from the thermodynamic point of view, the acyclic forms are predicted, except in the case of (**34**), to be more stable than the cyclic ones. Therefore, a significant concentration of (*E*)-iminoketene form should be present at equilibrium with the corresponding azetone. This conclusion probably cannot be applied to the equilibrium between benzazetones and the corresponding iminoketenes, since the aromaticity of the benzene ring is preserved in the azetone form.

Finally, analysis of the effect of the substituents R shows that the presence of a hydroxy substituent adjacent to the carbonyl group [in (**22**) and (**26**)] stabilises the azetone form both



Scheme 6.

Table 3. MNDO-calculated activation energies $\Delta H^{\ddagger}$ and reaction enthalpies ΔH_r° for the cyclisation of (*Z*)-*N*-acyliminoketenes to 1,3-oxazin-6-ones (**40**)—(**43**)

Reaction	$\Delta H^{\ddagger}$/kcal mol^{-1}	ΔH_r°/kcal mol^{-1}
(**36**) ⟶ (**40**)	8.5	−23.8
(**37**) ⟶ (**41**)	6.5	−23.2
(**38**) ⟶ (**42**)	11.3	−24.4
(**39**) ⟶ (**43**)	6.3	−26.1

Table 4. MNDO-calculated reaction enthalpies ΔH_r° for the overall conversion of azetones (**24**)—(**27**) into 1,3-oxazin-6-ones

Reaction	ΔH_r°/kcal mol^{-1}
(**24**) ⟶ (**40**)	−28.2
(**25**) ⟶ (**41**)	−31.1
(**26**) ⟶ (**42**)	−26.8
(**27**) ⟶ (**43**)	−29.0

Table 5. Fractional atomic co-ordinates (× 10^4) for non-hydrogen atoms of compound (**15**) with standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	10 466(2)	5 965(2)	6 668(2)
C(2)	9 772(3)	4 601(2)	6 805(3)
O(2)	10 438(2)	3 790(2)	6 708(3)
C(3)	8 365(3)	4 374(2)	7 055(3)
C(4)	7 774(3)	5 455(2)	7 020(3)
N(5)	8 519(2)	6 759(2)	6 860(2)
C(6)	9 808(3)	6 961(2)	6 700(3)
C(7)	10 728(3)	8 314(2)	6 589(3)
C(8)	11 948(3)	8 497(3)	6 076(3)
C(9)	12 806(3)	9 805(3)	5 989(4)
C(10)	12 442(4)	10 911(3)	6 432(4)
C(11)	11 219(4)	10 746(3)	6 923(4)
C(12)	10 353(3)	9 450(3)	7 013(3)
O(31)	7 575(2)	3 065(2)	7 120(2)
C(32)	7 719(3)	2 433(3)	8 542(3)
C(33)	9 342(5)	2 616(5)	9 377(5)
C(34)	7 046(7)	3 048(6)	9 468(6)
C(35)	7 029(15)	936(11)	8 206(17)
C(35′)	6 986(55)	915(25)	7 846(47)
O(41)	6 408(2)	5 195(2)	7 103(2)
C(42)	5 708(3)	6 244(3)	7 392(3)
C(43)	6 584(4)	6 988(4)	8 849(4)
C(44)	4 225(3)	5 352(4)	7 460(4)
C(45)	5 518(3)	7 178(3)	6 123(4)

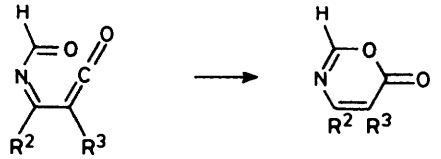
kinetically and thermodynamically. This seems to offer a clue for the preparation of 'stable' azetones by the interaction of an acetylenic ether with an isocyanate. Unfortunately, however, acyl isocyanates interact with acetylenic ethers in the opposite orientation, leading to 1,3-oxazin-4-ones by [4 + 2] cycloaddition.[8]

Our results may appear, *a priori*, to contradict the assumption of an iminoketene precursor in Olofson's synthesis of azetones. However, such iminoketenes have not been confirmed as *precursors* in this reaction. In any case, the presence of alkyl substituents at C(3) and C(4) of the azetone ring may perhaps modify the relative stabilities of the iminoketene and the azetone forms, allowing the iminoketene to be, at the same time, a precursor (through a rapid equilibrium) and the key intermediate for the decomposition of the compound through some irreversible process.

The conversion of the (*E*)-*N*-formyliminoketenes (**32**)—(**35**) into the 1,3-oxazin-6-ones (**40**)—(**43**) requires a previous isomerisation of the carbon–nitrogen double bond to give the (*Z*)-*N*-formyliminoketenes (**36**)—(**39**), in order to bring the *N*-formyl and ketene groups into proximity. In any case, it was expected *a priori* that such processes would not involve high-energy transition states, since the presence of the *N*-formyl group permits isomerisation in such a manner that the carbon–nitrogen double bond is preserved. When this isomerisation in (*E*)-*N*-formyliminoketenes (**32**)—(**35**) was studied by MNDO, this hypothesis was fully confirmed. The calculated activation energies $\Delta H^{\ddagger}$ and reaction enthalpies ΔH_r° are summarised in Table 2.

It is noteworthy that the transition states for these isomerisations exhibit a CNC angle of 152—177°, whereas the linear structures correspond to a second-order saddle point. From a kinetic point of view, the isomerisations are predicted to occur with great facility, and the small differences in the thermodynamic stability between the *E*- and *Z*-isomers ensure appreciable concentrations of both stereoisomers at equilibrium.

Therefore, it seemed clear that the isomerisation of the *N*-acyliminoketenes would not represent an insurmountable



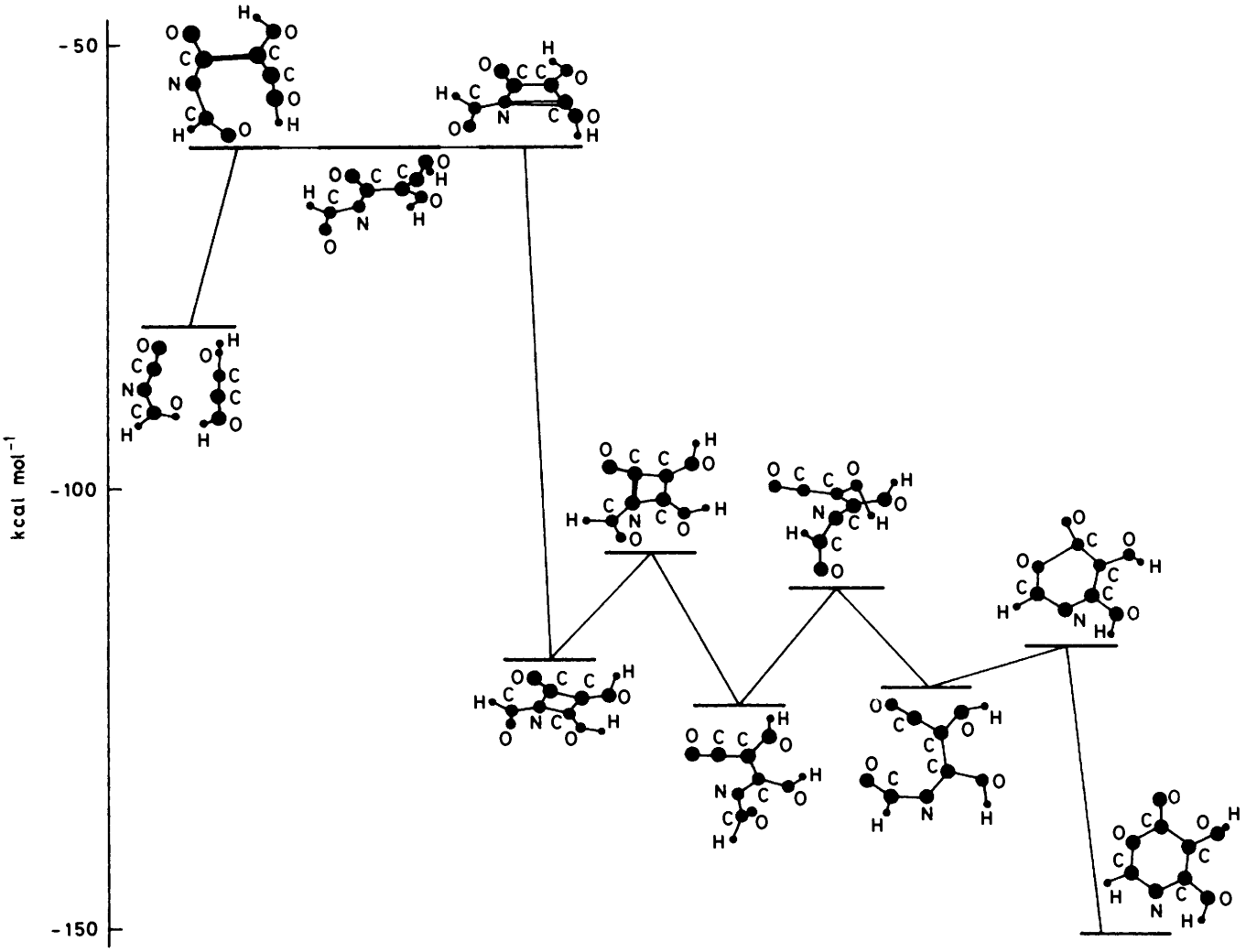


Figure 1. Calculated MNDO energy profile for the reaction between dihydroxyethyne and formyl isocyanate. Drawings are computer plots of the stationary points obtained on the reaction co-ordinate

problem in the conversion of a hypothetical *N*-acylazetone into a 1,3-oxazin-6-one. The only remaining point was to estimate, by calculation, the energetic barrier for the final cyclisation of the isomerised *N*-acyliminoketenes (**36**)—(**39**) to the 1,3-oxazin-6-ones (**40**)—(**43**). The MNDO study of these processes led to the results summarised in Table 3. As can be observed, the cyclisation processes are predicted to proceed very easily, and are highly exothermic.

If the overall conversion of azetones into 1,3-oxazin-6-ones (**40**)—(**43**) is then analysed, it can be seen that all four considered processes are predicted to be very favourable from a thermodynamic point of view (Table 4). Moreover, all individual steps implicated in the overall processes have low activation energies (<18 kcal mol^{-1}). Consequently, the conversion of *N*-acylazetones into 1,3-oxazin-6-ones is predicted by MNDO calculations to take place easily and completely, even at low temperatures, owing to the important difference in thermodynamic stability between the compounds.

A final question that deserves special attention is the comparison between the energetic barriers associated with the formation of an *N*-acylazetone by a cycloaddition between an alkyne and an acyl isocyanate and those associated with the conversion of the azetone into the 1,3-oxazin-6-one; the result of such a comparison could throw light on the intrinsic possibility of synthesising *N*-acylazetones by [2 + 2]cycloadditions between alkynes and isocyanates.

In the course of previous work on the reactivity of dihydroxyethyne in [2 + 2]cycloadditions, as a model for acetylenic diethers, we studied by MNDO the reaction of dihydroxyethyne with formyl isocyanate to give the corresponding *N*-formylazetone.[17] The process was predicted to take place stepwise, through a very short-lived intermediate, with a net activation energy of 26.3 kcal mol^{-1}. The calculated heat of reaction was -38.0 kcal mol^{-1}.

A complete representation of the energy profile for the reaction of dihydroxyethyne with formyl isocyanate, leading to 4,5-dihydroxy-1,3-oxazin-6-one (**43**), is given in Figure 1.

It is noteworthy that the energy barrier calculated for the cycloaddition between dihydroxyethyne and formyl isocyanate is greater than any of those implicated in the subsequent rearrangement steps. Although no entropy effects have been taken into account, such effects must likewise increase the barrier of the cycloaddition relative to those of the subsequent rearrangement. Consequently, MNDO predicts the impossibility of preparing 1-formyl-3,4-dihydroxyazet-2(1*H*)-one by a [2 + 2]cycloaddition without a concomitant rearrangement

Table 6. Interatomic distances (Å) for compound (**15**) with standard deviations in parentheses

O(1)–C(2)	1.403(3)	C(9)–C(10)	1.380(4)
O(1)–C(6)	1.348(2)	C(10)–C(11)	1.384(5)
C(2)–O(2)	1.205(3)	C(11)–C(12)	1.392(4)
C(2)–C(3)	1.438(3)	O(31)–C(32)	1.471(3)
C(3)–C(4)	1.373(3)	C(32)–C(33)	1.550(5)
C(3)–O(31)	1.368(3)	C(32)–C(34)	1.477(5)
C(4)–N(5)	1.371(3)	C(32)–C(35)	1.505(10)
C(4)–O(41)	1.334(3)	C(32)–C(35′)	1.603(31)
N(5)–C(6)	1.291(3)	C(35)–C(35′)	0.333(57)
C(6)–C(7)	1.463(3)	O(41)–C(42)	1.486(3)
C(7)–C(8)	1.391(3)	C(42)–C(43)	1.516(5)
C(7)–C(12)	1.405(3)	C(42)–C(44)	1.531(4)
C(8)–C(9)	1.397(4)	C(42)–C(45)	1.519(4)

Table 7. Angles (°) for compound (**15**) with standard deviations in parentheses

C(6)–O(1)–C(2)	121.4(2)	C(12)–C(11)–C(10)	120.3(3)
O(2)–C(2)–O(1)	115.9(2)	C(11)–C(12)–C(7)	119.3(3)
C(3)–C(2)–O(1)	115.0(2)	C(32)–O(31)–C(3)	119.7(2)
C(3)–C(2)–O(2)	129.2(2)	C(33)–C(32)–O(31)	110.5(2)
C(4)–C(3)–C(2)	118.8(2)	C(34)–C(32)–O(31)	111.1(2)
O(31)–C(3)–C(2)	118.5(2)	C(34)–C(32)–C(33)	108.2(4)
O(31)–C(3)–C(4)	122.2(2)	C(35)–C(32)–O(31)	106.3(6)
N(5)–C(4)–C(3)	122.4(2)	C(35)–C(32)–C(33)	107.7(6)
O(41)–C(4)–C(3)	117.6(2)	C(35)–C(32)–C(34)	113.1(8)
O(41)–C(4)–N(5)	119.9(2)	C(35′)–C(32)–O(31)	94.7(13)
C(6)–N(5)–C(4)	118.2(2)	C(35′)–C(32)–C(33)	110.8(17)
N(5)–C(6)–O(1)	124.0(2)	C(35′)–C(32)–C(34)	120.8(19)
C(7)–C(6)–O(1)	113.0(2)	C(35′)–C(32)–C(35)	11.8(20)
C(7)–C(6)–N(5)	122.9(2)	C(42)–O(41)–C(4)	124.5(2)
C(8)–C(7)–C(6)	121.8(2)	C(43)–C(42)–O(41)	108.8(2)
C(12)–C(7)–C(6)	118.4(2)	C(44)–C(42)–O(41)	100.8(2)
C(12)–C(7)–C(8)	119.8(2)	C(44)–C(42)–C(43)	112.0(3)
C(9)–C(8)–C(7)	120.3(2)	C(45)–C(42)–O(41)	110.9(2)
C(10)–C(9)–C(8)	119.4(3)	C(45)–C(42)–C(43)	113.5(3)
C(11)–C(10)–C(9)	120.9(3)	C(45)–C(42)–C(44)	110.2(2)

to the more stable 4,5-dihydroxy-1,3-oxazin-6-one. This prediction must also apply to any thermal [2 + 2]cycloaddition between an acetylene and an acyl isocyanate. Consequently, it is doubtful whether *N*-acylazetones can ever be obtained, at least by a cycloaddition of this type. In view of these ideas, it seems probable that the highly stable acylazetones of Arbuzov[4] are in fact 1,3-oxazin-6-one derivatives.

Crystal Structure of 2-*Phenyl*-4,5-*di*-*t*-*butoxy*-1,3-*oxazin*-6-*one* (**15**).—A computer-generated plot of the structure (**15**) is shown in Figure 2. Table 5 lists the final fractional co-ordinates; interatomic distances and bond angles are in Tables 6 and 7.

Some structure aspects of (**15**) deserve special comment. In the first place, the 6*H*-1,3-oxazin-6-one ring is not strictly planar, having C(2), C(3), and C(4), respectively, −0.022(3), 0.027(3), and −0.015(3) Å out of the plane defined by O(1), C(6), and N(5). On the other hand, the phenyl ring has typical geometry, being planar and exhibiting an average C–C distance of 1.391(8) Å, and CCC angle of 120.0(6)°. The torsion angle between the phenyl ring and the O(1),C(6),N(5) plane is 16.9(2)°. Most probably, the phenyl group adopts such a conformation in order to avoid steric interaction with the C(4) t-butoxy group which, in turn, is almost coplanar with the α,β-unsaturated carbonyl system [the torsion angle defined by C(42), O(41), C(4), and C(3) is 170.0(3)°]. This indicates that conjugation of the O(41) lone pair with the α,β-unsaturated carbonyl system is more stabilising in the crystal than the more extended conjugation of the phenyl ring through the C(6)–N(5) double bond. This fact is reflected in the C(4)–O(41) distance [1.334(3) Å], which is considerably shorter than C(3)–O(31) [1.368(3) Å].

MNDO calculations on the model molecule 4,5-dihydroxy-1,3-oxazin-6-one (**43**) (Figure 3) give an equilibrium geometry which is in good agreement with the crystal structure of compound (**15**). Remarkably, the conformation of the hydroxy groups in (**43**) is the same as of the t-butoxy groups in (**15**), the differences between the corresponding C(sp^2)–O bond distances being also well reproduced.

Experimental

Mass spectra were run with an electron-impact Hewlett-Packard 5930A spectrometer. U.v. and i.r. spectra were recorded with Perkin-Elmer spectrophotometers (Lambda 5 and 681, respectively). ^{1}H N.m.r. spectra were obtained with a Hitachi Perkin-Elmer R-24 B spectrometer, and ^{13}C n.m.r. spectra with a Varian XL-200 spectrometer. Benzoyl isocyanate (**13**) was prepared from benzamide and oxalyl chloride[18] and di-t-butoxyethyne (**14**) by a previously described procedure.[9]

Reaction of Di-t-butoxyethyne (**14**) *with Benzoyl Isocyanate* (**13**).—A solution of di-t-butoxyethyne (**14**) (1.00 g, 5.9 mmol) in toluene (20 ml) was added dropwise to a solution of benzoyl isocyanate (**13**) (0.88 g, 6.0 mmol) in toluene (15 ml) at 0 °C under N_2. The mixture was stored for 8 days at 4 °C. The unchanged reactants were then removed by distillation (20 °C; 0.05 Torr), leaving a residue (1.23 g). Repeated flash chromatography of this residue (elution with ether–hexane mixtures) allowed the isolation of two fractions. Fraction (a) was 4,5-*di*-*t*-*butoxy*-2-*phenyl*-1,3-*oxazin*-6-*one* (**15**) (299 mg, 16% yield), m.p. 77 °C (Found: C, 68.2; H, 7.7; N, 4.1. $C_{18}H_{23}NO_4$ requires C, 68.1; H, 7.3; N, 4.4%); *m*/*z* 317 (M^+, 0.01%), 261 (0.6), 246 (0.7), 205 (8), 149 (7), 105 (9), 104 (18), and 57 (100); $\lambda_{max.}$ (cyclohexane) 202, 240, and 338 nm (ε 25 700,

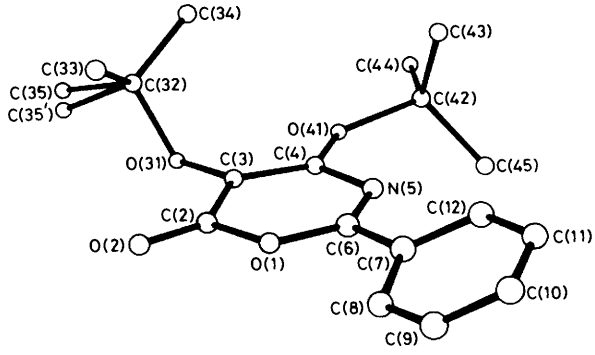


Figure 2. Computer-generated plot for compound (**15**) from the Cartesian co-ordinates of atoms in the crystal

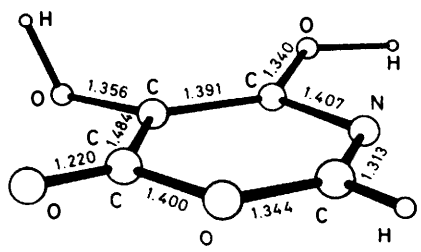


Figure 3. Computer-generated plot for model molecule (**43**) from the Cartesian co-ordinates of the equilibrium geometry obtained by the MNDO procedure. Relevant bond lengths (Å) are shown

16 600, and 9 400 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$ (CCl_4) 2 980, 1 760, 1 610, 1 580, 1 540, 1 395, 1 370, 1 335, and 1 155 cm^{-1}; δ_H (60 MHz; CCl_4; Me_4Si) 8.10—7.83 (2 H, m), 7.47—7.27 (3 H, m), 1.60 (9 H, s), and 1.33 (9 H, s); δ_C (50.3 MHz; $CDCl_3$; Me_4Si) 162.1 (s), 160.9 (s), 157.7 (s), 132.9 (d), 129.7 (s), 128.9 (d), 128.3 (d), 118.2 (s), 83.8 (s), 83.1 (s), 29.3 (q), and 28.7 (q). Pale yellow crystals of (**15**), suitable for *X*-ray crystallographic study, were grown by slow evaporation of a concentrated solution in pentane.

Fraction (b) was N-*benzoyl*-4-*hydroxy*-3,5,6-*tri*-*t*-*butoxy*-2-*pyridone* (**16**) (183 mg, 14%), m.p. 119—121 °C (Found: C, 66.75; H, 7.7; N, 3.25. $C_{24}H_{33}NO_6$ requires C, 66.4; H, 7.8; N, 3.3%); *m/z* 431 (M^+, 0.2%), 375 (1), 319 (6), 263 (4), 219 (33), 218 (20), 173 (20), 172 (15), 105 (30), 77 (33), and 57 (100); $\lambda_{max.}$ 208, 240, and 337 nm (ε 27 000, 13 800, and 13 300 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$ (CCl_4) 2 990, 2 965, 1 750, 1 690, 1 560, 1 370, 1 350, and 1 150 cm^{-1}; δ_H (60 MHz; CCl_4; Me_4Si) 8.10—7.90 (2 H, m), 7.57—7.43 (3 H, m), 5.63 (1 H, s), 1.50 (9 H, s), 1.46 (9 H, s), and 1.38 (9 H, s); δ_C (50.3 MHz; $CDCl_3$; Me_4Si) 169.8 (s), 166.5 (s), 165.0 (s), 152.9 (s), 132.7 (d), 131.5 (s), 129.3 (d), 128.5 (d), 126.4 (s), 108.1 (s), 84.3 (d), 82.5 (s), 82.4 (s), 29.0 (q), 28.1 (q), and 27.8 (q).

MNDO Calculations.—The calculations were performed with the standard MNDO semi-empirical SCF-MO method as implemented in the MOPAC program. All stationary points were characterised by calculating and diagonalising the Hessian matrix. Geometrical parameters for all stationary points are given in Cartesian co-ordinates in the Supplementary Publication.

Crystal Data for (**15**).—$C_{18}H_{23}NO_4$, M = 317.39. Triclinic, a = 9.910(2), b = 10.208(3), c = 9.503(2) Å, α = 88.56(2), β = 105.94(2), γ = 105.09(2)°, V = 891.4(6) Å^3 [by least-squares refinement on diffractometer angles for 25 independent reflections, λ(Mo-K_α) = 0.710 69 Å], space group $P\bar{1}$, Z = 2, D_x = 1.182 g cm^{-3}, F(000) = 340. Pale yellow tablets. μ(Mo-K_α) = 0.90 cm^{-1}.

Data Collection and Processing.—A crystal (0.2 × 0.2 × 0.1 mm) was mounted on a Phillips PW-1100 four-circle diffractometer. Intensities were collected with Mo-K_α radiation, monochromatised by reflection from a graphite crystal. Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay not being observed. The intensity data were corrected for Lorentz and polarisation factors but not absorption factors. 3 031 Independent reflections were measured in the range $2 \leqslant \theta \leqslant 30°$, of which 2 936 were considered observed with $I > 2.5\ \sigma(I)$.

Structure Analysis and Refinement.—The structure was solved by direct methods using the MULTAN system of computer programs.[19] Non-hydrogen atoms were isotropically and anisotropically refined by the full-matrix least-squares method, using the SHELX76 computer program.[20] The hydrogen-atom positions were computed and refined with an overall isotropic thermal coefficient. Atoms C(34) and C(35) gave the highest thermal coefficients, therefore disorder was checked in their localisation. Only for C(35) was it possible to determine an alternative site. Refinement of the occupancy factor for C(35) and C(35′) gave a value close to 0.70 for C(35). The final R factor was 0.069 (R_w = 0.086) for all observed reflections.

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